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**GALVANOPLASTIC MANIPULATIONS.**

**A PRACTICAL GUIDE**

FOR THE

**GOLD AND SILVER ELECTROPLATER**

AND THE

**GALVANOPLASTIC OPERATOR.**

COMPRISING

THE ELECTRO-DEPOSITION OF ALL METALS BY MEANS OF THE BATTERY AND THE DYNAMO-ELECTRIC MACHINE, AS WELL AS THE MOST APPROVED PROCESSES OF DEPOSITION BY SIMPLE IMMERSION, WITH DESCRIPTIONS OF APPARATUS, CHEMICAL PRODUCTS EMPLOYED IN THE ART, ETC.

BASED LARGELY ON THE

"MANIPULATIONS HYDROPLASTIQUES" OF ALFRED ROSELEUR.

BY

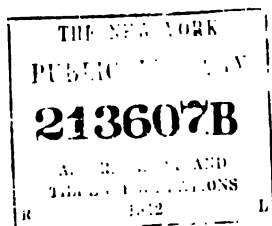
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## P R E F A C E.

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THE present work had its origin in a request of the publishers that the author would prepare a translation of the last edition of ROSELEUR'S well-known *Manipulations Hydroplastiques*—a treatise which has deservedly acquired a high reputation among galvanoplastic operators as a reliable and useful work of reference.

An examination, however, revealed the fact that it did not, in a number of important particulars, adequately represent the present state of the art, especially as developed and practised in the United States.

On this account, therefore, it was thought advisable to prepare a treatise, which, while it should have for its basis the admirable practical instructions of ROSELEUR, should, in addition, embrace also all the more recent and important processes, methods, and formulæ that have been proposed—in a word, to re-write the entire work, so that it should properly represent the present state of the galvanoplastic art.

As to how far this undertaking has been successful, the present volume must speak for itself. It has been prepared in the brief intervals of leisure snatched from other and absorbing professional occupations, and the writer is fully conscious of the fact that in many respects it could have been made more complete. He desires to express his indebtedness to the Meriden Britannia Company of Meriden, Conn., the William Rogers Manufacturing Company of Hartford, Conn., Messrs. Ledig & Herrlein of Philadelphia, and

Shulte  
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others, for courtesies extended to him in making personal examination of their processes and methods; and to the last named especially for opportunities afforded, and assistance rendered, in experimental work. He is also indebted to Prof. Edwin J. Houston, of Philadelphia, for the revision of the proof-sheets of the chapter on Dynamo-Electric Machines.

To facilitate reference and investigation, a copious list of patents—American and British—relating to the subject of electro-metallurgy has been carefully compiled and is given in the Appendix. The very full index will also be appreciated by those who may have occasion to consult it.

W. H. W.

PHILADELPHIA, Nov. 5, 1883.

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## GALVANOPLASTIC MANIPULATIONS.

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### HISTORICAL FACTS

#### RELATING TO ELECTRO-METALLURGY.

THE value of the galvanic current as an agent for effecting the dissociation of chemical compounds was established by Sir Humphry Davy as long ago as the year 1808, when with its aid he succeeded in proving that soda, potash, lime, etc., were metallic oxides, and not elementary substances, as had previously been the universal belief.

It was not, however, until many years after this that the decomposing power of the battery was applied to useful purposes in the arts. It was, however, soon observed that metals deposited by its agency, from their solutions, assumed various fantastical forms, which so closely resembled the growths of vegetation that they were not inaptly styled galvanic trees. But these observations might still have remained of no utility save to awaken the interest of students of chemistry by their beauty as philosophical experiments, had it not been for an accidental discovery by Professors Wagner and Jacobi in the year 1830, that the metallic deposits thus obtained might be used for plating and for copying.

The history of this interesting discovery is briefly as follows:—

These investigators were endeavoring to solve the enticing problem of utilizing electro-magnetism as a motive power in place of steam. Jacobi employed in these investigations the Daniell battery, which will be presently described, and which is distinguished for its constant and regular action. When this battery is working, the sulphate of copper solution employed is slowly decomposed, depositing metallic copper, which, after a certain quantity of it has accumulated, interferes with the action of the battery and must be removed. Once when Jacobi was busied in removing such a deposit from his battery, he noticed that there were several layers of copper, each having the form of the sides of his vessel. The fact that the disposition of these layers imitated, in a remarkably perfect manner, the shape of the surfaces of the vessel to which they adhered, suggested to Jacobi the idea that this troublesome phenomenon might be turned to profit by employing it for reproducing effects in metal. Meantime, several important observations bearing upon the same subject were made by other investigators.

Mr. De la Rue, for example (in 1836), noticed,\* that the deposit of copper precipitated upon the copper plate of a peculiar form of Daniell's battery that he had devised, "was covered with a coating of metallic copper which is continually being deposited, and so perfect is the sheet of copper thus formed that, on being stripped off, it has the polish and even a counterpart of every scratch of the plate on which it is deposited." The following year Dr. Golding Bird succeeded in decomposing, with the battery, solutions of the chlorides of sodium, potassium, and

\* Mr. W. De la Rue, "On Voltaic Electricity, and on the Effects of a Battery charged with Sulphate of Copper." Lond. and Edinb. Philos. Mag., ix. (1836), p. 484 *et seq.*



ammonium, and deposited these metals on a negative pole of mercury.\*

These observations, however, were followed by no practical results; and it remained for Prof. Jacobi, to whom the idea of utilizing his observations first occurred, to give them practical form. This noteworthy event took place in 1838, when he communicated to the Academy of Sciences of St. Petersburg, a description of his discovery of the utility of galvanic electricity as a means of reproducing objects in metals. This galvanoplastic process was claimed to be a method of converting any line, however fine, engraved on copper, into a relief by galvanic process, applicable to copper-plate engravings, medals, stereotype plates, ornaments, and to making calico-printing blocks, and patterns for paper hangings. The merit of having been the first to apply the electro-deposition of metals to useful purposes, and of having originated the galvanoplastic art, appears, therefore, to be due unquestionably to Jacobi. His discovery attracted at the time such attention that the Emperor Nicholas, after satisfying himself of its great value, gave its author the means of making the new art the common property of the world.

In the year 1839, Mr. C. J. Jordan described (*Mechanic's Magazine*, June 8, 1839) a series of experiments for the purpose of obtaining by galvanic means casts in copper from various metals; in which reference is made to Jacobi's earlier work in this field.

Mr. T. Spencer read a paper before the Liverpool Polytechnic Society on the "Electrotype Process," in the same year in which, among other things, he describes a method

\* Golding Bird, F.L.S., F.G.S., etc., "Observations on the Electro-Chemical Influence of Long-continued Electric Currents of Low Tension." *Philos. Transactions*, 1837, p. 37.

of depositing "a metallic surface on a model of clay, wood, or other *non-metallic* body," by coating the surfaces of these models with a thin coating of mastic varnish, rendered conductive by means of bronze powder, and by means of which he was enabled to deposit a surface of copper on the prepared surface of the mould by the voltaic method.

About the year 1840, Prof. Boettger succeeded in producing handsome relief plates of copper with the aid of the battery, and employed this apparatus also for gilding silver, copper, and brass. About the same time, Mr. John Wright, of Birmingham (Gore, *Electro-metallurgy*, 1877, p. 19), was engaged in experiments with the view of obtaining, with gold and silver, similar results to those already obtained by Jacobi, Spencer, and Jordan with copper, viz., thick deposits of firm, coherent metal, bright, and of good color. Led thereto by a suggestion of Scheele's, respecting the solubility of the cyanides of copper, silver, and gold, this experimenter made the important observation that a solution of the cyanides of gold and silver in the alkaline cyanides was capable of yielding a solid, coherent deposit of these metals by electrolytic action. Shortly after this (1841) Prof. Boettger succeeded in making a copy of one of Felsing's copper-plates (the *Ecce Homo* of Guido Reni,  $12\frac{1}{2} \times 9\frac{1}{2}$  inches) which proved to be so perfect that the engraver admitted that proofs printed with it were not to be distinguished from those taken from the original.

Meantime, [in 1840, M. de Roulz, a French electro-depositor (Gore, *Electro-metallurgy*, 21 *et seq.*), had taken out a patent in France for electro-gilding] and silvering by means of solutions of the double cyanides and ferro-cyanides. His patent also included the use of similar solutions for the electro-deposition of platinum, copper,

lead, tin, cobalt, nickel, and zinc (*Encyclopædie, Roret, Galvanoplastie*, tome ii. p. 114). From this time forward the galvanoplastic art made rapid progress. American experimentalists appear to have been among the earliest in the field in applying the new art to letter-press printing, a branch of the art to which the name of electrotyping is generally given. In 1842, Daniel Davis, of Boston, made and used electrotype plates of the engravings and letter-press of his *Manual of Magnetism*. In the previous year, Mr. Joseph A. Adams, of New York, is credited with having reproduced and printed an engraving in a magazine published by James J. Mapes, of that city; and in 1843, he electrotyped the various borders around the larger engravings in Harper's Illustrated Bible.

From these beginnings the galvanoplastic art has developed into an industry of inestimable value to the printer, the publisher, the engraver, the artist, and the antiquarian. Its employment in reproducing copies of engravings and letter-press, coins, medals, etc. is almost universal, it is even successfully employed for the reproduction, in copper, of works of art of great size. In another direction, also, the galvanoplastic art has originated a great industry, the value of which, from the vast variety, popularity, and utility of its products, it would be difficult to over-estimate. Reference is made, in this connection, to the electroplating of artistic and useful articles of every conceivable description with gold, silver, copper, bronze, nickel, etc., to enhance their beauty and artistic value, or to protect the underlying surfaces from the action of destructive agencies. The developement of this branch of the art has of late been simply enormous, and it has placed within the reach of all classes objects of utility and beauty of the most artistic designs, which rival in

tastefulness and serviceability the most precious works of art in gold and silver, which are of necessity the exclusive property of the rich. The recent great improvements in dynamo-electric machines, which have been so far perfected as to have almost completely replaced the troublesome and expensive chemical battery for the electro-deposition of metals, have given an immense impulse to the art, and bid fair to work an important revolution in the metallurgical arts.

## PART I.

### THIN METALLIC DEPOSITS.

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#### CHAPTER I.

##### OBJECT OF THE HYDROPLASTIC ART.

THE art of depositing metals by the wet way comprises two orders of phenomena, which, though apparently identical in their results, are nevertheless essentially different in respect to the causes of their production. The one, as, for example, gilding by simple immersion in a liquid or bath prepared for the purpose, is directly the result of the action of chemical affinities; the other, on the contrary, as, for instance, electro-gilding, cannot take place without the simultaneous concurrence of chemical reactions, and of that form of energy called dynamic electricity, which, though only recently discovered, has become of great practical importance.\*

\* Physicists recognize two modifications of electricity. They call *static electricity* that which, when accumulated on an insulated conductor, as, for example, in the prime conductor of an electrical machine, or in the Leyden jar, manifests its presence, in the form of sparks, on the approach of another conducting body.

They call, on the other hand, *dynamic electricity*, or current electricity, that modification which manifests its effects with or without the disengagement of light, as, for example, when contact is established between the two electrodes of a galvanic battery, or when a conductor of any description is interposed between the extremities of these reophores. This subject will be more fully discussed in the chapter on Batteries.



The frequent use in the same workshop of metalloplastic methods, both with and without the aid of electricity, renders it necessary that we should not separate these two orders of facts; in support of which opinion we have the additional reasons that the manipulations and chemical preparations are very nearly identical in both cases, and the results obtained are sensibly the same.

In the operations of deposition by simple immersion, where the dissolved metals are reduced to their metallic state by the sole agency of chemical affinities, the results obtained are, in most cases, very similar, the metallic deposits thus obtained being generally characterized by their extreme thinness.

On the other hand, we may by electro-deposition attain two different objects.

It may be desired, for instance, to coat a common metal with a layer of another metal which is more precious, more resisting, less oxidizable, or which has a more pleasing appearance; but this layer, generally, borrows its strength from the underlying metal, as is the case in gilding or silvering copper, or in coating zinc with copper, etc.

Or, we may design to reproduce a given article with scrupulous exactness, by means of a metallic deposit, which, after its separation from the mould, shall have sufficient firmness to constitute a fac-simile of the original; of this nature are the galvanoplastic reproductions of basso-relievos, medals, etc. Or, we may wish to impart a metallic hardness to a material without firmness, and retain at the same time as nearly as possible its original shapes and dimensions, as when we deposit metallic coatings upon small statues, flowers, fruits, insects, etc.

We shall examine first the thin electro-deposits, and

principally those of gold and silver, as their applications present great variety, and are of general interest.

The following definitions may be found useful to students of this subject:—

*Electro-chemistry* is that branch of the science of chemistry which treats of the agency of electricity in producing chemical changes. The branch of electro-chemistry with which we are here specially interested is,

*Electro-metallurgy*, which deals with the deposition of metals from their compounds held in solution, by the agency of galvanic (or current) electricity. According to the object sought to be attained, the following subdivisions are recognized:—

*Electro-metallurgy* proper, which relates to the extraction of metals, on the commercial scale, from solutions of their ores or other compounds, by means of the galvanic current, the resulting product being placed in merchantable form (ingots, bars, sheets, wire, etc. etc.).

*Electrotyping*, by which term is understood the reproduction and duplication of useful and artistic objects (medallions, coins, statues, and other works of art), and the reproduction and duplication of printing surfaces (engravings, letter-press) in copper, by means of the galvanic current. The resulting electro-deposited metal is usually removed from the surface on which it has been deposited.

*Electro-plating*, which is confined to the coating of any metallic or other conducting surface, by means of the galvanic current, with an adhering deposit of another metal, either for the purpose of enhancing the beauty and value of the object thus treated, or to protect the underlying surfaces from the action of corrosive agents, or for both of these purposes.

## CHAPTER II.

### CLEANSING.

CLEANSING COPPER AND ITS ALLOYS—CLEANSING BY FIRE OR BY ALKALIES—DIPPING—DIPPING IN OLD AQUA FORTIS—DIPPING IN AQUA FORTIS AND SOOT—AQUA FORTIS FOR BRIGHT DIPPING—BRIGHT DIPPING IN MIXED ACIDS—WHITENING BATH—MIXED ACIDS FOR A DEAD LUSTRE—DIPPING IN NITRATE OF MERCURY.

BEFORE undertaking to lay a thin electro-deposit of one metal upon another, it is absolutely necessary that the latter should be chemically clean, as the presence of the slightest impurity is sufficient to prevent the adherence of the two metals.

The operation or series of operations by which this result is reached is called *cleansing*.

The mode of cleansing varies with the metals operated upon; the cleansing of copper and its alloys presents the greatest difficulties, and requires to be done with the greatest care and thoroughness. The cleansing of other metals, such as silver, iron, lead, tin, etc., is more a mechanical than a chemical operation.

We shall examine successively the preparation which metals and their alloys should receive before they are ready for a metallic deposit, following substantially the mode of procedure recommended by Roseleur.



*Cleansing Copper and its Alloys.*

The mode of cleansing copper, brass, bronze, maillechort, oreide, similar, French gold, Mannheim gold, British metal, German silver, and, generally speaking, all alloys in which the proportion of copper predominates, is the same. It comprises six operations:—

1. *Cleansing by fire or by alkalies.*
2. *Dipping.*
3. *Dipping in old aqua fortis.*
4. *Dipping in fresh aqua fortis.*
5. *Dipping in mixed acids for a bright or dead lustre.*
6. *Dipping in nitrate of mercury.\**

*Cleansing by Fire or by Alkalies.*

The articles for electroplating are generally soiled by adhering greasy matters, derived during the operations of manufacture, such as rolling, spinning, soldering, polishing with oil, etc., or simply from contact with the hands. The foreign substances, and especially those of organic nature, are destroyed by heating the pieces on all sides over a gentle fire of charcoal. A muffle furnace, heated up to a dull red heat, is to be preferred; but small articles may be cleansed in a heated revolving cylinder.

This operation is not adapted to very delicate articles, such as filigree and spangled work, neither to table-forks and spoons, which must retain their sonorousness and toughness, nor to those pieces the different parts of which are united by solders which are fusible below the temperature to which they would be subjected in reheating. In such cases, the articles are submitted to a more or less

\* Of these six operations, four only are indispensable; the third and sixth may be dispensed with in many cases, which we shall examine further on.

prolonged boiling in alkaline solutions, either of potassa or soda, which saponify the fatty substances and thus render them soluble in water.

The operation is performed in a cast-iron kettle, in which a more or less concentrated solution of carbonate of potassium or sodium, or of American potash, is maintained at the boiling-point, usually with the use of a coil of pipe through which steam is passed. Roseleur gives the preference to caustic potassa dissolved in ten times its weight of ordinary water. This solution lasts quite a long time, and, when it has lost part of its power, it may be revived by the addition of a few fragments of caustic potassa. At the boiling-point this solution will cleanse copper completely in a few seconds. If the articles to be cleansed are joined with tin solder, they must not be allowed to remain too long in the caustic liquor, which may dissolve the solder and strongly blacken the copper. The lye kettle should be provided with a lid, or cover, to retard the otherwise rapid absorption, by the caustic liquor, of carbonic acid from the air, or of the acid vapors of the workshop, which would diminish its alkalinity, and consequently its cleansing qualities.

#### *Dipping.*

The articles are then dipped in a mixture of from five to twenty parts (by weight) of sulphuric acid of 66° Baumé to one hundred parts of water.

Copper articles may remain any length of time in the dipping bath without suffering any injury; but it is absolutely necessary that they should not be removed until the black coating of oxide of copper (cupric oxide), caused by the heating operation above described, is entirely dissolved. The remaining coat of red oxide of copper (cuprous oxide) is unacted upon by the sul-

phuric acid. <sup>1</sup> It should be remarked that articles having parts made of iron or zinc, should not be submitted to the action of sulphuric acid, as such parts will be entirely dissolved; therefore, the use of all implements, wires, or hooks of iron, zinc, or steel must be avoided. A dipping bath which, from previous operations, contains copper in solution, will not suit for such articles as contain iron, tin, tin solder, antimony, bismuth, or lead. In these cases, a newly made dipping bath with a small proportion of acid must be used.

The articles cleansed by alkalies must be washed before being plunged into the dipping bath, or pickle, as it is sometimes called; and we cannot insist too much on the necessity of thoroughly and rapidly rinsing in fresh water all the articles, both before and after each of the operations that are to follow.

The various manipulations which we shall presently indicate, and which complete the cleansing, should succeed each other without interruption; and the articles should be actively moved about in the acid bath (pickle) and also in the rinsing-water.

In order to prove the importance of these operations, we do not hesitate to state, that, even with very inferior electroplating solutions, good results may be arrived at if the cleansing is perfect, while the converse is not true.

After dipping and rinsing, the various pieces are attached to a brass wire, or simply hooked upon copper hooks represented by Figs. 1 and 2. Small articles of jewelry are simply suspended to a stout copper wire, as seen in Figs. 3 and 4.

For the construction of these hooks copper is to be preferred to brass, and for careful workers, we recommend the use of hooks of glass, which are not expensive

and not liable to be acted on by the acids. Any one can make such hooks or supports, by bending glass rods, by

Fig. 1.

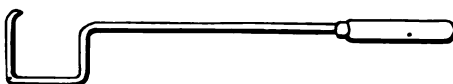
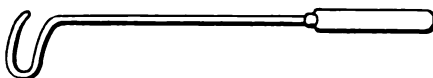


Fig. 2.



the heat of a charcoal fire, or of a gas-burner, into the shape shown in Fig. 5, which is handy for the manipulations required in the cleansing vessels.

Fig. 3.



Fig. 4.

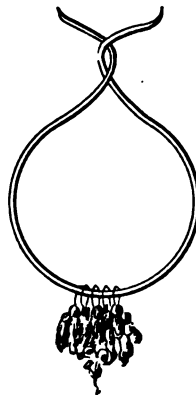
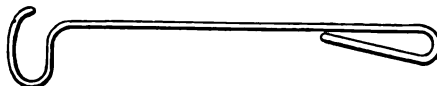


Fig. 5.



Those objects which cannot be suspended or attached to hooks, are placed in baskets or perforated ladles of

stoneware or porcelain (Figs. 6, 7, and 8), or what is less economical, but sometimes absolutely necessary, into

Fig. 6.

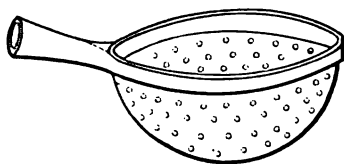
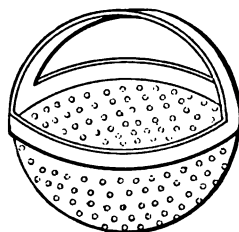


Fig. 7.



baskets of brass wire cloth (Fig. 9), having the mesh fine or coarse, according to circumstances.

Fig. 8.

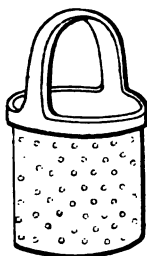
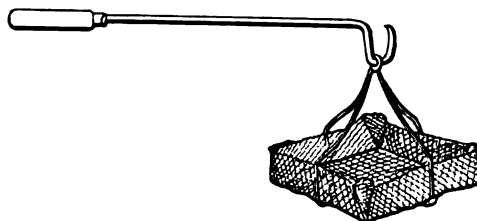


Fig. 9.



Those who have frequently to cleanse very small articles, will find it advantageous to employ a basket of platinum wire cloth, which, although expensive in first cost, will be found cheaper in the end, on account of its indifference to the action of the chemical substances used in the cleansing operations.

#### *Dipping in Old Aqua Fortis.*

The material employed for this purpose is the *spent aqua fortis* (nitric acid), already weakened by previous dippings, and of which there is always a supply on hand. After thorough rinsing in water, the articles that have



passed through the sulphuric acid bath just described are next immersed in a bath of this kind. They should be allowed to remain in this until the red coating of suboxide of copper has entirely disappeared, leaving, after rinsing, a uniform metallic lustre.

The dipping in old aqua fortis is not absolutely necessary, although we recommend it for two reasons, the last being the more important: First, it is economical in saving the cost of fresh acids; second, as its action is slow, it prevents the too rapid corrosion of those portions of the copper already cleansed, during the time that the solution of the oxide, which still adheres to certain parts of the surface, is being effected. If some operators frequently complain of the burned or pitted appearance of their pieces, it is due to the neglect of this operation, and direct dipping in strong aqua fortis.

We shall indicate further on the processes for utilizing and extracting all that can be saved from old aqua fortis and other dipping baths.

#### *Dipping in Strong Aqua Fortis.*

After a preliminary rinsing in fresh water, the absolute necessity of which has already been pointed out, the articles, well shaken and drained, are plunged into a bath composed of—

Nitric acid of 36° Baumé (straw-colored aqua fortis)	. . . . .	100 parts (by volume).
Sodium chloride (common salt)	. . . . .	1 part “
Calcined soot	. . . . .	1 “ “

This mixture attacks the metal with the greatest energy, and the pieces should therefore not remain in it more than a few seconds. The volume of acid should be from twenty to thirty times as great as that of the articles to be cleansed, for the chemical action being energetic a small

volume of the liquor would become heated, and the acid would be rapidly weakened or "spent."

After this bath, and rapid rinsing before the acid has time to give off reddish nitrous vapor, the pieces present a fine red color, sometimes gold-yellow or greenish-yellow, according to the alloy employed, and one might be led to suppose that they had been entirely deprived of foreign matter. It is not so, however; for, if the pieces in this state are plunged into a gilding or silvering bath, they become entirely black and without any metallic lustre.

If, on the other hand, we put aside without rinsing, the pieces removed from the dipping bath, there is produced on their surfaces a greenish froth, with the evolution of abundant nitrous vapors, which indicate the complete decomposition of the acid which remains upon them. When the vapors have disappeared, the pieces, even after washing, remain black and tarnished, on account of the formation of a basic copper salt, which is not soluble in water.

This last mode of operating, called blackening by aqua fortis, is preferred by a few gilders, varnishers, and color fixers, who find it economical to allow the production of nitrous vapors while the pieces are draining on top of the vessel which contains the acids. At all events, any subsequent operation is to be prefaced by rinsing in fresh water.

When small objects, such as pins, caps, eyelets, pearls, etc., are to be dipped, they are often put into a stoneware pot with a small quantity of aqua fortis, and then rapidly shaken and stirred. In this case, the acid is entirely used up with the production of abundant vapors, and the objects remain blackened and ready for further cleansing.

The soot in the above bath acts as a reducing agent. The carbon and hydrogen which it contains deoxidize a small proportion of the nitric acid, transforming it into

nitrous acid, which, uniting with the chlorine of the sodium chloride present, forms a small quantity of *aqua regia*, which is necessary in the operation above described.

The operator is required to be careful in the choice of his aqua fortis. Three kinds of nitric acid of 36° are to be found in the market:—

One is perfectly colorless.

The other is colored straw-yellow.

The last is of a more or less dark-red color.

The colorless acid does not cleanse well, especially when freshly used.

The red acid, which often contains chlorine, bromine, or iodine, acts too powerfully and pits the copper.\*

The straw-yellow acid, on the contrary, is to be preferred to the others. Nitric acid of 40° is too energetic and costly; certain operators however, who have to cleanse large quantities of copper-ware daily, prefer it on account of the rapidity of its action.

Aqua fortis is spent when its action on the articles of copper becomes too slow, and when the objects removed from the bath are covered with a kind of bluish-white film. Such acid is then preserved for the preceding operation, that is to say, dipping in old aqua fortis; or for dipping in the whitening bath, which will be described at the proper time.†

\* Certain gilders have taken advantage of this property of bromic and iodic acids to pit copper surfaces, to produce what they call "*mat anglais*," which has a fine effect on smooth surfaces.

† Very good aqua fortis may cleanse imperfectly when the temperature is too low or too high. This accounts for the difficulty in cleansing in frosty weather, or during the great heat of summer.



*Aqua Fortis for Bright Dipping.*

Before quitting this subject, we may indicate an excellent method of restoring the brilliant lustre of metallic surfaces that have been dulled by bad dipping, or slightly pitted or otherwise injured by the acids used for "stripping" or removing the gold or silver from plated articles. For this purpose it is sufficient to allow them to remain for a few minutes in a bath composed of—

Old aqua fortis, nearly spent . . . . .	1 volume.
Hydrochloric acid . . . . .	6 volumes.
Water . . . . .	2 "

The pieces, when removed from it, are entirely black, and must be thoroughly rinsed in clear water to remove the black slime which covers them. They are then cleansed and dipped anew.

This bath is in constant use by varnishers on metals, and though scarcely known to electrogilders, will certainly be found useful by them. It will be found to answer admirably for removing the moulding sand adhering to castings of copper and its alloys. With pieces of considerable size, however, it will be necessary to prolong the immersion for 20 or 30 minutes and sometimes much longer, as this mixture acts very slowly on copper and its alloys.

*Acid Mixture for "Bright" Dipping.*

These acids, which were rightly considered as indispensable by the first gilders by simple immersion, are of two kinds according to the object in view.

If the pieces must have a bright lustre, they are stirred for one or two seconds in a liquid (prepared the day previous, and cold) composed of—

Nitric acid of 36° (yellow aqua fortis) . . .	100 volumes.
Sulphuric acid of 66° (oil of vitriol) . . .	100 “
Common salt (chloride of sodium) . . .	1 volume.

On removing the articles from the bath they should be thoroughly swilled in an abundance of water. (*gilding*)

In the preparation of this dipping liquid, the acids should be added in the following order: First, the nitric acid should be poured into the containing vessel, and then the sulphuric acid, as otherwise the latter, by reason of its superior density, would remain at the bottom of the vessel without mingling with the former.

While the acids are being mixed, and especially when the common salt is added, considerable heat is developed, accompanied by the disengagement of an abundance of acid fumes, which are dangerous to inhale. For these reasons it is prudent to conduct this operation in the open air, or under a good chimney-hood provided with a movable glass sash. As this mixture must be used cold, it will therefore be necessary to prepare it some time in advance.

In an emergency the mixture may be used the same day that it has been prepared, by placing the containing vessel in ice or cold water until the acid mixture is cooled off.

Copper articles, after this dipping, are lighter colored and much brighter than after the passage through aqua fortis. They may then be considered as completely cleansed.

The above acid mixture is too energetic for small articles, such as pins, hooks, pearls, etc., which are generally cleansed in stoneware colanders, the holes of which are more or less obstructed, so that the acid liquid shall not drain off too rapidly, but if permitted to remain too long in contact with the copper, it becomes heated, fumes,

and blackens the articles before it is possible to rinse them. To obviate this inconvenience, the above acid mixture should be diluted with one-eighth of its volume of water. This mixture bears the name of "bitter water for bright dipping."

Frequently, in place of dipping the objects in the "bitter water," they are put in a stoneware pot, covered with a small quantity of the cleansing liquid, briskly agitated, and the whole plunged into a large volume of fresh water, as soon as the acid has acted sufficiently, and threatens to fume. This method is not economical, since the acid is lost, but it has the advantage that the entire mass of the dipping liquid is not heated.

#### *Whitening Bath.*

Varnishers and the majority of gold and silver platers, in place of frequently preparing fresh baths of the above mixed acids for bright dipping, use in place of it a mixture composed of variable proportions of—

Old aqua fortis,

Sulphuric acid,

Common salt,

and Soot,—which is called the "whitening bath. It is prepared about as follows:—

Into a large stoneware vessel, a certain quantity of old aqua fortis from previous dippings ("strong pickle") is poured, to which is added twice its volume of sulphuric acid of 66°.

The mixture becomes heated, and is allowed to cool off until the next day. The nitrate of copper contained in the old aqua fortis is converted into sulphate of copper, which is much less soluble, and which in cooling crystallizes upon the sides of the vessel. The liquid portion is decanted into another vessel, and then about two or three per cent.

(by volume) of sea salt, and as much of calcined soot, are added. This mixture is much less active than the above described mixed acids for bright dipping, and may often replace them advantageously. The crystallized sulphate of copper may be preserved for use or sold.

This whitening bath is now and then strengthened, as the operator may find it desirable, by the addition of aqua fortis or of oil of vitriol. To replace the portion used up during the day, equal volumes of old aqua fortis and oil of vitriol are added at the end of the day. The next morning the liquor is decanted, and a new crop of sulphate of copper crystals is gathered. Soot and salt in sufficient proportions are also added. In this manner a perpetual and cheap whitening bath is prepared.

Some operators heat this bath, and replace the salt of the formula with hydrochloric acid.

*Acid Mixture for Dead Dipping.*

If, instead of a bright appearance, it is desired to impart to the objects a dead lustre, they are, after dipping in aqua fortis and rinsing, plunged into a bath prepared the day previous and composed of—

Nitric acid of 36° (yellow aqua fortis)	. . . 200 volumes.
Sulphuric acid of 66° (oil of vitriol)	. . . 100 "
Common salt (chloride of sodium)	. . . 1 volume.
Sulphate of zinc (white copperas)	. . . 1 to 5 volumes.

It will be noticed that in this mixture the proportion of nitric acid is double that of sulphuric acid.

The copper articles may remain from five to twenty minutes in this cold mixture, and the dead lustre will be the more decided as the immersion has been more protracted.

When they come from this bath, and after a prolonged and thorough swilling in water, the objects present an



earthy appearance which is disagreeable to the eye. This objectionable dulness may be cleared up without causing the "dead" lustre to disappear, by passing the pieces rapidly through the acid mixture for bright dipping previously described, followed by an immediate rinsing. If they are permitted to remain too long in the bright lustre liquid, the dead lustre will disappear, and the operation must be begun anew.

If the bath for bright dipping be not conveniently at hand, it will suffice to rapidly pass the objects again, after rinsing, through the bath for dead dipping, which will clear up the dull appearance caused by their first immersion in the same bath.

The acid mixture for bright dipping may, after a long use, be employed, to a certain extent, for a dead lustre bath. The mode of operation remains the same.

A few varnishers employ a hot bath for dead lustre, prepared as follows:—

Old aqua fortis	. . . . .	4 to 5 volumes.
Sulphuric acid	. . . . .	1 volume.
Sulphate of zinc	. . . . .	8 to 10 per cent.

The last substance being gradually added when needed for increasing the deadness of the lustre.

The lustre thus obtained at first appears dull, ochreous, and yellowish; but after a thorough rinsing, a passage through the same bath for one or two seconds, and a final rinsing, it becomes clear enough.

The proportions which we have indicated for this bath need not be rigorously adhered to. They may be made to vary with the fancy and the habits of the operator, and will depend somewhat on the degree of energy of the old aqua fortis employed.

*Dipping in Nitrate of Mercury ("Quickening" Solution).*

In order to cause the deposited silver, etc. to adhere firmly, electroplaters have borrowed from the fire-gilders an operation which will be found of some importance in practice.

This operation consists in plunging the cleansed articles for a few seconds into a solution composed of—

Nitrate of mercury . . . . .	1 part (by weight).
Nitric acid, or preferably sulphuric acid . . . . .	2 parts " "
Water . . . . .	1000 parts " "

In dissolving the nitrate of mercury in water, a heavy, yellowish-white precipitate ensues, from the formation of a basic salt. By the addition of the acid, the precipitate disappears, and the solution becomes clear. It is well to stir the mixture before using it.

Certain authors recommend the nitrate of the sub-oxide of mercury (mercurous nitrate); but experience has shown that it is inferior to the nitrate.\*

The proportion of mercury salt above indicated will be modified with the size of the pieces and the nature of the alloy. For instance, less mercury will be needed for light pieces of jewelry which need a very thin deposit. On the other hand, more mercury is advisable for heavy objects, such as spoons, forks, and table ornaments, which should receive a thick deposit of gold or silver. The latter must come from the mercurial solution with a perfectly white and bright appearance, looking like silver, while the color of the former should show but little change.

\* In this case theory is confirmed by experience, since the exchange of bases takes place between oxides, analogously constituted (HgO and CuO).

It may be laid down as a rule that the behavior of the articles in the "quicking" solution is the test of the thoroughness of the preceding cleansing operations. If the cleansing has been properly done, the articles will come out of the "quicking" solution perfectly white and bright like silver. Where the cleansing has not been thorough, on the contrary, they will come out blackened or colored of various shades and generally without metallic lustre.

When the "quicking" solution becomes exhausted by use, it may be revived by the addition of a few drops of pernitrate of mercury; but it is more prudent to discard it and prepare a fresh solution.

We cannot insist too strongly on the necessity, especially when gilding or silvering by dipping, of allowing no intervals between the various operations of cleansing, which, excepting the time necessary for cleansing by fire or by alkalies, ought to take place in less time than is needed to read the following *résumé* :—

1. Cleansing by fire or by alkalies.
2. Dipping and rinsing in water.
3. Dipping in old aqua fortis and rinsing.
4. Dipping in strong aqua fortis and rinsing.
5. Dipping in the liquid for a bright lustre, or in the whitening bath, and rinsing.
6. Dipping in nitrate of mercury, and rinsing.

And, lastly, immersing the articles in the depositing vat.

This treatment, preparatory to obtaining the desired metallic deposit, answers equally well for copper, and all the alloys rich in this metal. German silver, however, on account of the nickel it contains, will sometimes be a little difficult to manage, and may require freshly prepared dipping baths. But in this, as in many other cases, the operator will quickly learn by practice all the slight

modifications which may be needed. As a rule, copper and its alloys must not be cleansed by mechanical means. But, if, notwithstanding the proper care, German silver does not cleanse well, it should then be cleaned with alkalis, carefully scoured with pumice powder and a hard brush, then passed through a moderately strong "quicking" solution, and introduced into the depositing vat.

The cleansing baths are commonly kept in covered vessels of glass, stoneware, porcelain, or other ceramic ware that will resist corrosion by the acids employed. Common earthen-ware or lead-glazed pottery must be rigorously excluded. The cleansing pots should be deep and comparatively straight in shape, and should be provided with a cover, or in lieu of this a plate of glass, to avoid loss by evaporation when the liquids are not in service (Fig. 10). The shallow dishes, usually called

Fig. 10.



Fig. 11.



capsules, present a large evaporating surface, and should be rejected for this purpose. Vessels of this form, however, are excellent for rinsing (Fig. 11).

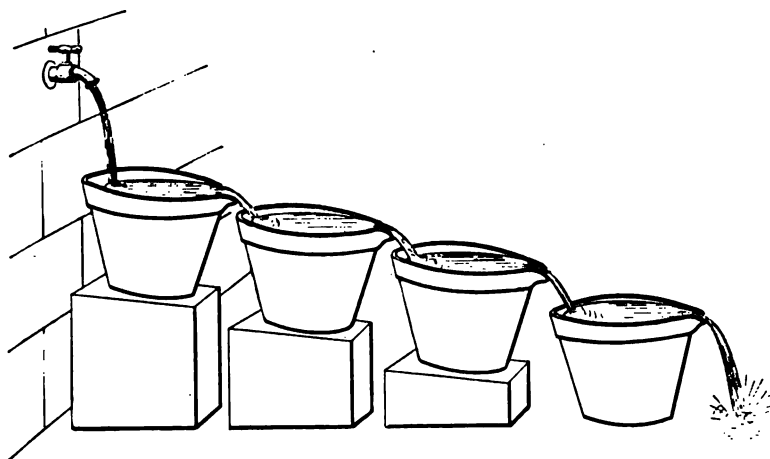
Electroplaters and varnishers should be provided with a considerable number of dipping pots of various sizes and



shapes, in order to accommodate articles of every description that they may not be obliged to clean the same piece in two operations for the need of a suitable vessel.

In some well-arranged establishments, a series of rinsing vessels is provided arranged in cascade form, the overflow of one flowing into the next lower one, and so on. The rinsing is begun in the lowest vessel and is completed in the highest, which is placed under the delivery cock (Fig. 12).

Fig. 12.



All the cleansing pots, as well as the swilling vessels, should be disposed in two rows in a deep trough lined with pitch or lead and furnished with a waste-pipe to carry off the foul water. The whole is placed beneath a hood communicating with a chimney, provided, for greater precaution, with a sliding glass-door, which the operator can raise or lower at pleasure, to facilitate the carrying off of the acid fumes. If the draft of the hood is not sufficient, a small fire may be kindled beneath it when at work; a lighted gas-jet is often sufficient for the purpose.

The "stripping" liquids, for removing the precious metal from old gilded or silvered ware, are likewise troublesome because of the acid vapors they give off, and for this reason should also be kept beneath the hood, and kept covered with a cover of plate glass. As to the "quicking" solution it is best to place it near to the gilding or silvering vats, and alongside of one or two large rinsing vessels of fresh water, for thoroughly swilling the articles immediately before transferring them to the depositing vat.

### CHAPTER III.

#### CLEANING SILVER.

FOR cleaning the metals to be mentioned further on, neither science nor practice furnishes us with methods as perfect as those we possess for cleansing copper and its alloys. In nearly all cases, we shall be obliged to have recourse to mechanical agents, which are much less favorable to success, since with their aid we cannot, as with acids, act simultaneously on every part of the subject. By such means, therefore, it is impossible to entirely avoid exposure of the cleansed surfaces, for a longer or shorter time, to the influence of the air, moisture, and injurious gases. We shall, however, proceed to describe the most perfect and expeditious processes for arriving at the best possible results.

In order to prepare this metal for receiving a deposit of any other metal, it must, as in all other cases, be freed from any surface impurity. We begin by heating the object to a dull red heat upon a slow fire. If the silver is pure, which very seldom happens, it becomes covered

with a thin bluish film resulting from the decomposition of organic matter, the result of handling. If, on the other hand, and as is nearly always the case, the silver is alloyed with a variable proportion of copper, the latter becomes oxidized and covers the piece with a grayish-black coating. While the piece is still hot, it is plunged into a boiling pickle of diluted sulphuric acid, which transforms the oxide into sulphate and dissolves it, while not sensibly attacking the silver.

If the heat has been sufficiently protracted for oxidizing all the copper on the surface, the object, when removed from the pickle, will present a perfectly dead white appearance. It is grayish, on the contrary, if the heating has been too short, and the operation must be repeated as many times as is necessary until success is attained. This is especially necessary with silver alloys of a low degree of fineness.

A few gilders, instead of heating silver over a naked fire, as above described, place it in sheet-iron boxes filled with a mixture of powdered borax, lime, and charcoal dust. In this case the borax dissolves the oxide of copper as fast as it is formed; as for the chalk and charcoal dust, we do not understand their utility, unless they are intended to prevent the formation of a small quantity of oxide of silver, which would also have been dissolved in the pickle. It is possible that these substances aid in distributing the heat uniformly over the entire surface of the article.

We derive this method from the gold and silver-smiths, who employ it for whitening and giving a dead lustre to their silverware.

If the objects to be cleansed are hollow, as certain medals formed of two shells soldered along their edges, it is absolutely necessary, before heating, to make a small hole which will allow of the escape of the confined air

which will be expanded by the fire. Without this precaution, the piece will certainly burst open, and possibly result in injury to the operator.

This aperture, though necessary for the above-named purpose, presents the inconvenience that when the piece is put into the pickle, the acid liquor takes the place of the air between the shells, and is difficult to remove. In order to prevent the spotting of the piece by this liquor, it is dipped for a few minutes into a very dilute solution of ammonia or of carbonate of sodium (sal-soda), which neutralizes the acid and prevents any injurious action upon the silver. It is then sufficient simply to place the rinsed article between layers of well-dried and warm sawdust which will absorb the saline solution which it still contains.

Certain operators use nitric in preference to sulphuric acid for this pickle. Where this is done, however, the water must be distilled, and the acid free from chlorine or hydrochloric acid, as otherwise the silverware will be covered with a bluish film of chloride of silver.

This method of cleansing silver is not suited for articles in which iron, zinc, etc. may be present. In this case it will be necessary to employ alkalies, and to polish afterwards with very fine sand or pumice powder, with the aid of a stiff and short brush or with the scratch-brush alone.

Silver, perfectly cleansed by the above operations of heating and pickling, is in condition to receive, without further treatment, a deposit of another metal; but it is evident that as it comes from the depositing vat, it will present the same dead lustre that the object had. We may take advantage of this fact to produce certain agreeable contrasts between different parts of the surface. To effect this, certain parts only of the surface may be pol-



ished with the aid of the burnisher, which we will describe further on. It is the general usage, however, before introducing articles of silver into the gilding vat, to submit them to the operation known as "scratch-brushing."

## CHAPTER IV.

### SCRATCH-BRUSHING—VARIOUS KINDS OF SCRATCH-BRUSHES— SCRATCH-BRUSH LATHE.

#### *Scratch-brushing.*

SCRATCH-BRUSHING is one of the indispensable and constantly recurring operations of the galvanoplastic art. It often precedes, and nearly always follows the operation of deposition, and therefore requires a special description.

"Scratch-brushing" consists in brightening the surface of an object, by the rapid and long-continued friction of the points of a collection of stiff and straight metallic wires.

The instrument used for this purpose is called a "scratch-brush," and its shape varies with the articles to be operated upon.

The hand "scratch-brush" consists of a bundle of fine wires of hardened brass, which should be selected from a large coil in order that the single wires which compose the bundle may have less tendency to bend or curve when in place.\*

To make a good hand scratch-brush, proceed as follows: select a coil of brass wire of the proper degree of fineness

\* Scratch-brushes of spun glass, with fibres of extreme fineness and elasticity, are also used for scouring highly delicate objects.

(Fig. 13), and bind it tightly with strong twine for about two-thirds of the intended length of the brush (6 or 8 inches) (Fig. 14). Then, with a chisel, cut the bundle of wire close to the cord at one end, and about 2 inches from it at the other end. Then dip the close cut end into a neutral solution of chloride of zinc, and plunge it into melted tin, which solders all the wires, and prevents their separation and injury to the hand of the operator.

The tool thus made may be used as it is, but it is preferable to fix it, by means of another string, to a thin wooden handle which projects above the soldered end (Fig. 15).

Fig. 13.



Fig. 14.



Fig. 15.



Fig. 16.



Scratch-brushes are also made by cutting a coil of wire for a length of from 12 to 16 inches, binding it in the middle, and doubling it so as to unite the two ends (Fig. 16). This process is less economical, and the wires have a tendency to become entangled.

Very small scratch-brushes are necessary for reaching sinuosities and depressions in the work, and other parts difficult of access.

An old scratch-brush, the wires of which have been bent in every direction, when fixed to a long handle, is useful for scouring the interior of certain pieces, such as Etruscan vases, coffee-urns, etc. (Fig. 17).

The varnishers on metals use, for rapid work, a kind of brush (Figs. 18 and 19) with long and stiff brass wires. Such brushes are only used for the preparation of articles of considerable size, such as clock dials, hearth furniture, and the like.

Fig. 17.



Fig. 18.



Fig. 19.

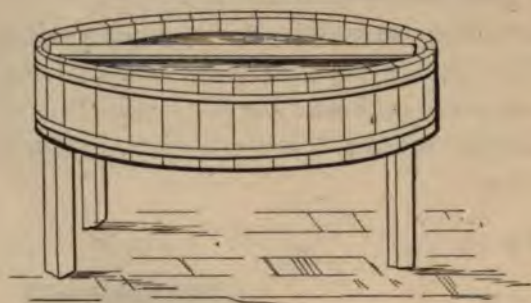


Scratch-brushing is scarcely ever done dry; the tool, as well as the pieces, must be constantly wet with a solution, which may set up a chemical action, but which most generally acts simply as a lubricant, and which, at the same time, carries away the impurities that the brush detaches.

The scratch-brush affords an excellent test of the quality of the metallic deposits; when good they are only polished by the friction; when bad they scale off, from defective adhesion to the subjacent metallic surfaces.

A good adjunct for scratch-brushing is a shallow wooden tub for the solution employed, with a board laid across it, nearly level with the edges, which, however, project a little above. This board serves as a rest for the pieces (Fig. 20).

Fig. 20.



The liquid employed is water and vinegar, or sour wine (stale beer), or solutions of cream of tartar or alum when we desire to brighten a gold deposit which is too dark. But that most generally used is a decoction of liquorice root, of horse-chestnut, of marshmallow, of soapwort, or of the bark of Panama wood, all of which, being slightly mucilaginous, allow of a gentle scouring with the scratch-brush, with the production of an abundant froth.

The board on which the piece is rested while being scoured, should be above the surface of the liquid. It suffices to frequently wet the scratch-brush and the piece by dipping in the solution.

Every five or six days the old liquid is removed by careful decantation, so as not to carry away the sediment at the bottom, which always contains a little of the precious metals, and these, together with various residues of the workshop, are collected to be treated afterwards, as we shall explain further on.



With small objects and articles of jewelry, the operator holds the scratch-brush as he would a writing pen, and moves it over the article with a back-and-forward motion imparted by the wrist only, the forearm resting on the edge of the tub (Fig. 21).

Fig. 21.



For larger articles of bronze, on the contrary, the operator holds his extended fingers close to the lower part of the scratch-brush, so as to give the wires a certain support, and, with raised elbow, strikes the piece repeatedly, at the same time giving the tool a sliding motion. When a hollow is met which cannot be scoured longitudinally, a twisting motion is imparted to the tool. These various motions are better understood when seen than when described.

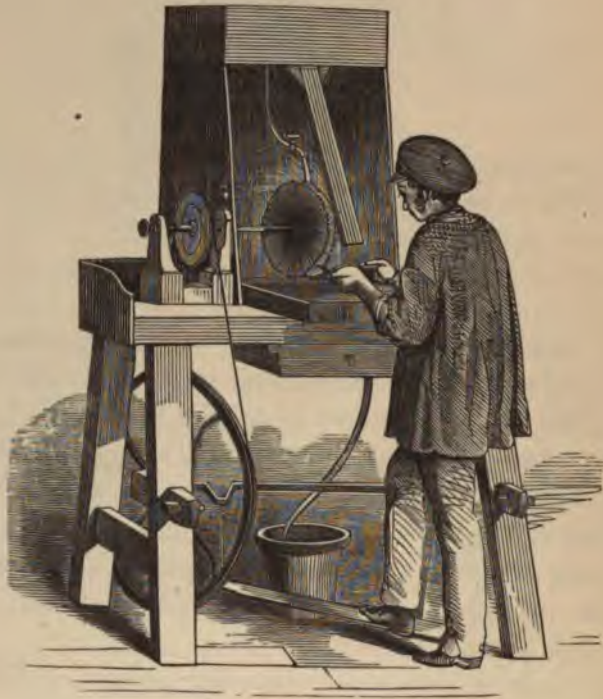
This mode of hand scratch-brushing is slow and tedious; besides, it is open to the inconvenience, on account of the irregular motion of the arm, of leaving on soft metals cross marks which have a bad appearance.

Circular scratch-brushes, in which the wires are arranged radially, are used for scouring articles that admit of their use, such as table-ware and plated wares in general. These circular scratch-brushes are attached to the spindle of a lathe, and the wires consequently all receive a uniform motion in the same direction.

*Scratch-brush Lathe.*

The scratch-brush lathe shown in Fig. 22 consists of a circular brush of brass wires, with a metal or wooden

Fig. 22.



case, mounted upon a spindle running in two bearings, and driven either by foot or by steam power. The wires

are from 2 to 3 inches long, and the form of the brush is shown in Fig. 23. The top of the brush revolves towards the operator, who presents the object to be scratched, to the bottom.

Fig. 23.



The brush is surrounded by a wooden cage or screen, to prevent splashing. It is open in front, and above it is placed a reservoir of one of the liquids above named (generally, stale beer), from which a slender jet of the liquid is allowed to dribble upon the top of the brush. In order to protect the operator against the water projected by the rapid motion, there is fixed to the top of the frame a small inclined board, which reaches a little lower than the axis of the brush, without touching it. This board receives the projected liquid and lets it fall into a zinc trough which forms the bottom of the box. Through an outlet provided in one of the angles of the trough a gum tube conveys the waste liquid to a reservoir below.

Fig. 24 represents a lathe of different form, which is well adapted for pieces of small size. It is likewise surrounded by a screen, to avoid splashing the operator and neighboring objects.

The above described hand and lathe scratch-brushes are made of wire of various gauges, from coarse to very fine, according to their intended uses.

When a hand scratch-brush becomes too short, the

twisted ends are cut off with a cold-chisel, and a new portion of wire is uncovered by removing part of the string wrapping. The best way to remove the twisted wire ends

Fig. 24.



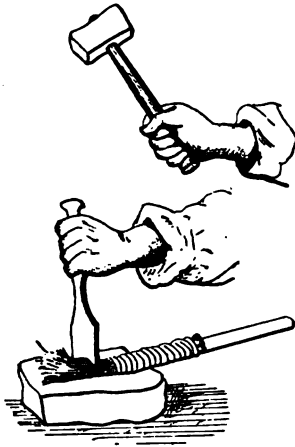
is by resting the scratch-brush upon a lead block, and cutting them off with a sharp cold-chisel, if possible with one stroke of the hammer. This operation is represented in Fig. 25.

Scratch-brushes must be carefully looked after and the wires kept in good order.



When they begin to curl, they are now and then beaten with a mallet of boxwood, upon a small block held between the knees, so as not to produce a dead stroke.

Fig. 25.



Scratch-brushes kept too long in water become hard.

If they become greasy, they are cleansed in caustic potassa; when oxidized, they must be cleansed in the mixed acid bath. This last operation, and even the dipping in aqua fortis, are sometimes resorted to for diminishing the size of the wires, and to soften the brush.

The lathe-brush is now and then turned over, face for face, in order to change the direction of the wires.

A few practical men have tried, by means of suitable devices, to run the lathe-brush constantly immersed in the liquid. But the resistance offered by the liquid requires so much more power to drive it that the method has been abandoned. If it were practicable this method of running the lathe-brush would be very desirable both on the score of cleanliness and because it would afford a more complete

protection against the oxidation of the wires by the acid fumes of the workshop.

Scratch-brushing is an important operation, the more so that many articles are delivered to the trade without any further manipulation. It is therefore advisable for beginners to become thoroughly practised in it before they venture to experiment upon articles of considerable value.

Another apparatus employed for scratch-brushing and polishing consists of a quantity of disks of muslin held together by side washers and nuts, and mounted upon a mandrel or arbor revolving with great velocity. These buffing wheels, as they are called, are flexible, and follow the irregularities of shape of certain articles. They receive now and then a small quantity of rouge or pumice-stone, or any other suitable polishing or abrading material.

## CHAPTER V.

### CLEANING BY ATTRITION (TUMBLING)

*plating*  
 VERY small articles, that cannot be scratch-brushed, are cleaned by attrition, either dry or wet. For this purpose the articles are placed in a long and narrow sack, to which a regular to-and-fro motion is given, thus occasioning a constant friction by the rolling of the articles over each other. In some cases, as where, for example, it is desired to lighten the gilding of pearls, diluted vinegar is used in the operation. In other cases sawdust from fir or box-wood is employed for drying the small articles, and at the same time increasing their brightness.

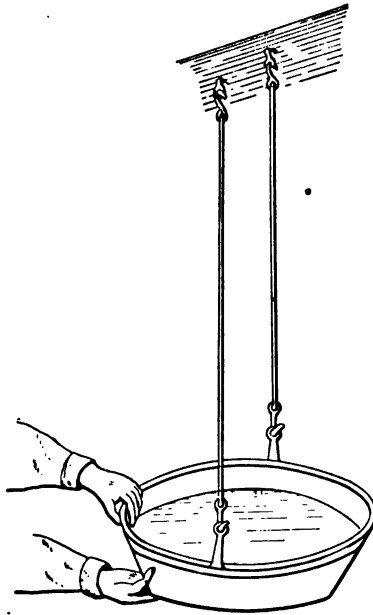
The operation is sometimes performed by hand. The articles to be brightened are introduced, together with



sawdust, bran, or sand, into a cloth sack about 4 feet in length; then, the ends being gathered into the hands with the thumbs inwards, a regular motion with both arms from right to left and from left to right is given to the bag, so that one of its extremities is alternately raised while the other is lowered. The inclosed articles must follow this motion, and by rolling over each other become gradually polished.

When it is deemed preferable to perform this operation in water, which is frequently the case, a device like that shown in Fig. 26 is found to be very serviceable. It con-

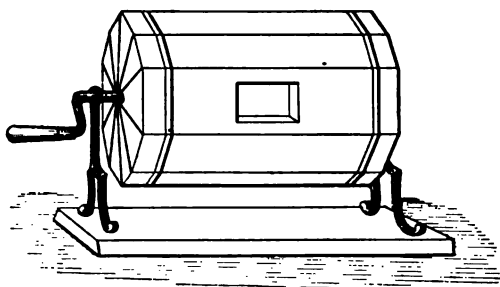
Fig. 26.



sists of a small tub suspended by long cords to a beam of the ceiling, to which the operator imparts a to-and-fro motion whereby the articles to be polished are made to roll one over the other.

Another apparatus for cleaning by attrition, is the tumbling-box shown in Fig. 27. It consists of a cylindrical or polygonal box, having a side door for the introduction of the work, and is mounted horizontally on

Fig. 27.



an axis furnished with a winch or pulley, so as to be revolved either by hand or power as may be desired. In order to prevent certain objects, like hooks for ladies' dresses and the like, from catching each other and accumulating into a mass, a number of nails or wooden pegs are fixed in the interior of the drum.

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## CHAPTER VI.

### GOLD-VARNISH.

ALTHOUGH, strictly speaking, this work should be confined to subjects relating to the deposition of metals, we assume that most of our readers will be interested in a description of those processes by which those magnificent varnishes are obtained which imitate so completely the appearance, freshness, and rich tones of real gilding. In

general, varnish is applied only upon copper and its more or less yellow alloys.

Gold varnishers operate as follows: After the pieces have been perfectly cleansed, scratch-brushed, and burnished if necessary, they are completely dried in the hot sawdust, and wiped clean with a fine cloth. A light coat of varnish is then applied with a fitch-pencil, and all excess of varnish removed or levelled with another flat brush of badger-hair or bristles. / The two brushes are kept together in the same hand, the varnish brush between the thumb and first two fingers, while the flat one (without a handle) is held between the other fingers and the palm of the hand. (Fig. 28.)

Fig. 28.



In this manner there is no interval in the use of the two brushes. The varnish is kept in a jelly-pot or other

similar vessel, across the top of which a string has been stretched. This string is intended for removing, by wiping, the excess of varnish taken up by the brush or pencil. (Fig. 29.)

Fig. 29.



The varnish which covers the burnished parts of the piece may be removed with a clean rag wetted in alcohol and wrapped around the finger. Another dry cloth finishes the drying. Sometimes the burnished parts are also varnished, but the operation is very difficult when their surface is considerable. Round wares, polished or burnished, may be varnished in the lathe.

After the varnish has been applied as uniformly as possible, the wares are put into a drying stove heated from about  $140^{\circ}$  to  $175^{\circ}$  Fah., or supported upon wires on top of a small furnace heated with smouldering charcoal-dust. The alcohol or essential oils of the varnish are rapidly volatilized, while the resins or gums melt and cover the objects with a glassy lustre. The heat must be sufficient to melt these gums, but low enough to avoid burning them. When the operation has been well performed, the pieces present a beautiful and uniform golden appearance, with no disfiguring red patches, which latter indicate an unequal thickness of varnish.

Varnishers have always at their disposition four varnishes of different shades,—*red gold*, *orange-yellow gold*, *green gold*, and *colorless varnish for mixtures*. This last is employed for diluting the first three and diminishing

the depth of their colors. Each of these various varnishes gives to copper the gold color peculiar to it, and, when mixed, intermediary shades. It often happens that the various parts of a large piece are different in composition and color, and the varnisher is obliged to impart the same shade of gold all over, by skilful combinations of varnishes. He thus succeeds in giving the same gold color to half-red copper, and to alloys of yellow and green brass.

But a small quantity of varnish is poured into the varnish pot at one time, in order to prevent it from thickening by evaporation, and, after the operation, the residue is poured back into the flask from which it was taken and kept well stoppered. The brushes and pencils must be often washed in alcohol, which may afterwards be used for diluting thick varnishes.

These varnishes are made by dissolving various resinous substances, like sandarach, benzoin, dragon's-blood, elemi, gamboge, etc., and tinctorial matters, such as saffron, annatto, alkanet, etc., in a mixture of alcohol with essence of lavender or of spikenard. All qualities of varnishes are to be found, but the more expensive are often the more economical.

To remove the varnish from an imperfectly varnished piece, or from an old one, it is immersed in alcohol or concentrated sulphuric acid, or, better still, in a boiling solution of caustic lye. The varnishing is then begun anew.



## CHAPTER VII.

CLEANSING ZINC—LEAD—TIN—CAST IRON—WROUGHT IRON  
—STEEL—ETC.*Cleansing Zinc.*

ZINC, next to copper and silver, is the metal that the electroplater has most frequently to deal with. This substance, which the ancient chemists had ranged among half metals (*i. e.* those whose brittleness unfitted them for many uses in the arts), has for some years past received so many improvements in its preparation that, at the present day, there are few metals applied to more various uses than zinc. It may be drawn out into quite tenacious medium-sized wire, which takes the place of lead and brass wire for many uses, and into wire so fine that it is possible to sew and embroider with it; it is rolled into plates whose properties of resistance and lightness render them often preferable to sheet lead, iron, or copper; it may be cast into all kinds of shapes and patterns, and the castings are sufficiently sharp and economical to permit the production of a great number of ornamental objects, such as were formerly made of copper, bronze, or brass. The clocks, cups, candelabras, chandeliers, statues, and ornaments of all kinds cheaply obtained with this metal have made these useful and artistic objects very common. It is sufficiently strong and sonorous for such uses, but its appearance is not prepossessing, and we cannot do better than to study the processes by which its surface is modified and rendered similar to that of more precious metals.



Objects of zinc are occasionally coated with gold or silver; but the common practice is to give them a coating of copper or of brass, which, after certain chemical manipulations to be described further on, may be made to present the various shades of bronze known as *verd antique*, Florentine, medallion, artistic, etc. But before undertaking any of these operations, the zinc, like all other metals, must first be cleansed of all its surface impurities.

The cleansing of zinc is performed as follows: it is dipped into a boiling solution of caustic potash, in which it should only remain a short time, since this liquid readily attacks the metal. It is then rinsed in fresh water; then immersed for a few minutes in water acidulated with from one-tenth to one-twentieth of sulphuric acid; then thoroughly swilled (in hot water if possible); and if it should be necessary, scoured with a stiff brush and pumice powder, or vigorously scratch-brushed. This last operation is especially useful when parts have been united with tin solder, which becomes black and dull by the action of the alkaline and acid baths.

These processes never give entirely satisfactory results, and the cleansing is much more thorough when the object is rapidly dipped into a cold mixture of—

Sulphuric acid . . . . .	100 volumes.
Nitric acid . . . . .	100 “
Common salt . . . . .	1 per cent.

and then still more rapidly rinsed in water perfectly free from copper salt, which will blacken the zinc.

If, instead of this quick cleansing of the zinc, we allow it to remain a little longer in the above mixture of acids, it acquires a fine “dead” lustre, which, in some cases, may be utilized for producing agreeable contrasts between the various parts of the same piece.

The “dead” lustre disappears and gives place to a

“bright” one, when the piece is replunged a number of times in the acid mixture, and rinsed rapidly after each immersion. When, as frequently happens, the different members of which a zinc article is made up, are united by tin or plumbiferous solder, these portions of the surface will come out of the cleansing liquor blackened; but the inconvenience is trifling, as a few strokes of the scratch-brush before immersion in the depositing vat suffice to remove it.

Zinc should be lightly amalgamated by passing through the “quicking” solution (nitrate of mercury), previously indicated for copper. This treatment insures greater density to the electro-deposits.

When, as often happens, in consequence of careless or defective cleansing of the pieces, the copper or brass deposit is unsatisfactory, having only a slight adherence at many points of the surface, it becomes necessary to repeat the operation of brassing or coppering. In such cases it is always prudent to completely “strip” the zinc of its cupreous coating. This is best accomplished by immersing it in strong nitric acid until on removal it appears completely black, which indicates the complete solution of the copper. An immersion, then, into the acid mixture above named will render the surface perfectly white, and in condition to receive a new deposit of copper. But, if the defective deposit was of considerable thickness, the “stripping” will be attended with much difficulty, and it rarely happens that we can succeed in saving the piece, for the reason that the zinc will be rapidly corroded in those places that are first stripped of their copper coating.



*Cleansing Lead, Tin, etc.*

Tin, lead, the alloy of these metals called solder, Algiers metal, Boulogne silver, Britannia metal, etc., are much more difficult to cleanse than zinc. The usual process is a rapid cleansing in potash lye and subsequent friction with a hard substance. The objects are sometimes plunged into diluted hydrochloric acid, but the first operation is nearly always necessary.

*Cleansing Cast Iron.*

Cast iron is cleansed by immersion for two or three hours in water containing one-hundredth part of sulphuric acid. After this bath, the metal is rinsed in cold water, and scoured with fine sand with the aid of a brush or a coarse rag, then again immersed in the acid pickle, rinsed, and plunged into the depositing vat. If more than one per cent. of sulphuric acid be added to the water, the length of the immersion must be shortened, otherwise the cast iron will be deeply corroded, and the carbon of the metal, which is insoluble in the pickle, can only with great difficulty be removed by the friction of the sand. In fact, cast iron that has been injured by too prolonged an immersion in the pickle, or by the use of a pickle unnecessarily strong, cannot be made to yield good results in the depositing vat.

For cleansing cast iron some operators prefer to use hydrochloric acid (muriatic acid) in place of sulphuric. A solution containing 5 per cent. of muriatic acid will be found to answer best; but the operation is more costly and more uncertain. A one per cent. solution of sulphuric acid will last for a week, and at the end of that time can be revived again by the addition of a fresh hundredth of acid.

In fact, we prefer a pickle thus revived, and consequently charged somewhat with sulphate of iron, to an entirely fresh one, for the former has the advantage over the latter of attacking the cast iron more uniformly. The action of hydrochloric acid, on the other hand, is much more energetic, and a portion of it is volatilized with the hydrogen gas disengaged during its action.

If it be desired to keep cast iron thus cleansed for some time before submitting it to the depositing bath, it is necessary to keep it immersed in a water rendered alkaline by the addition of caustic lime, potassa, or soda, or their carbonates; but caustic lime-water is the cheapest and simplest method, and cast iron which has remained in it for a few hours will not rust after quite a long exposure to a damp atmosphere.

#### *Cleansing Wrought Iron.*

The cleansing of wrought iron is effected in the same manner as that of cast iron, with the difference that it will bear a stronger pickle and a longer immersion. Reference is made here to ordinary wrought iron covered with a film of black magnetic scale or of red rust. Whitened, filed, or polished irons should be treated like steel.

#### *Cleansing Steel.*

Articles of polished iron or steel are usually cleansed by boiling in caustic lye (soda or potash), and afterwards gently scouring with pumice powder to slightly roughen the surface, and thus provide points of attachment for the metal to be subsequently deposited. They are then passed rapidly through a solution composed of—

Water	. . . . .	1000 parts (by weight.)
Hydrochloric acid	. . . . .	300 " "
or Sulphuric acid	. . . . .	100 " "



They are then well washed in fresh water to free them from adhering acid, and placed at once in the depositing bath. It is particularly necessary to guard against substituting nitric acid in place of the hydrochloric or sulphuric acid in the above named acid solution.

Referring to the gilding and silvering of iron and steel, Roseleur remarks, that, while they may be well gilded without an intermediary coating of copper, in the hot gilding baths to be described further on, the direct silvering is always imperfect and without adherence, on which account he considers it necessary to coat such articles with a preparatory coating of copper. As regards steel, as we shall show in the special chapter on silver-plating, Roseleur is evidently not familiar with what has been done in this country, and, if we mistake not, also in England. In all the large plating factories in the United States, not only is irreproachable silver-plating done upon table-knives directly on the steel, but such has been the practice for the past twenty-five years. The same may also be said in the case of Britannia metal so largely employed for articles of table service and artistic uses, of which Roseleur makes the assertion that "the direct deposit of the precious metals is difficult and does not adhere well." Not only is the direct silver-plating of such wares the universal practice in this country with the most admirable results, but it is questionable if coppered goods could command a market.

We shall, under Silvering, describe certain methods for preparing work, in use in some of the leading American establishments.

## CHAPTER VIII.

GALVANIC BATTERIES—DANIELL'S BATTERY—MODIFIED DANIELL — BUNSEN'S BATTERY — BICHROMATE BATTERY — GROVE'S BATTERY—MARIE-DAVY BATTERY—SMEE'S BATTERY—THE SAME MODIFIED—LÉCLANCHÉ BATTERY.

*Galvanic Batteries.*

THIS name is applied to certain forms of apparatus devised for the purpose of generating an electrical current of more or less intensity and quantity and with more or less constancy and uniformity.

As in static electricity and magnetism, so likewise in the production of the electrical current in the battery, the action is accompanied by the phenomenon of polarity; the current presenting properties conveniently known as *positive* (corresponding to the vitreous of static electricity) and *negative* (or resinous); the former manifesting itself at one extremity of the apparatus, and the latter at the other. A galvanic *couple* or *element* is constituted by the union of a single electro-negative agent with a single electro-positive agent. A number of such elements, coupled, as we shall see further on, constitutes a *battery*. The agents employed are commonly two dissimilar metals, which, when brought in contact by suitable means with a liquid capable of acting chemically on one of them, become electric. The degree of electric disturbance will depend on the nature of the dissimilar metals, and is termed *electro-motive force*. This electrical disturbance manifests



itself by the phenomenon of polarity in the two agents employed in the cell. The *positive* pole is designated by the + sign, and the *negative* by —.

The electrical current generated in a cell may be conducted to any desired point by means of metallic bands or wires, which are called *conductors*.

When the two poles or the metallic conductors are united, the *galvanic circuit is closed*, and a continuous flow of the opposite electricities takes place in opposite directions, in virtue of the disposition to re-establish electrical equilibrium. As rapidly, however, as the opposite electricities passing through the conductors are neutralized, the electro-motive force in the cell originates a fresh electrical disturbance. The consequence of this continuous production of electrical tension and its equalization, is the formation of a continuous flow of electricity, which is called a *galvanic current*.

When the extremities of the two conductors (not in contact) are plunged into a liquid that is capable of transmitting the current, the liquid in question completes the circuit, and is termed an *electrolyte*.

It is nearly always to the wire which proceeds from the negative pole of the battery (generally zinc) that we attach the object which is to receive the galvanoplastic deposit, and the object takes the name of *cathode*. The positive conductor is generally terminated by a plate or wire of platinum, or by a plate of the metal which the bath contains in solution, or by any other good conductor of electricity, like the graphite (carbon) of gas-retorts, for instance. This wire, plate, or conducting body is called the *anode*.

There are two classes of batteries: One class depends for its action upon physical agents solely, the thermo-

electric battery for example, and is comparatively feeble. On this account such batteries are rarely employed.

Batteries of the other class derive their action from chemical processes, decompositions, and recompositions, more or less energetic. It is with batteries of this class that we are specially interested.

There are many varieties of these batteries in use to-day. They have been modified extensively both in their shape and in the nature of their constituents. But we may summarize the subject by stating that the best battery is that which exhibits in the smallest volume the greatest energy, constancy, regularity, and economy.

We proceed, in the following, to describe the more important varieties of batteries which one may purchase, or, in case of necessity, construct for himself.

#### *Daniell's Battery.*

This battery develops quite a constant and lasting current; it is, however, wanting in intensity. It is especially adapted to those slow deposits which require to be thick and of uniform texture. A great advantage of this battery is that it will work without acids, and, therefore, without the production of gases or odors. It may be used in a private apartment without inconvenience.

Each cell of this battery is made of an exterior vessel of copper (Fig. 30), which is partially filled with a saturated solution of sulphate of copper (blue vitriol), and within which is placed a diaphragm of sail cloth, or hog's bladder, or, better still, a cup of porous porcelain or earthenware (Fig. 31), which causes the solution of sulphate of copper to rise to within about one inch of the top of the copper vessel. This diaphragm or cup is charged with a saturated solution of chloride of sodium

(common salt), into which is plunged a well-cleansed zinc plate (Fig. 32).

Fig. 30.



Fig. 31.



Fig. 32.



For the proper working of the apparatus, it is necessary that the levels of the two solutions should be practically the same. If there be any difference, the solution of chloride of sodium may be slightly above the other, as little inconvenience will result if a small quantity of salt becomes mixed with the sulphate of copper. On the contrary, if from a higher level the solution of sulphate of copper passes through the diaphragm, or porous cell, the zinc is immediately corroded and blackened, and the battery may cease to work.

When a single Daniell's element is employed, which seldom happens on account of the feeble intensity of the current, the conducting wire which supports the article to be electro-plated is connected with the zinc plate by a binding screw of brass, and the other wire supporting the anode is connected with the exterior vase of copper.

The solution of sulphate of copper must be kept constantly saturated with crystals of this salt, which may be laid upon a perforated shelf or box of copper in the upper portion of the solution, or suspended therein in a bag of linen or hair cloth. A similar process may be employed to keep the solution of common salt in a state of satura-

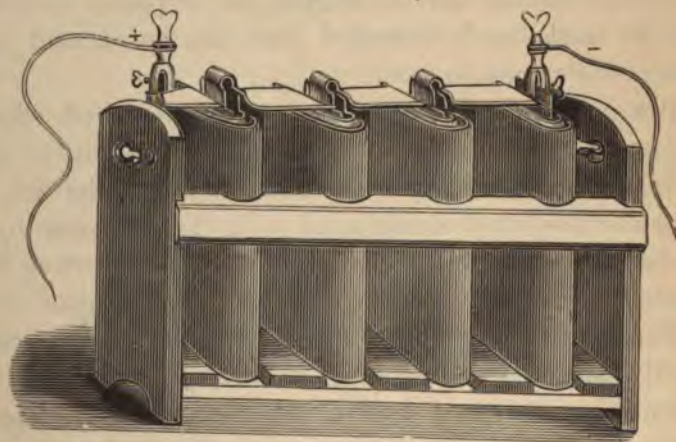


tion. A battery thus disposed may be kept in operation for three weeks, or a month, and sometimes longer.

When this battery is working, the copper of the decomposed sulphate is deposited upon the copper of the vessel, which thus increases in weight and in value. The zinc is slowly dissolved in the solution of common salt, and forms a double chloride of sodium and zinc, of no value.

When two, or a greater number, of Daniell's elements are to be coupled to form a battery, the zinc of the first element is connected with the copper of the second element by means of a well-cleansed metallic ribbon or wire, then the zinc of the second with the copper of the third, and so on, until the whole apparatus (Fig. 33) presents at one end a copper vase, and at the other a zinc plate, unconnected. A metallic wire, or ribbon, connects the anode with the free copper end, and a similar wire is attached to the zinc end and supports the cathode or objects to be electro-plated.

Fig. 33.



The battery of Daniell is susceptible of many modifications. One of these is shown in Figs. 34 and 35. In

this, the copper solution is placed in the porous cups, from each of which proceeds a copper rod with a perforated

Fig. 34.

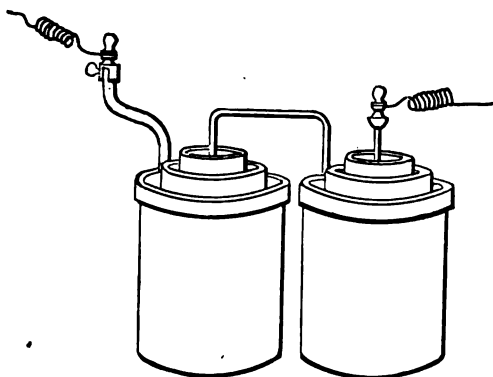


Fig. 35.

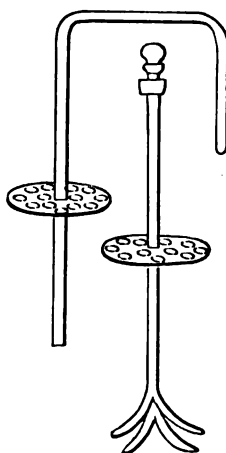


plate supporting crystals of sulphate of copper. Surrounding each porous cup is a cylindrical plate of zinc immersed in acidulated water or solution of common salt, contained in a cup of stoneware or glass.

In another modification, much used by electro-gilders of watch- and clock-works, and for telegraphic purposes, each element is composed of—

1. A cylindrical vase of stoneware, glass, or porcelain (Fig. 36);
2. A cylinder of zinc to which is soldered or riveted a ribbon of copper (Fig. 37);
3. A porous cell of baked clay (Fig. 38);
4. A glass balloon with a short neck, filled with crystals of sulphate of copper, and closed with a cork perforated with two holes, or having two notches cut on the surface along its length (Fig. 39).

These various parts are united in the following manner

to form a battery: the zinc plate is placed concentrically in the stoneware jar, then the porous cell is introduced.

Fig. 36.

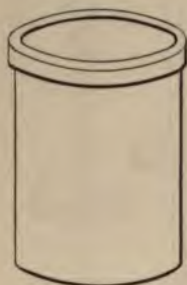


Fig. 37.

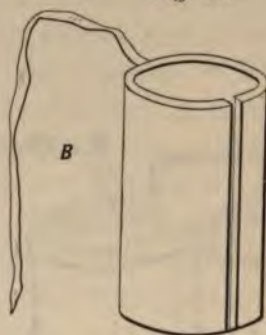


Fig. 38.



Fig. 39.



Fig. 40.

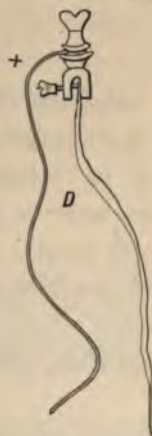
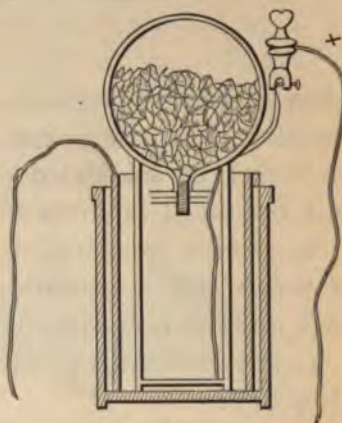


Fig. 41.

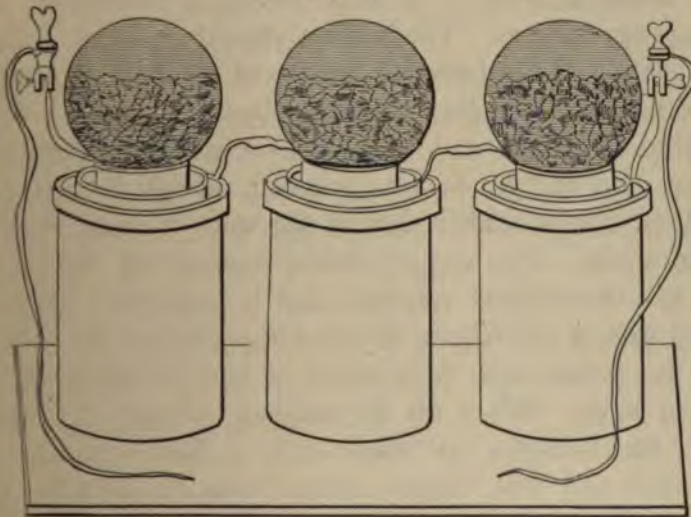


The copper ribbon of the zinc of the first element dips to the bottom of the porous cup of the next element in such a manner that when several elements are connected there will be at one end a free ribbon of the last zinc plate, and at the other end a free ribbon extending from the bottom of the last porous cup (Fig. 40). Then, the porous cell and the stoneware jar are filled to the same



level with water. The balloon containing the crystallized sulphate of copper receives as much water as it can hold, and the notched cork being put in place, the balloon is quickly inverted with its neck in the water of the porous cell. The battery is ready to work twenty-four hours after. The ribbon of the zinc end is attached to the conductor which supports the objects to be electroplated, and that of the other end of the cell is connected with the anode. Fig. 41 shows a vertical section of a single cell of the kind just described; and Fig. 42 represents a battery of three such cells.

Fig. 42.



This form of the Daniell battery operates as follows: the copper sulphate contained in the balloon dissolves in the water surrounding it, and, as this saline solution is denser than water, it descends into the porous cells through one of the notches of the cork, while at the same time an equal volume of the lighter water ascends through the other notch of the cork. In this manner

the sulphate of copper in this balloon is gradually dissolved, and a constant current is established, the denser liquid, more heavily charged with sulphate of copper, descending through one notch of the cork, while the lighter liquid ascends through the other. Simultaneously with the closing of the circuit, chemical action sets in. The sulphate of copper is decomposed, the sulphuric acid passes through the porous cup by exosmose, and acts upon the zinc in the outer vessels, and copper is deposited upon the copper bands in the porous cups, which are connected by conductors, as above described, with the zincs.

In order that this battery may work regularly for six or seven months, it is only necessary to replace the evaporated water. The balloon should be large enough to contain at least several pounds of sulphate of copper crystals, and the zinc cylinders should be from 7 to 8 inches in height and from 4 to 5 inches in diameter. The zinc should be amalgamated, in which case the action, though a little slow at the start, is more regular afterwards. The copper ribbon receives all the metal of the decomposed sulphate, and it sometimes happens that part of the copper becomes deposited on the bottom of the porous cell, from which it may be removed by aqua fortis. When all the sulphate of copper is used up, the balloons are filled with a fresh quantity of crystals and new copper ribbons inserted to take the place of those rendered too voluminous. This variety of battery is in extensive use, and properly so, for telegraphing and electric signalling. If gilders were willing to employ such batteries, with elements sufficiently large and numerous, they could dispense with acid batteries which require fresh charging every day; but, whether right or wrong, they still prefer the Bunsen battery,

which, while much less bulky, is more energetic in its action.

If it be desired to start this form of the Daniell battery at once, it is sufficient to add a small quantity of sulphuric acid or of common salt to the water in which the zinc is immersed.

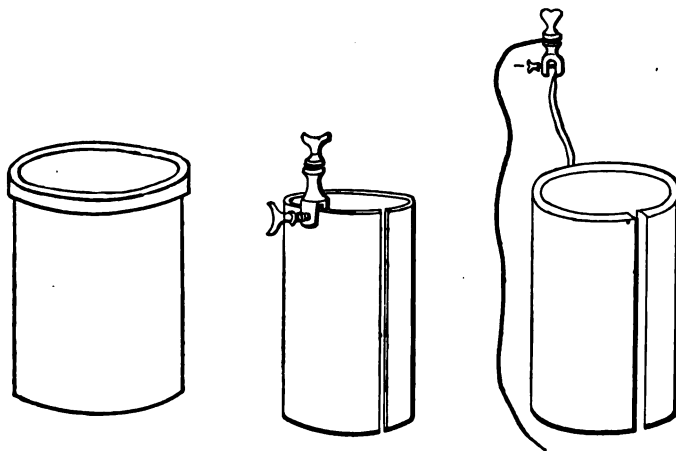
### *Bunsen's Battery.*

The Bunsen battery, which, like the Daniell, is susceptible of many modifications, is shown in its usual form below. It consists of an outer vessel of stoneware or glass, Fig. 43, which is half filled with diluted sulphuric

Fig. 43.

Fig. 44.

Fig. 45.



acid (about  $\frac{1}{10}$  acid). In this is placed a cylinder of amalgamated zinc, furnished with a brass binding screw (Figs. 44 and 45) where a single cell is employed or where it forms one of the terminals of a battery, or with a copper band (Fig. 46) where connection must be made with another couple. Within this comes a porous cup of baked clay (Fig. 47), and within this diaphragm again, a prism of gas-carbon (Fig. 48), with binding screw of one



or the other of the several forms shown in Figs. 49 to 52, according as it is to form the terminal of the battery,

Fig. 46.

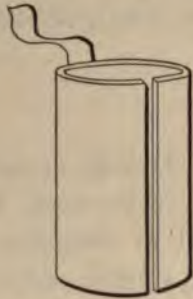


Fig. 47.



Fig. 48.



or to be united with the band of a zinc of the adjacent element. Fig. 53 shows the binding screw of a zinc terminal.

Fig. 49.



Fig. 50.



Fig. 51.



Fig. 52.

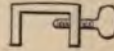


Fig. 53.



The wire conductors of copper, for greater precaution, should be insulated by a covering of cotton, silk, caoutchouc or gutta percha, and their extremities alone should be denuded of their insulating covering to permit of making the necessary metallic connections.

The carbon having been placed in the diaphragm, this is filled with strong nitric acid, the proper connections made as before indicated, and the battery is ready for use.

#### *Coupling a Number of Cells.*

When several elements are to be connected, they are placed near each other, though without touching, and

the first carbon is left free for the attachment of the wire conductor of the anode. The ribbon or band of the first zinc is bent over and clamped between the jaws of the brass binding screw and the carbon of the second element, and so on, in such a manner that the terminals of the battery will be, at one end a free carbon, and at the other an independent zinc. This zinc, for greater convenience, is furnished with a double binding clamp such as is shown in Fig. 53, from the upper binding post of which proceeds the conducting wire, establishing connection with the objects to be electro-plated.

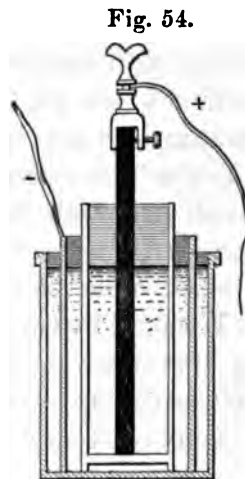
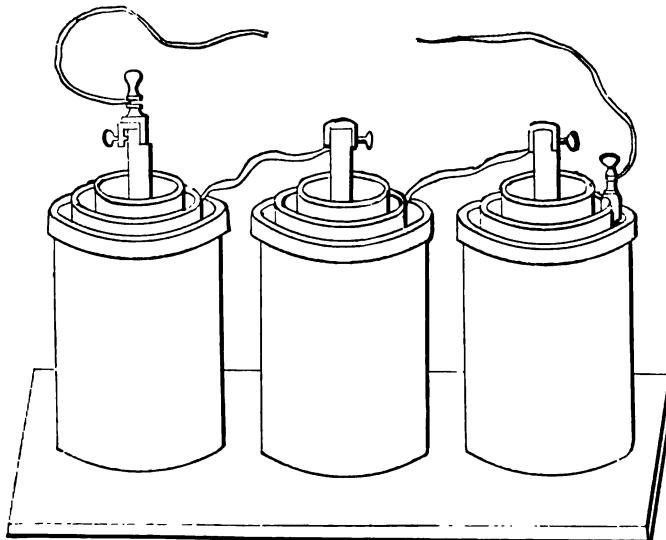


Fig. 54 represents a vertical section of a single cell of this description; and Fig. 55 a coupled battery of three cells.

Fig. 55.





Roseleur prefers the use of a small quantity of his amalgamating salt (the formula of which is given further on), as an addition to the sulphuric acid in the outer vessel in which the zinc is placed, to the usual method of amalgamating with mercury direct, since the salt only affects the zinc below the liquid, and the risk of rendering the metallic connections brittle is thereby obviated.

The ordinary usage, however, is to provide a wooden trough sufficiently large to rest one of the zincs in it, to place some mercury in the bottom of the trough, and cover it with a small quantity of diluted sulphuric acid. By laying the zincs successively in this trough and turning them around, so that all parts of them shall in turn come in contact with the mercury, they are rapidly and perfectly coated with the metal.

#### *Bringing Batteries into Action.*

The battery will generate an electrical current as soon as the *circuit is closed*; that is to say, as soon as the two extremities of the conducting wires proceeding respectively from the last zinc and the last carbon of the battery, are brought into electrical communication, which may be either by direct contact of the wires, or through the intermediation of a bath or liquid conductor of any description. It will often happen that a battery which appears to be properly set up, will not work. On examination, this will generally be found to be due either to the presence of foreign substances (oxide) preventing clean metallic contacts, or to improper connections in setting up, and the like. Difficulties from these causes disappear on removing the cause.

Before using a battery, it is always necessary to test its working condition. For this purpose, the end of the negative wire should be brought in contact with the terminal

carbon, when, if the battery is working properly, a spark should be seen at the instant contact is made. A similar experiment made with the positive wire should produce the same result. A simpler plan is to rest the ends of the terminal wires a short distance from each other upon a piece of battery carbon or upon a file, and then to scrape with one wire over the surface while the other remains in contact. Numerous sparks should immediately appear.

When one element of a battery is wrongly put up, the defect may be located by successively presenting the end of the negative wire to the carbon of each element. That which does not produce a spark belongs to the defective element.

A common cause of the stoppage of the current is an excessive porosity of the porous cells. This will generally be indicated by the deposition of a whitish coating of zinc salt upon the surface of the carbons, which speedily checks the flow of the current. When this defect is observed, it is necessary to substitute a fresh porous cell for the defective one, and to thoroughly remove the deposit from the carbon by scraping. This state of things is generally observed only after the battery has been working for several days without renewal of the liquids, or when the same has been too strongly acidulated.

It may also happen that the battery will cease working from too great an accumulation of sulphate of zinc, which, when the solution becomes saturated, crystallizes upon the zinc, and prevents any further action. The acid solution is then removed, a fresh one substituted, and the zinc cleaned and returned. Rolled zinc is preferable to cast.

#### *Keeping the Battery in Order.*

Every twenty-four hours, and sometimes oftener, the losses of the battery must be made good by adding, with-

out taking the elements apart, a quantity equal to about two teaspoonfuls of amalgamating salt and about two tablespoonfuls of sulphuric acid to the liquid of the outer vase in which the zincs are placed, and stirring with a glass rod. Nitric acid, to replace that evaporated, is put into the porous cell. This manner of operating may be kept up for five or six days, after which it will be necessary to take the battery apart, to empty out the old liquors and to recharge afresh.

We may conveniently introduce, at this point, the accompanying table (after Ferrini) exhibiting the electromotive force of a number of the better known forms of batteries, which may be useful for comparison. Several of the forms of batteries named in the table, notably those of Grove, Smee, and Léclanché, will be found described in detail, farther on.

TABLE OF THE ELECTRO-MOTIVE FORCE OF BATTERIES.

(AFTER FERRINI.)

Name of element.	Constitution.	Electro-motive force in VOLTS.	Authority.
Wollaston	Amalgamated zinc and copper in dilute sulphuric acid (1 : 12)	{ 0.886 0.861 0.719	Clark and Sabine. Sprague. De la Rive.
Smee	Amalgamated zinc in sulphuric acid; platinized silver, or platinum in sulphuric acid (1 : 12)	{ 1.098 1.107 0.541 1.192	Clark and Sabine. Sprague. De la Rive. Naclari.
Daniell	Amalgamated zinc in sulphuric acid (1 : 4); copper in saturated solution of copper sulphate	{ 1.079 do. do. do.	Clark and Sabine. Sprague. De la Rive. Naclari.
do.	Zinc in dilute sulphuric acid (1 : 12); copper as above	{ 0.978 0.98	Clark and Sabine. Du Moncel.
Léclanché	Zinc in sal-ammoniac, carbon with manganese peroxide in sal-ammoniac	{ 1.481 1.561 1.942 1.259	Clark and Sabine. Sprague. De la Rive. Beetz.
do.	Zinc in solution of common salt; carbon with manganese peroxide in common salt solution	{ 1.498 1.360 1.34	Sprague. Naclari. Du Moncel.
Marie Davy	Zinc in dilute sulphuric acid (1 : 12); carbon in mercurous sulphate	{ 1.524 1.542 1.482 1.440	Clark and Sabine. Sprague. Naclari. Du Moncel.
Grove	Zinc in dilute sulphuric acid (1 : 12); platinum in fuming nitric acid	1.956	Clark and Sabine.
do.	Zinc as above; platinum in nitric acid of 1.38 sp. gr.	{ 1.524 1.542	Clark and Sabine. Sprague.
Bunsen	Zinc as above; carbon in fuming nitric acid	{ 1.964 1.95	Clark and Sabine. Du Moncel.
do.	Zinc as above; carbon in nitric acid of 1.38 sp. gr.	{ 1.888 1.941 1.880	Clark and Sabine. Beetz. Naclari.
do.	Zinc as above; carbon in bichromate of potassium	{ 2.028 1.905 2.120	Clark and Sabine. Sprague. Naclari.
Grenet	Zinc and carbon in bichromate of potassium	1.825	Naclari.

Although amalgamated zinc is scarcely corroded, even in a very acid solution, when the circuit is not closed, that is to say, when the two poles are not electrically connected by direct contact, or through a conducting liquid, it is nevertheless preferable to take the batteries apart every evening, which should be done in the following manner:—

Fig. 56.



1. All the binding screws are loosened, and, if necessary, cleaned.
2. The carbons are removed, and, *without washing*, deposited in a vessel especially provided for them.

3. The porous cells are removed, and their acid poured into a special vessel. The cells are *not washed*.

4. The zincs are removed from acidulated water, and simply placed in an inclined position upon the edges of the stone-ware jars as shown in Fig. 56. To set up the battery again, these operations are performed in reverse order.

#### *Important Observations on Batteries.*

It is prudent to have a duplicate set of cells, or, at least, a supply of those parts which are easily broken.

Batteries should be kept in a place where the temperature does not greatly vary, as cold arrests their action, and extreme heat increases it too much, and lessens their constancy.

Where it is possible, they should be placed in a box or other receptacle about as deep as the height of the



jars, so that they may be readily manipulated. They should not, however, be placed above the depositing vats, for the reason that, should any of the mercurial solution be spilled in handling the cups, it may run down the wires into the metallic baths, and contaminate them. This box or closet should have means of ventilation, in such a way that the air coming in at the lower part, will escape at the top through a flue, and carry away with it the acid fumes constantly disengaged.

It is well, when possible, to keep the batteries in an apartment separate from the operating room, where the depositing vats and the metals to be treated are located, for the reason that these are always injuriously affected by the acid vapors given off. The current is then conducted into the work-room by wires passing through holes in the wall, and covered with *gutta-percha*.

It is permissible to establish branch circuits, by leading branch conductors from the main conductors, for the purpose of operating several baths with the same battery, either at the same time or alternately. But it is preferable to appropriate a separate battery to each metallic solution, because, of two baths thus connected, that which furnishes the better conductor will take nearly all the current.

#### *Grove's Battery.*

This battery is analogous to that of Bunsen, and differs from it only in having a strip of platinum foil which plunges into the nitric acid, and replaces the prism of carbon. This foil is supported by a small brass arm (Fig. 57) attached in turn to a round band fitting on a collar at the top of the outer cup. This arm is provided with a binding screw of brass, soldered to its upper part, when several couples are to be united. Fig. 58 shows a

vertical section of a single Grove element, and Fig. 59 represents three such elements coupled.

Fig. 57.



Fig. 58.

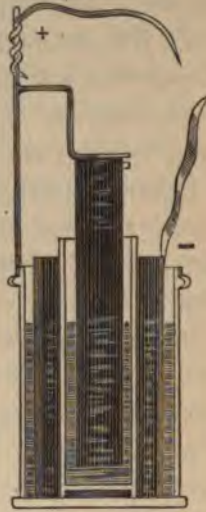
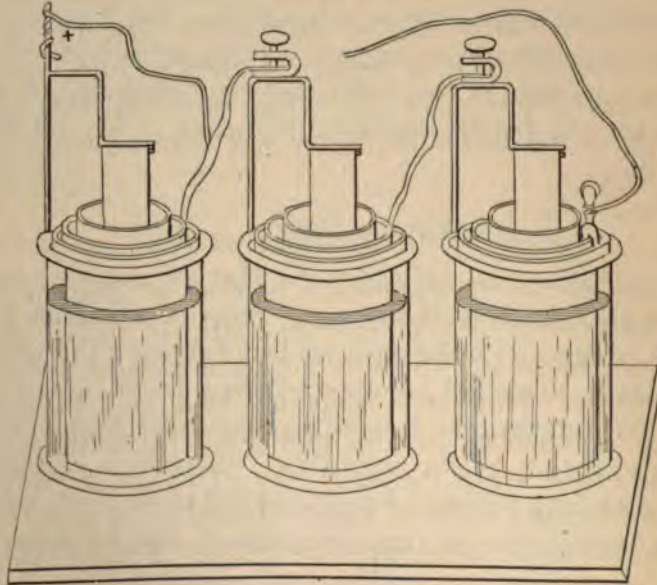


Fig. 59.



The only objection to this battery is its high cost, due to the platinum employed. Mr. Hulot has proposed to substitute a foil of aluminium for that of platinum. In spite of this substitution, however, the price is still too high, and prevents the extensive use of the battery, which, otherwise, gives satisfactory results.

We may mention, among batteries having some analogy with that of Bunsen—

1. The Grenet battery, in which a solution of 100 parts of water, 10 of bichromate of potassa, and 10 of sulphuric acid in the porous cell, replaces the nitric acid employed by Grove and Bunsen. This battery does not emit acid fumes, but this advantage does not compensate for the rapid incrustation of the carbon with oxide of chromium, which quickly arrests the galvanic current.

2. The Marie-Davy battery, in which sulphate of mercury, slightly damp, replaces the nitric acid in the porous cell. The working expenses of this battery are very high, and it is used only in the telegraphic service, and there but little, the preference being given to the Daniell battery with balloon, previously described, or to the Lécanché battery, which will be described further on.

#### *Smee's Battery.*

This battery is very simple in construction, requires only one liquid, easily procurable everywhere, and does not emit any smell or acid fumes. All these advantages adapt it especially to the needs of provincial electro-platers and jewellers who often practise their gilding and silvering operations in their work-rooms.

It is composed (Fig. 60) of a rectangular wooden frame, of moderate thickness, open at the top, with three internal parallel grooves, parallel to its longest diameter. The middle groove receives a plate of silver, platinum,



gold, or copper which has been strongly gilt, silvered, or platinized. The surfaces of this plate should be rough or matt. Two plates of strongly amalgamated zinc are placed in the other two grooves, each presenting, there-

Fig. 60.



fore, one of its faces to the central plate. They should be placed at a very slight distance from, but not in contact with, the central plate which they inclose, and should be connected with each other by a metallic wire or ribbon. The positive wire proceeds from the central plate, and the negative from any point of the zincs, and the whole apparatus is immersed in a solution containing common salt, or in water acidulated with one-tenth of sulphuric acid. Several of such elements may be united together by connecting the zinc of the first with the central plate of the second, and so forth. This battery, therefore, operates with a single liquid and without diaphragm or porous cell.

Roseleur has modified this battery in the following manner: In place of the wooden frame he provides a trough of gutta-percha. The two narrow sides (Fig. 61) have three parallel grooves half an inch deep, and about a

quarter of an inch distant from each other. The central groove receives a plate of gas-carbon (Fig. 62), which

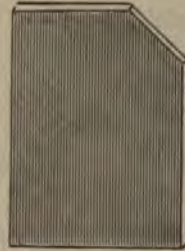
Fig. 61.



Fig. 62.



Fig. 63.



advantageously replaces the plate of silver, etc., of the previously described forms. The two other grooves receive

Fig. 64.



two plates of amalgamated zinc with one of the upper corners cut away, as seen in Fig. 63. A double binding



screw, for the positive wire, is attached to the plate of carbon where the two zinc corners have been cut away, and another large binding screw unites the two zinc plates, and carries, at the same time, the negative wire.

This battery will work by filling the cell with water saturated with common salt, or acidulated with one-tenth of sulphuric acid. It is evident that batteries of several elements may be disposed (Fig. 64) by arranging them like the ordinary Smee batteries, from which they differ but slightly.

When acidulated water is employed as the excitant, the addition of amalgamating salt is recommended to keep the zincs in good condition, and to avoid the disengagement of hydrogen gas; if, on the contrary, a saturated solution of common salt is used, no amalgam is necessary.

#### *The Léclanché Battery.*

Within the past few years, a new order of battery has been developed, which combines to a high degree, in its operation, all the desirable conditions of economy, inoffensiveness, and constancy.

Like the Daniell, these batteries operate without acid, they evolve neither gases nor vapors, and they maintain their activity for more than a year, requiring no other attention than to replace the water as it evaporates. They have the advantage over the Daniell, of requiring only a single exciting liquid, of consuming very little zinc, and of not giving rise to objectionable crystallizations, which, in time, clog up the porous cup and interrupt the current.

As an offset to all these advantages, it is proper to state, that the Léclanché battery is much less powerful (with equal surface) than the battery of either Bunsen, Archereau, or of Grove, which require the use of acids,

and which, when the circuit is closed, depolarize themselves very rapidly, and which consequently require to be frequently recharged.

The battery here referred to, though insufficient for the requirements of the great workshops where the work is incessant, will, nevertheless, be very serviceable to provincial jewellers and platers, and to the gilders of watch movements, who only occasionally need the battery, or who, on account of the smallness of the surfaces of the objects they need to gild or silver, require only a feeble and sluggish current.

Léclanché constructs his battery as follows:—

1st. The exterior vessel is of glass, is rectangular in shape, thus permitting the battery to be disposed in the smallest possible space, the adjacent vessels fitting snugly the one against the other. This exterior vessel is provided with a cylindrical neck, prolonged at one side after the fashion of a spout. This serves as a convenience in filling or emptying the vessel of liquid, and for the reception of a rod of zinc.

2d. A rod of zinc, rolled or cast, which passes through the spout just spoken of, to the bottom of the vessel (this zinc may be amalgamated). It is provided with a wire conductor covered with gutta-percha except at its extremities.

3d. In the centre of the glass vessel there is a diaphragm or porous cup in which there is permanently fixed a strip of gas carbon, with a metal piece carrying a binding-screw at the top, soldered to the carbon by means of lead poured into the joint. Into the empty space left between the wall of the porous cup and the carbon strip there is solidly pressed a mixture of equal parts of wood charcoal and binocide of manganese, both finely pulverized; and, as this portion of the cell should serve for an

almost indefinite period, the mixture in the porous cup is covered with a species of resinous mastic, which covers up the powder, and intimately unites the carbon and the diaphragm. It is only necessary to leave a very small opening, say about a quarter of an inch, in this mastic in order that the liquid of the battery may be able to gain access to it. The metallic cap at the top of the carbon

Fig. 65.



strip is likewise covered with this varnish except at the binding-screws. Fig. 65 gives a very good idea of the appearance of this battery, which is charged with the following simple solution:—

Ordinary water	. . . . .	1000 parts.
Sal ammoniac	. . . . .	80 "

If a more concentrated solution of sal ammoniac is used than that indicated above, the double chloride of ammonium and zinc which is formed by the action of the battery, will crystallize on the rod of zinc, and by interfering with the action of the liquid, interrupt the current.

It is sufficient, once in about two weeks or once a month, to add a little water to each of the cells, to replace that lost by evaporation.

When, in the course of time, it is found that the battery ceases to give a current, when the sal ammoniac solution is used up, or the zincs have become incrustated and inert, the battery is taken apart, the zincs are washed and scraped clean with an old knife or other convenient tool. Having thus removed from the zincs the coating of double chloride which incrustated them, and which the sal ammoniac could not penetrate, it is sufficient to couple the elements anew, and to refill the vases with the sal ammoniac solution. It is also necessary from time to time to look after the cleanliness of the binding-screws. Lastly, if the leaden top of the carbon loses its resinous coating, it becomes necessary to re-varnish it, without which precaution it will become covered with a coating of white chloride of lead, and rapidly destroyed.

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## CHAPTER IX.

### DYNAMO-ELECTRIC MACHINES.

THE art of electro-plating has received a great impulse within the past decade by reason of the great improvements that have within this period been made in the construction of dynamo-electric machines, by which me-



chanical energy, generated by the steam-engine or other convenient source of power, may be directly converted into electrical energy. The advantages of these machines as the source of electric current over the voltaic batteries just described are numerous and decided. The latter, at the very best, are troublesome to manage; they only give out their full power when freshly charged, and, as the chemical actions, upon which they rely for their power, progress, they deteriorate in strength and require frequent additions of acids or salts, or to be freshly charged; and their use demands constant vigilance and attention. From these and other objectionable features the dynamo-electric machine is almost entirely exempt. The source of power is under such control that electrical currents of any desired strength may be instantly generated by simply throwing on a belt, and maintained with practically perfect uniformity for hours at a time. The amount of attention required in its operation is infinitesimal as compared with the constant watchfulness demanded by the battery, rendering the machine vastly more convenient to use, and the rapidity with which large quantities of metal may be deposited with the machine with a comparatively small consumption of mechanical power renders it a much more economical source of electrical current. The importance of adapting machines of this class for the work of electrotyping and electro-plating has been steadily kept in mind by successive inventors, and the result has been the production of plating machines that answer so satisfactorily, every reasonable requirement of the electro-plater, that to-day there is scarcely an electro-plating establishment, worthy to be called by this name, in the United States, that has not discarded the voltaic battery and adopted one or the other of many varieties of the dynamo-electric machine in its place. As a surplus of

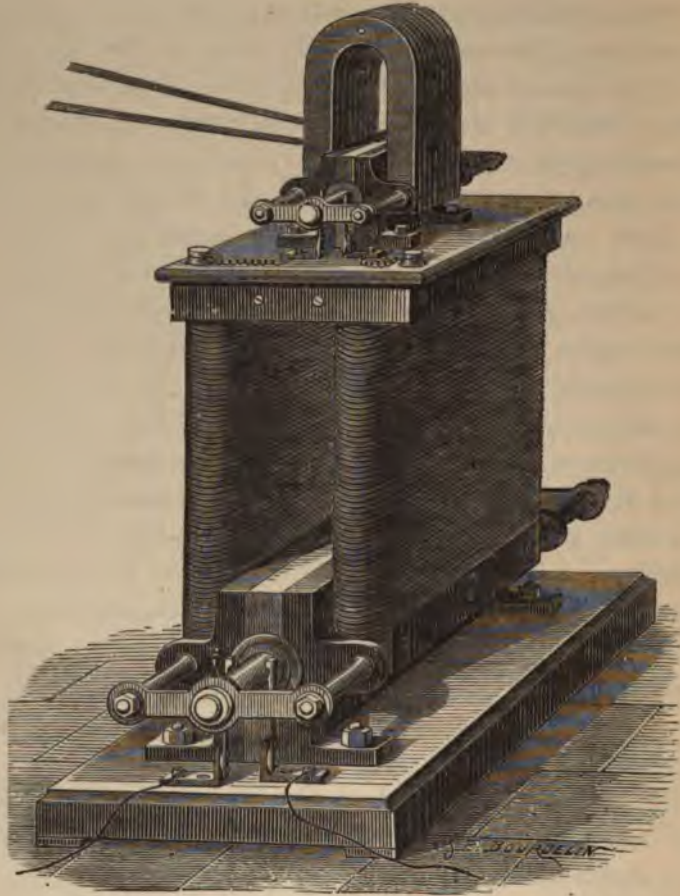


steam power is frequently at hand in all the larger establishments, for driving presses, lathes, grinding and polishing wheels, etc., the few horse-powers, more or less, taken off by one or several plating machines is an item that scarcely makes itself felt in the expense account. It would be manifestly out of place in a work of this character to enter into a lengthy discussion of the theory and action of these machines, for which the reader is referred to special treatises on the subject. We shall only refer to the subject in connection with a brief description of the several more prominent machines. In all these machines the currents developed in the armature, by its rotation, flow alternately in opposite directions. This change in the direction of the current, while not unfitting the machine for certain applications of electric lighting, would of course render it useless for the purposes of electro-metallurgy, since what it would deposit at one moment it would dissolve at the next. In order, therefore, to commute these alternating currents, that is, to change them into direct currents, or those flowing in one and the same direction, appliances called commutators are necessary.

Dynamo-electric machines, therefore, may be divided into two classes, viz., those with alternating, and those with direct currents.

The Wilde machine, Fig. 66, which was one of the first, if not the first, to be applied to the practical use of electroplating, consists of two machines, namely an excitor, in the form of a magneto-electric machine, in which a current is generated by means of a series of permanent magnets, and a revolving Siemens armature. The current thus generated in the excitor, is passed around a large electro-magnet, between the poles of which a large armature of the same kind is made to revolve. By this means a current is

Fig. 66.



induced in the large armature which is utilized for electroplating purposes.

The Wilde machines, which at one time were in use in a number of establishments in the United States, principally, however for electrotyping, have been almost entirely superseded by machines of simpler construction and greater efficiency. In England, it would appear that they are still to some extent in use. (See Gore,



*Electro-metallurgy*, p. 349.) As to the efficiency of the Wilde machine, this authority states, that "a single multiple armature machine of Wilde's (at the smelting works of the Messrs. Elkington & Co. at Pembrey near Swansea) deposits four and a half hundred-weights of copper in 24 hours. The machines have also been successfully applied to the economic production of coppered rollers for calico printing." (Power consumed not stated.)

An important step in the simplification of these machines was taken, when it was discovered that the exciting apparatus could be dispensed with, and that the slight amount of residual magnetism, remaining in the electro-magnet after it has once been charged, is sufficient to induce a current in the armature, which may be made in turn to excite the magnet, and this in turn to induce a still stronger current in the armature; this mutual reinforcement, known technically as "the reaction principle," going on until the point of magnetic saturation is reached, beyond which the current cannot be increased except by increasing the speed of the machine.

In endeavoring to apply this principle to the construction of machines for electro-plating, a serious difficulty was encountered in the tendency of the machine to suffer a reversal of its polarity by reason of a polarization of the electrodes of the depositing solution. As such depositing solution when charged and properly connected plays the part of a battery, tending to generate a current flowing in opposition to that generated by the machine, it is obvious that, unless some means of prevention were discovered, whenever from any cause, whether by an accident or by stoppage, the electro-motive force at the electrodes became greater than that of the machine, the current from the bath will flow back through the field magnets of the machine, reversing their polarity. When the ma-

chine is started again, the direction of the current will consequently be reversed, and the result will be to strip the metal already deposited, from the work, and to dissolve the work also, if the difficulty is not promptly discovered and remedied. This tendency of the dynamo to reverse has been a source of serious annoyance and loss to electro-platers, and much ingenuity has been expended by inventors in devising means to prevent it.

M. Gramme, a French inventor, was the first to introduce a substantial improvement in the construction of the dynamo-electric machine, by employing the idea first suggested by Dr. Pacinotti of Florence, of using an iron ring as a revolving electro-magnet, which, in place of having fixed revolving poles, had poles which travelled continuously through the whole circumference of the ring.

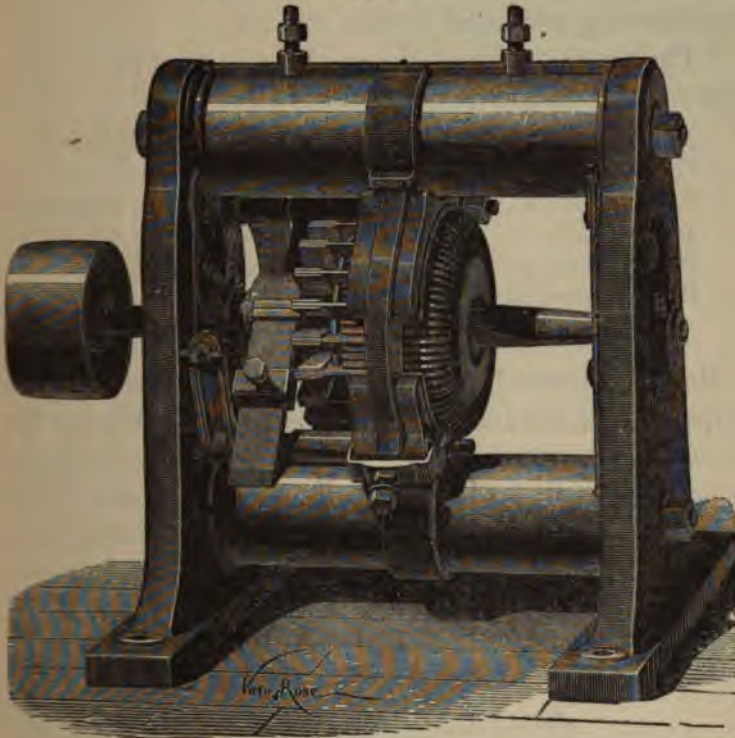
The Gramme machine in one of its many forms is shown in Fig. 67.

The essential parts of this machine are the annular armature of soft iron surrounded by numerous coils of insulated copper wire, the ends of which are suitably joined to the separate sections of the commutator. This commutator, together with the annular armature and its coils, is attached to the axis of the machine, and revolves with it between the poles of an electro-magnet. The machine of Gramme, which was brought out in the year 1871, was so great an advance in the construction of this class of machines, that its invention may properly be said to have originated the present very general public interest in the subject of electric lighting, and to have given the impetus to the investigation of the applications of electricity that has led to the invention of a host of improvements upon the dynamo-electric machine.

To start his machine Gramme resorts at first to a preliminary magnetization with the aid of a chemical battery. After this the slight residual magnetism retained by the



Fig. 67



electro-magnets suffices to set the machine in action. Reporting upon this machine, the *Telegraphic Journal*, (i. 94) (quoted by Gore, *Electro-metallurgy*, 349 *et seq.*, 1877) has the following, viz., "To deposit 600 grammes of silver requires one horse-power and a speed of 300 turns per minute; the tension of the current being equal to that of 2 Bunsen cells, and its quantity equal to 32 such cells of ordinary size. At a speed of 275 revolutions per minute it has deposited 525 grammes (16.87 oz. Troy) of silver per hour; at 300 turns, 605 grammes (19.45 oz.); and at 325 turns, 675 grammes (21.72 oz.). The weight of the copper wire on the fixed electro-magnets was 135 kilogrammes (297 pounds), and on the movable ones 40 kilogrammes (88 pounds)." The same



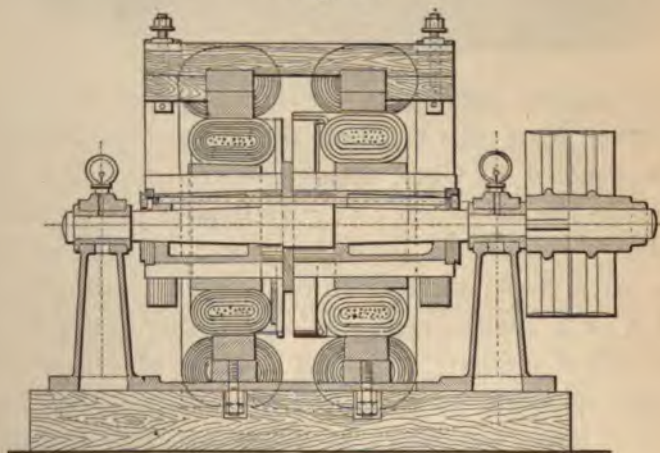
journal (iii. 198) (also quoted by Gore, see *ante*) gives the following additional details, viz. :—

“The present form of the machine as used for electro-deposition is composed as follows :—

Total weight . . . .	117.5	kilogrammes	(258½ lbs.).
Copper coils . . . .	47.0	“	(103 “).
Total height . . . .	0.6	metre	( 23.6 inches).
Total width . . . .	.55	metre	( 21.6 “ ).
Deposits silver per hour .	600.	grammes	( 19.3 oz. Troy).
Power required to work .	50.	kilogrammetres	( = .65 horse-power). ”

Roseleur quotes from the *Revue Industrielle* (1873) an extended notice of the Wilde and Gramme machines, from which, however, we abstract simply the portion relating to the comparative performance of the Gramme and Wilde machines in the large electro-plating establishment of the Messrs. Christofle, in Paris. “The three following cuts represent, a longitudinal section (Fig. 68), a plan (Fig.

Fig. 68.



69), and elevation (Fig. 70) of the special form of the Gramme machine referred to.

Fig. 69.

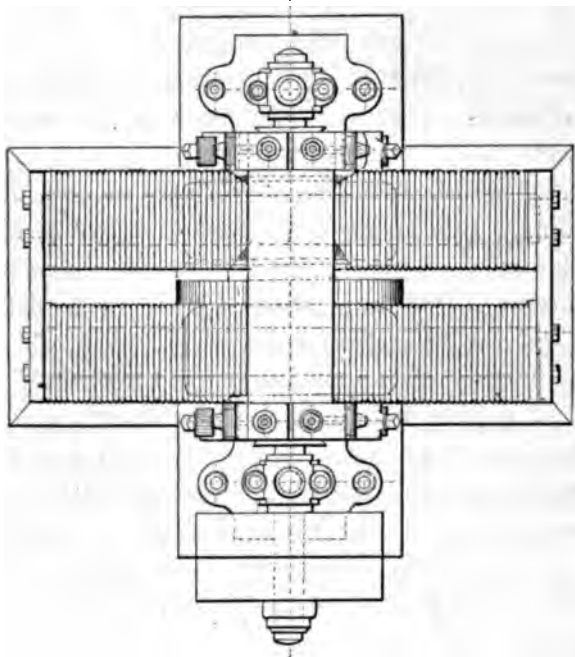
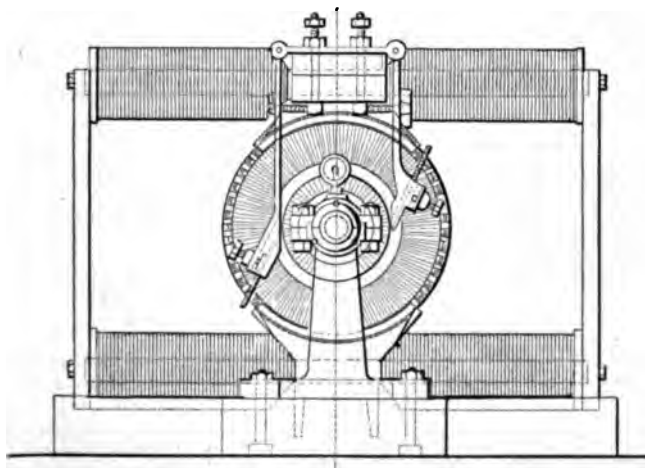


Fig. 70.



The total weight of this machine is 460 kilogrammes (1012 pounds). The wire wrapping on the stationary electro-magnets weighs 135 kilogrammes (297 pounds). The power required to drive it when working normally is about one horse-power; the speed is 300 revolutions per minute.

The tension of the current produced is equal to that of 2 ordinary Bunsen elements; the quantity corresponds to 32 elements. This current is powerful enough to fuse an iron wire of 0.003 m. (about  $\frac{1}{8}$  inch) in diameter, and 0.30 m. (about 12 inches) in length.

The collectors of the currents are composed of a great number of copper wires held in a flat sheath which gives them the shape of a brush. The elasticity of these brushes, while giving a gentle contact, at the same time prevents any interruption of the continuity of the circuit that might otherwise be caused by the vibrations of the machine, and which gives rise to rapidly destructive sparks of the extra current.

The tables given below embody the results of comparative experiments made by Messrs. Christoffe & Co. with the Gramme and Wilde machines.

## GRAMME MACHINE.

Number of experiment.	Date.	Metal deposited in kilogr. = 2.2 lbs.	Time of deposition.		Surface of the anode.	Metal deposited per hour.		Remarks
			h.	m.		kilogr.	kilogr.	
	1873.	kilogr.	h.	m.	sq. metre,*	kilogr.	kilogr.	
1	Aug. 27	5.973	7	50	5.3550	0.766	0.143	Speed 305 revolutions.
2	" 28	5.905	7	50	id.	0.757	0.141	
3	" 29	5.972	7	50	id.	0.766	0.143	
4	" 30	6.117	7	50	id.	0.784	0.146	6 baths.
5	Sept. 6	1.980	2	50	3.5700	0.707	0.198	Speed 300 revolutions.
6	" 6	1.985	2	45	id.	0.732	0.203	Deposit good.
7	" 6	2.614	2	43	id.	0.732	0.203	4 baths.
8	" 7	1.557	2	35	2.6775	0.603	0.225	Speed 300 revolutions.
9	" 7	1.598	2	45	id.	0.581	0.217	Deposit granular.
10	" 7	1.540	2	40	id.	0.578	0.216	3 baths.



## WILDE MACHINE.

Number of experiment.	Date.	Metal deposited in kilogrammes	Time of deposition.		Surface of anode.	Metal deposited per hour.		Remarks.
			h.	m.		sq. metre.*	kilogr.	
1	1873. Sept. 9	1.481	3	30	2.6775	0.423	0.158	Speed 2400 revolutions.
2	" 9	1.144	2	30	id.	0.457	0.170	
3	" 10	1.481	3	05	id.	0.480	0.179	
4	" 10	1.689	3	35	id.	0.472	0.176	

It is scarcely necessary, in connection with the foregoing figures, to dwell on the disadvantages of excessively high speeds. It need only be said that a speed of 2400 revolutions per minute is so destructive to the machine that it cannot be practically maintained.

On the other hand, the manipulation of batteries presents a number of serious difficulties; it is, besides, difficult to always procure acids of uniform quality, and, consequently to obtain a current of uniform intensity. When to all this we add that the cost of depositing a given weight of silver is considerably less with the new machine than with the battery,† the reasons that induced the house of Christoffe & Co. to negotiate with the *Société*

\* 1 sq. metre =  $10\frac{3}{4}$  sq. feet; 1 kilogramme = 2.2 pounds.

† By actual comparison of the relative amounts of work done by the battery and by the magneto-electric machines, it has been ascertained that for equal quantities of metal deposited the Gramme machine is nearly eight times more economical, and the Wilde machine about four times as economical as the battery. It is probable that with the improved machines now in use, the figures of comparative economy will be still further increased. An exhaustive series of experiments with the view of determining the actual duty of a number of these machines would be very desirable. At the present time we are dependent for this information on the statements of the makers, which are likely to diverge somewhat from the results obtained in actual practice.

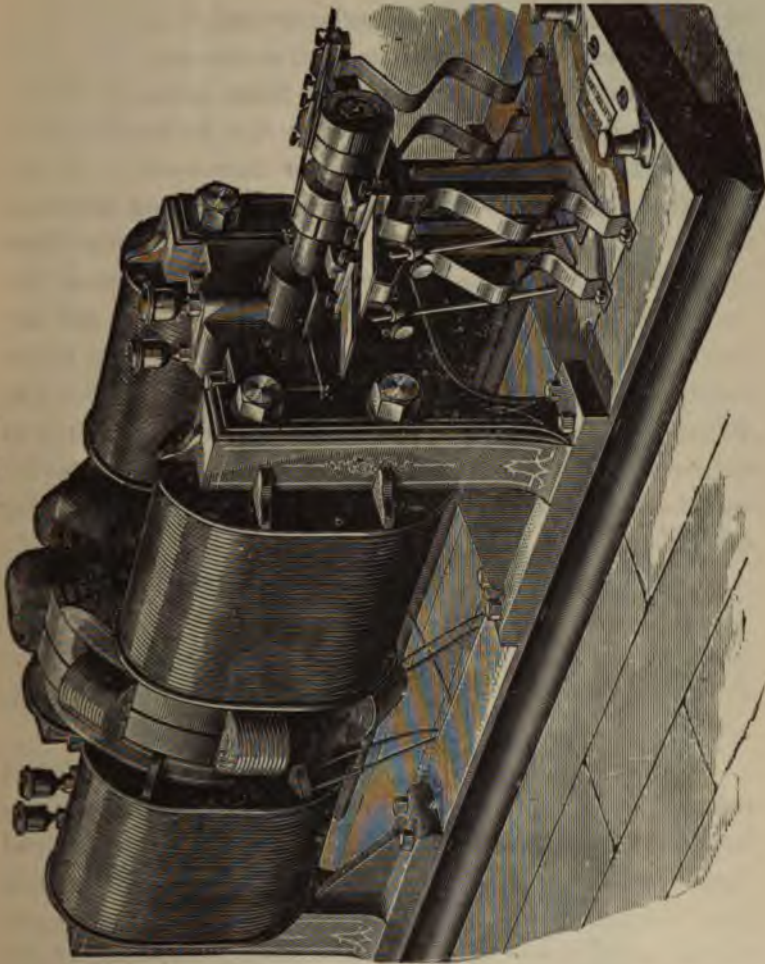
*des Machines Gramme*, for the use of so remarkable a machine, are apparent.”

The Gramme machine is a very efficient one, and in various modifications is extensively used in Europe, and to some extent in the United States, for electric lighting and electro-plating. The machines about to be described, however, are those in more general use in the United States, viz.:—

The Brush machine is similar in principle to that of Gramme above described, but has many features of construction in which it differs from its prototype. The Brush machine is shown in Fig. 71. It employs the annular armature, but this differs from the Gramme ring, in the fact that it is divided into sections by a series of rectangular grooves or recesses, which correspond in number to the number of bobbins employed. The coils are wound in these grooves until they are filled out to the surface of the intermediate thicker portions of the ring. These intermediate portions also are grooved out to lessen the weight of the armature and for the purpose of preventing the heating of the ring and coils by induced currents set up in the iron core of the armature. Allison (see *Dictionary of Electricity*, p. 94) refers to “the arrangement of the magnets by which magnetic field is produced, and by which the armature coils are during their revolution almost continually passing through a very intense magnetic field,” as an important feature of the Brush machine. “The armature ring is closely embraced on each side by large horizontal electro-magnets, whose poles are expanded so as to be presented to three of the armature coils on each side, leaving one pair of coils free from their direct influence, and this is the pair which is passing through the neutral region of the magnetic field. The disposition of the magnets towards the armature may



Fig. 71.



be described as two horseshoe electro-magnets placed opposite in horizontal position, their similar poles being towards one another, and having a small space between them in which rotates the armature ring." The machine contains other special features which would consume too much space to describe in detail.

Van der Weyde makes the following comparison between the Gramme and Brush machines. "In the

Gramme, the coils of the annular armature are, as in the Pacinotti machine, tapped in such a way that the whole of it is always in the circuit, even those parts which are over the neutral part of the ring; this unnecessarily increases the internal resistance of the current in the machine. Brush corrected this, by connecting the ends of the coils in such a way to the commutator, that those parts of the coils passing over the neutral parts of the magnets, in which no current is developed, are cut out from the circuit so as to diminish the internal total resistance. This adds to the efficiency of the machine." The Brush machine is one of the most popular machines in this country for electric lighting, and with certain modifications in the manner of winding has been adapted for electro-plating.

In response to a letter of inquiry addressed to the manufacturers of this machine, we have received, through the courtesy of Mr. G. W. Stockly, Vice-President of the Brush Electric Company, Cleveland, Ohio, the following reply:—

"We have delayed sending to you the information you asked for, regarding the performance of our plating machines, in order that we might compare the theoretical figures of the work capable of being done by them with their actual work in practice. From the data thus collected, we are able to deduce the general rule (which we presume is what you wanted to know) that for each horse-power absorbed by the machines, we are able to deposit in suitable baths *at least* one pound per hour in *each bath*. The number of baths that can be run in series (with this amount being deposited in *each*) will be governed by the electro-motive force of the machine, the size of the plates in the bath, the character of the solution, the distance apart of the plates, etc. In the case

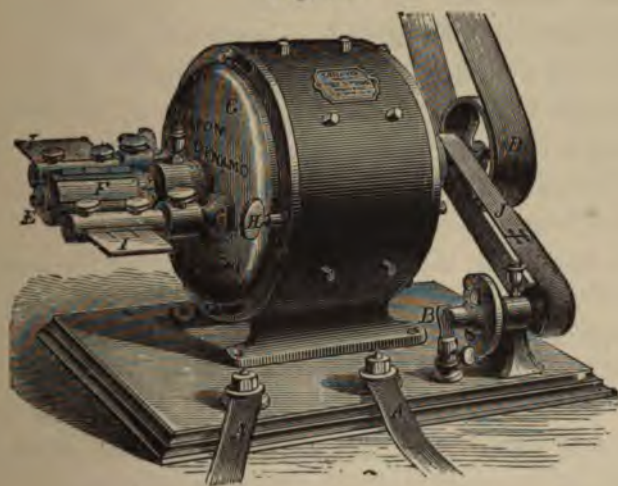


of our No. 8 light machine, wound suitably for copper-plating and requiring about thirty-five horse-power to drive it, we could, with large surfaces of copper, both for anode and cathode, in an acid solution of sulphate of copper, with plates say an inch apart, with twenty baths in one series and suitable conducting wires, deposit about eight tons of copper per day of twenty-four hours.

“These figures will enable you to estimate the capacity of any one of our machines when wound for electro-plating. Any of our machines on the list inclosed can be wound for electro-plating, and, when so wound and run at their maximum capacity, absorb the same horse-power as when wound and used for electric light.”

The accompanying cut, Fig. 72, represents the Weston machine. An iron ring or cylinder attached to an iron base forms the outer shell of the machine. The con-

Fig. 72.



struction, which is not visible from the engraving, will be readily understood from the following brief description. From the interior of the cylinder above named, and pro-

jecting radially towards the centre of the apparatus, are arranged a number of magnets (usually five), which consist of a core of iron to which are fastened a number of thin tempered steel plates, and they are wrapped with insulated copper wire, and so connected that the poles shall be alternately north and south. In the central space left between the inward ends of these magnets is arranged a shaft carried by bearings, which, to secure greater strength and perfect alignment, are cast on the iron disks or heads, which are accurately fitted and bolted to the ends of the cylinder. To the shaft is secured a series of armatures made in segments. The armatures are of iron, and are also wrapped with wire. When revolved, the outwardly projecting ends of these armatures will pass closely to, but without touching, the inwardly projecting ends of the magnets. The commutator is made in two pieces, and requires but two springs to carry the currents from all the armatures. These springs or brushes are clamped in sockets projecting from the front disk of the cylinder. An automatic switch or governor is attached to this machine for the purpose of preventing it from reversing by the polarization of the electrodes. The Weston machine is exceedingly compact in form, and has been extensively introduced for plating.

We have had the opportunity of noting the performance of one of these machines in the large electrotyping establishment of Messrs. Hanson Bros., Philadelphia, where it was introduced several years ago to take the place of thirty large cells of Smee battery, with which about 66 $\frac{2}{3}$  square feet of moulds could be covered with copper, of the usual thickness for electrotype shells, in ten hours. The Weston dynamo, consuming three horsepower, covers 100 square feet of moulds with copper of the required thickness in the same time, and without the

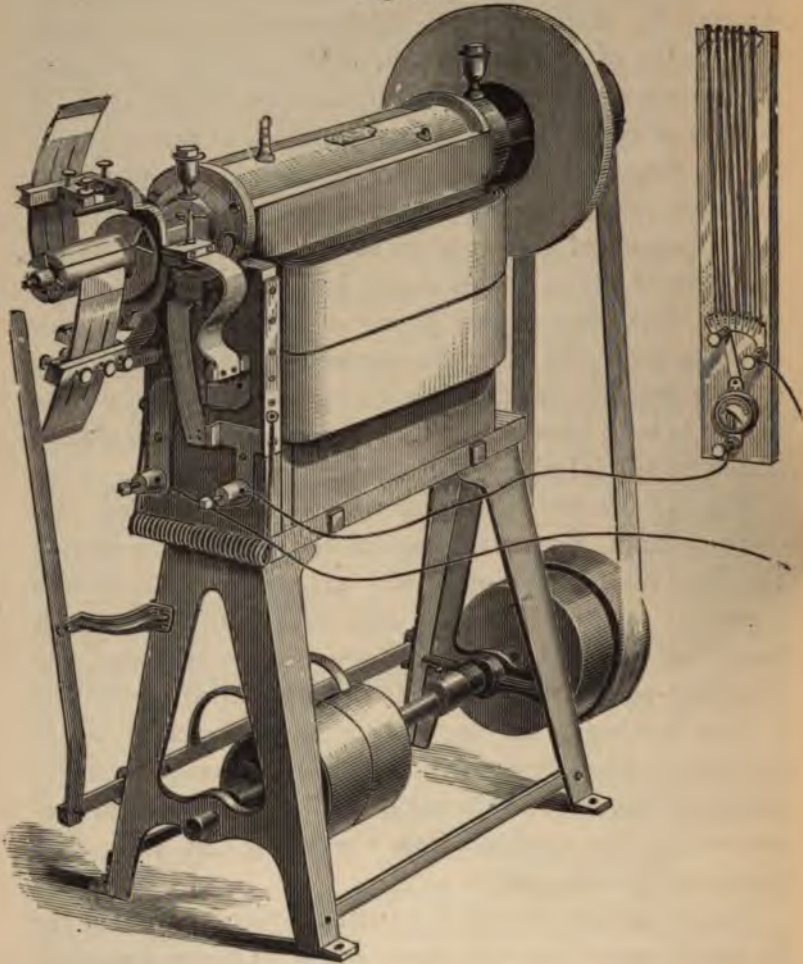


care and attention that the voltaic battery constantly demanded. Estimating the thickness of the copper shells at  $\frac{6}{1000}$ ths of an inch, which is the average thickness, the surface above named will represent a weight of 27.72 pounds of copper; and, taking the cost of steam power at the usually accepted figure of four cents per hour per horse-power, the machine in question actually deposits 27.72 pounds of copper at an average cost of one dollar and twenty cents. This result is practically equivalent to the deposition of one pound of copper per hour per horse-power. The attention required by the machine is so trifling that the machinist in charge of the steam engine is able to look after it, without neglecting his other duties, hence no special charge for this item is made.

Fig. 73 shows the Arnoux-Hochhausen plating machine with a Siemens armature, as recently improved. To avoid undue heating of the armature coils, which is a serious source of trouble and of loss of power with many forms of the dynamo, these makers surround the armature with a water jacket in which a current of water is kept flowing. Another feature of the machine is an automatic switch for regulating the current according to the surface of the work in the bath, and for the purpose also of preventing the machine from "reversing" by the polarization of the electrodes.

The resistance board or "switch" with galvanometer shown in connection with the above is, in this or an analogous form, an indispensable adjunct to the dynamo-electric machine, for controlling the amount of current generated. It consists of a rectangular board of convenient size, to which is attached a series of brass or German-silver wires of varying thicknesses, from very fine to thick. These wires are each attached at one end to a flat plate of German silver below, and are stretched over a pin

Fig. 73.

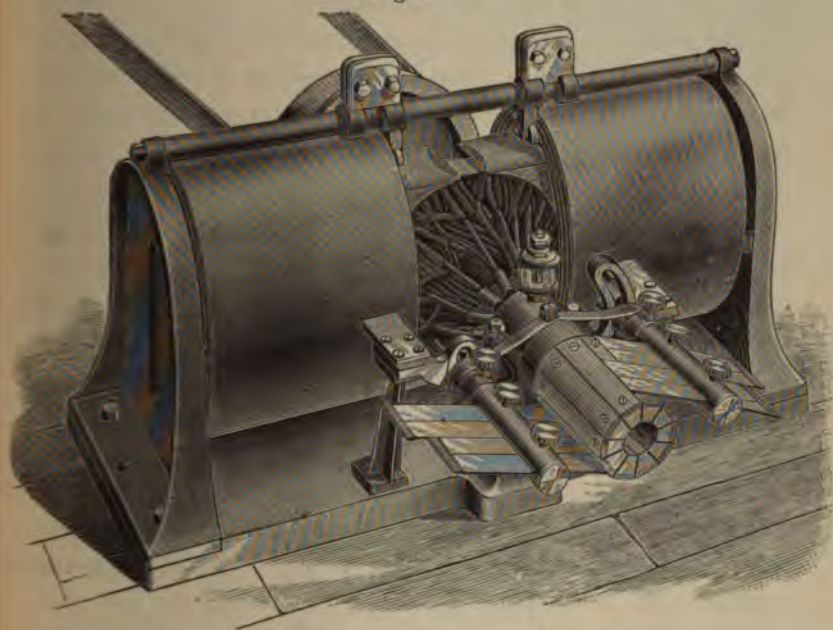


above and attached below to the next plate, the successive plates being separated from each other. This board is placed in the circuit, and, by means of a metallic key which may be shifted from one of the plates to another, the full current of the machine, or any proportion of it that may be required, may be passed into the bath.



The accompanying cut, Fig. 74, represents the Mather Dynamo-Electric Machine. This machine uses a single

Fig. 74.



magnet, of which the base of the machine forms a part, and which is so formed as to secure a much greater length than is commonly used. The purpose of the designer in introducing this feature is to interpose as great a resistance as possible to reversal. The opposite poles of the magnet inclose the armature which thus occupies and fills the magnetic field. The fixed magnet is wound in the usual manner; and its form is such as to allow a free circulation of air through longitudinal recesses in the outer surfaces of the core, which, when it is wound, become passages open at each end for the transmission of a current of air produced by the rotation of the armature. Much stress is laid by the maker of this machine upon the

method of constructing the armature, by virtue of which, it is claimed, the local currents produced by induction in an ordinary core are so far prevented, that the heating from this cause is very inconsiderable. The armature is wound with insulated wire in substantially the same manner as other machines; and its disposition is such that its face is surrounded by the masses of iron composing the magnets with their coils; and the endeavor has been made in its form and the relation of its parts to provide that there shall be a strong magnetic action on its sides as well as on its face, and at the same time to have a free circulation of air around it and through the recesses in the magnet in order to counteract the heat that may be developed. It is further claimed that the method of construction adopted renders it possible to leave much more space between the armature and the magnets than has usually been possible. One-eighth of an inch is allowed, and it is affirmed that up to three-sixteenths of an inch, the results obtained show a gain in power without loss of current. If this space between the armature and the magnets can be allowed without detrimental effect upon the power of the machine, it will have the advantage of avoiding the danger of actual contact between the face of the armature and the magnets, which happens in some cases by wear of the journal boxes or other causes, and with disastrous results. The commutator differs in some minor details from those commonly used. The junction of the coil wires with the segments of the commutator is made through large copper plugs, which are "sweated" in to secure perfect contact. The segments of which it is composed are separated from each other entirely by longitudinal slits, which permit of rapid cleaning by simply passing a string through an opposite pair of the slits and working it back and forward.



The Müller Machine, which has also been introduced to a considerable extent for electro-plating in the United States, and several forms of the Siemens machine, which have been largely adopted abroad for plating as well as for the metallurgical extraction of copper on the large scale, are worthy of mention as successful machines in connection with this subject. Detailed descriptions of these, however, would needlessly lengthen this chapter, and the reader is referred for such descriptions, should they be desired, to the technical journals.

Respecting the comparative merits of these and other machines, there is much diversity of opinion among those who use them, some preferring one and others another. As remarked elsewhere, there is great need of a series of tests with these machines, in order to determine which type of machine is best adapted for electro-metallurgical purposes. Meantime, the claims of rival makers, and widely differing testimony of electro-platers, render the selection of a machine a task of no little difficulty.

In conclusion, we may be allowed to briefly reaffirm that the dynamo-electric machine has now practically become the sole source of electric current in the art of electro-plating. In one or another of its numerous modifications it has supplanted almost entirely the cumbersome, troublesome, and expensive voltaic battery. By reason of the economy, certainty, and rapidity of its operation it has contributed very largely to the considerable extension of the art of electro-plating, and cheapened the cost of this class of work, and it may safely be credited with having called into existence one of the most extensive and important branches of the art; we refer to nickel plating, which without its aid could never have come into general use.

## CHAPTER X.

### DEPOSITION OF COPPER—BY SIMPLE IMMERSION—BY BATTERY.

#### *Deposition of Copper.*

WE have said, in the articles on cleansing, that it was often useful, and sometimes absolutely necessary, to effect a primary deposit of copper, brass, and sometimes of tin, upon common metals or alloys, such as wrought and cast iron, zinc, Algiers metal, etc., before they receive the precious metals. But these various operations are often not simply the complement of the cleansing process, but furnish products ready for the trade without any further operations. We shall carefully describe the various formulæ, by the aid of which we arrive at these results.

#### *Deposition of Copper (by simple immersion).*

Copper deposits are obtained, according to the metals employed or the object in view, either by simple immersion or by the galvanic method.

The deposition of copper by immersion is seldom practised except upon iron, and the deposits obtained are generally wanting in lasting qualities. They are intended to please the eye only, since, from the thinness of the deposit, the iron is not protected against atmospheric influences. It may even be rendered more liable to oxidation.

We employ a bath composed of—

Sulphate of copper (blue vitriol)	.	10 parts.
Sulphuric acid (oil of vitriol)	.	10 "
Water	.	500 to 1000 "



If the iron is immersed in this solution for a short time only, it immediately becomes covered with a bright film of pure copper having a certain adherence; but should it remain there for a few minutes, the deposit of copper is thicker and muddy, and has such slight adherence that the least friction is sufficient to detach it. In this case, we are obliged to compress it by means of rollers or a draw plate, in order to impart a certain cohesion to the molecules of copper. Small articles, such as hooks, pins, steel pens, etc., are coppered by tumbling them for a certain length of time in sand, bran, or sawdust, impregnated with the above solution, diluted with three or four times its volume of water.

An improved method of coppering by simple immersion, and which is reputed to be in common use in Paris, for coating such large objects as cast-iron fountains, lamp-posts, etc., is that of F. Weil. It is, briefly described, as follows:—

The depositing solution consists of—

Sodio-potassic tartrate . . . . .	150 parts.
Soda-lime (containing 50 per cent. free soda) . . . . .	80 “
Sulphate of copper . . . . .	35 “
Water . . . . .	1000 “

The above named substances are dissolved in water with the aid of heat, if necessary, and the articles of iron, or steel, properly cleansed, are immersed in the bath in contact with a piece of zinc, or lead, or suspended therein from zinc slinging wires. The articles themselves should not touch each other. The action is slow, iron articles requiring an immersion of from five hours to several days, according to the thickness, color, etc. of the deposit desired; but the deposited copper is affirmed to be strongly adherent, and to be capable of acquiring considerable thickness. When the coating is satisfactory, the articles

are withdrawn, well rinsed in water, dried in hot saw-dust, and afterwards in a stove. In operating with this solution on the large scale, Weil recommends, in order to keep the bath of uniform strength, that it be constantly renewed from below, the overflow passing off in a small stream from the top. As the copper becomes exhausted the solution is strengthened from time to time by additions of hydrated oxide of copper. When, after prolonged use, the bath has become saturated with zinc, it will be necessary to revivify it by precipitating the zinc with sulphide of sodium, being careful to avoid an excess, and charging the liquid drawn off from the precipitate, afresh with copper salt.

#### *Electro-Deposition of Copper.*

Electro-deposits of copper may be obtained by two different methods: First by decomposing a simple salt of copper, the sulphate for instance, which is suitable for those metals only which are not decomposed by the acid solution; and second, by decomposing a double salt of copper, such as the double cyanide of potassium and copper. This latter process is equally well adapted to all metals and metallic alloys.

It is obvious that the sulphate solution cannot be used for obtaining electro-deposits of copper upon such metals or alloys as zinc, iron, tin, lead, Britannia-metal, etc., which decompose the solution without the galvanic current, precipitating its copper by simple immersion. For these metals or alloys, therefore, the alkaline cyanide solution, or its equivalent, is used. Brass, German-silver, etc., which do not precipitate copper from the sulphate, can be electro-coppered in this solution. It may be added, in this place, that the practice sometimes obtains, where a copper deposit of considerable thickness is desired, upon



iron, zinc, etc., of laying a thin coating of copper in the cyanide bath, and thereupon transferring the article to the sulphate bath to complete the deposit to the desired thickness.

The first method of obtaining electro-deposits of copper, *i. e.*, by a simple salt of copper, will be treated *in extenso* in the second part of this work, under the caption of GALVANOPLASTY proper. | The deposition of copper by the galvanic decomposition of double salts, is, on the other hand, the subject which will occupy us in this place. ✓

The deposition of copper from solutions of the double salts is a process, as we have already said, well adapted to all metals and alloys; the deposits are fine, lasting, and their thickness is entirely under the control of the operator.

The most simple, although not the most economical, process consists in dissolving any salt whatever of copper in water in the presence of a sufficient quantity of the cyanide of potassium. The mode of procedure is about as follows: Dissolve 50 parts of sulphate of copper in 1000 parts of water, and add a solution of carbonate of soda until no more precipitate is formed: collect the green precipitate (carbonate of copper) thus obtained, upon a cloth filter, and wash it several times with water; then stir the washed carbonate of copper in water, to which cyanide of potassium is added until the carbonate is entirely dissolved, and the solution is colorless. It is advantageous to add a small excess of cyanide, which will increase the electric-conducting power of the liquid.

This bath may be employed indifferently, hot or cold, and requires for its decomposition quite an intense electric current.

A copper plate or sheet forms the anode, and, slowly

dissolving, nearly makes up for the loss of the bath in copper which has deposited on the negative pole. This anode must be removed when the bath is not in action, as the cyanide will continue to dissolve it even without an electric current; and, should the bath become overcharged with copper, which will be indicated by a blue or green color, it will require a fresh addition of cyanide to be restored to good working order.

This bath, we repeat, is not economical, and is likewise uncertain in its action. We have found by experience that either of the following formulæ is preferable to it under all circumstances:—

*First Formula.*

EQUALLY WELL ADAPTED FOR ALL METALS OR ALLOYS, AND TO BE EMPLOYED INDIFFERENTLY, COLD OR WARM.

Water . . . . .	1000 parts.
Acetate of copper (crystallized) . . . . .	20 “
Carbonate of soda (crystals) . . . . .	20 “
Bisulphite of soda . . . . .	20 “
Cyanide of potassium (pure) . . . . .	20 “

For preparing this bath, the acetate of copper is put first into the vessel, and moistened with sufficient water to make a homogeneous paste. This salt, like flour, is wetted with difficulty, and will float on the surface of too great a body of water.

The carbonate of soda and two hundred parts of water are added to this paste, and, after stirring, a light green precipitate is formed. Two hundred parts more of water are then added with the bisulphite of soda, when the magma becomes of a dirty-yellow color.

Lastly, the remaining six hundred parts of water and the cyanide of potassium are introduced. When this has completely dissolved, the result will be a colorless liquid, which is the coppering bath. If, after the complete

solution of the cyanide, the liquid is not entirely colorless, we must add a little more cyanide. But this is never necessary save when the cyanide is impure, or has begun to decompose.

If we desire a perfectly limpid bath, we may pass it through filtering paper, or decant it after settling.

This bath, for its decomposition, requires an electric current of moderate intensity.

The copper anode should have a surface about equal to that of the objects to be coppered.

Large pieces are generally kept hanging and motionless in the bath; on the other hand, small articles are moved as much as possible, which is always to be preferred when practicable, especially with warm baths.

The following formulæ are adapted for a cyanide of from 70 to 75 per cent. purity. These formulæ are applied to various uses.

*Second Formula.*

COLD BATH FOR IRON AND STEEL.

Bisulphite of soda . . . . .	50 parts.
Cyanide of potassium . . . . .	50 "
Carbonate of soda . . . . .	100 "
Acetate of copper . . . . .	47 "
Aqua ammonia . . . . .	35 "
Water . . . . .	2500 "

WARM BATH.

Bisulphite of soda . . . . .	20 parts.
Cyanide of potassium . . . . .	70 "
Carbonate of soda . . . . .	50 "
Acetate of copper . . . . .	50 "
Aqua ammonia . . . . .	30 "
Water . . . . .	2500 "

*Third Formula.*

## HOT OR COLD BATH FOR TIN, BRONZE, OR LARGE PIECES OF ZINC.

Bisulphite of soda . . . . .	30 parts.
Cyanide of potassium . . . . .	50 "
Acetate of copper . . . . .	35 "
Aqua ammonia . . . . .	20 "
Water . . . . .	2500 "

Lastly, for small articles of zinc, which may be coppered in a perforated ladle, and at nearly boiling temperature:—

*Fourth Formula.*

Cyanide of potassium . . . . .	70 parts.
Bisulphite of soda . . . . .	10 "
Acetate of copper . . . . .	45 "
Aqua ammonia . . . . .	15 "
Water . . . . .	2000 to 2500 "

In order to prepare these different baths, we dissolve in two thousand parts of water (preferably rain or distilled water) all of the salts, except the acetate of copper and the ammonia, which are dissolved in the remaining five hundred parts. The two solutions are then mixed, and that of the copper and ammonia, which was of a magnificent blue, must become entirely colorless when mixed with the first.\* The bath is ready to work when subjected to the action of the electric current.

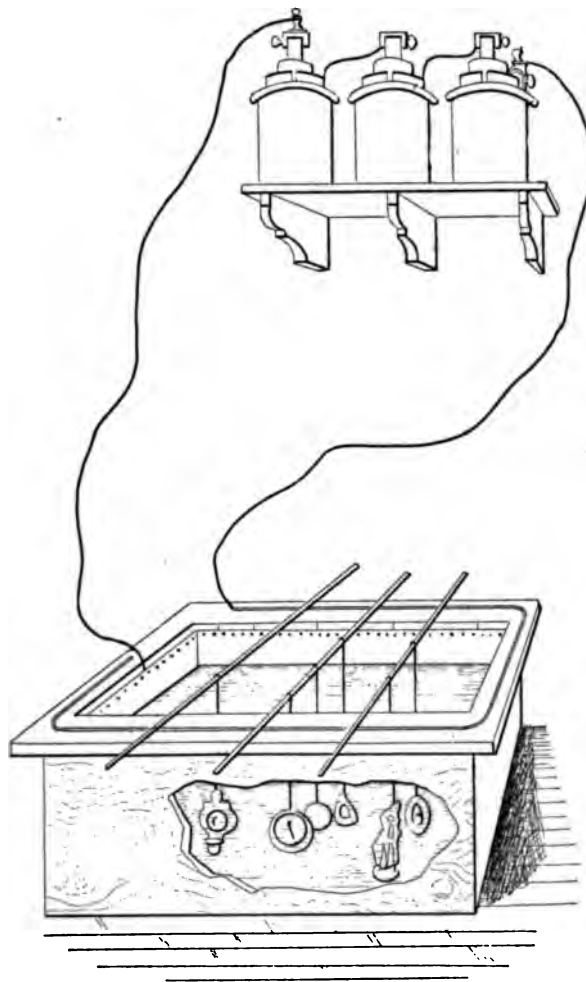
The baths intended for working in the cold are contained in well-joined tanks of oak or fir wood (Fig. 75), and, for greater precaution, lined inside with gutta-percha.

\* It should be understood that, when these baths are not colorless, it is because of a deficiency of cyanide of potassium, which should be added, until complete decolorization takes place, and even in slight excess. We should state of the baths of these four formulæ, that they work more regularly the older they are, and the more frequently they have been recharged.



The vertical sides are also covered with one or several sheets of copper, which constitute the soluble anode,

Fig. 75.



and the height of which is somewhat below the level of the edge of the tank. This anode is connected by the clean extremities of a conducting wire to the last copper

or carbon (according to the kind of battery employed), that is to say, to the positive pole of a battery, or machine, as the case may be.

A stout brass wire is fixed upon the top of the tank, well insulated from the anode, and is connected by a second wire with the last zinc, or negative pole, of the battery, or machine.

The objects to be coppered are suspended in the bath by means of copper wires, or hooks, of convenient length, which in turn are supported upon a stout and clean brass rod, the two extremities of which rest upon the brass conducting wire fixed upon the tank. A number of such rods carrying objects are placed parallel to each other, and the greatest care must be observed to prevent any of the objects to be coppered from touching the anode, as the slightest contact of this kind would at once arrest working of the bath. It is needless to say that the objects must have been cleansed in the manner already described.

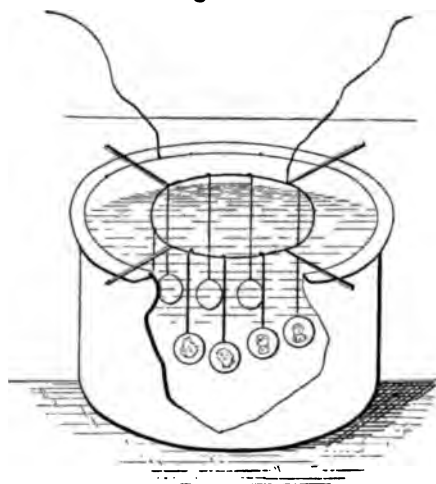
When the thickness of the deposited copper is very slight, the deposit is sufficiently bright to be considered finished after drying. But if the operation is more protracted, the deposit appears with a more or less dead lustre on account of its thickness, and, if a bright lustre is desired, we must use the scratch-brush.

The baths intended for working hot are contained in stoneware vessels (Fig. 76) heated on the water or steam-bath, or simply in an enamelled cast-iron kettle placed directly over a fire.

The interior of this vessel is also lined with an anode of copper, connected with the positive pole of the battery, and the edges of the vessels are varnished, or support a wooden ring, upon which rests a brass ring commu-

nicating with the negative pole. The rods supporting the objects to be electro-plated, rest upon this circle.

Fig. 76.



The hot process is much more rapid than the cold, and is especially adapted to those articles which are difficult to cleanse, because any remaining superficial impurity of grease is dissolved by the alkaline bath.

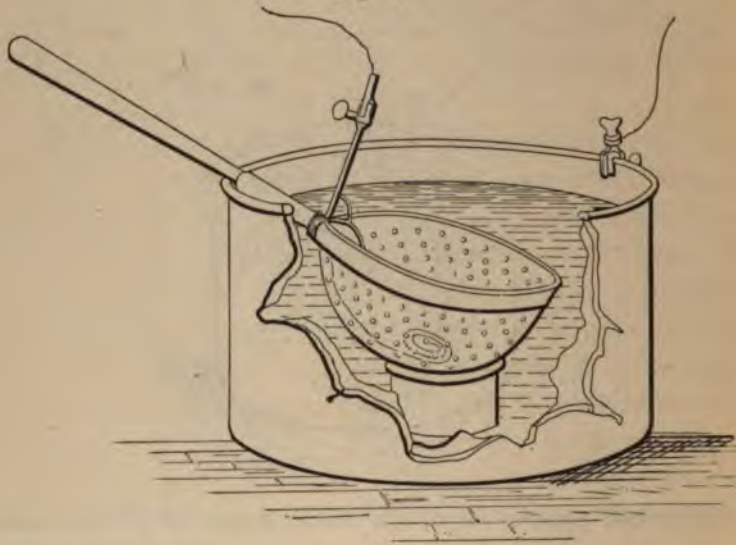
The squares of watch-keys, the metal parts of portemonnaies, and other small articles, are coppered by this method, if a firm coating is required.

Packages of pierced articles that may be threaded on a wire, as for instance metallic pens, are not suspended in the bath; but are simply connected with the negative wire in the hand of the operator, and moved about in every direction in the bath. This agitation permits of the employment of quite an intense current, without danger of impairing the beauty of the deposit.

Small articles of zinc, such as hooks, nails, etc., are disposed in a perforated stoneware ladle (Fig. 77), at the bottom of which is placed a spiral of zinc or copper wire,

which is wound up around the handle, and is connected with the negative pole of the battery. It is sufficient

Fig. 77.



that a single one of these small articles shall touch the wire, for all of the others to be affected by the current, since they are all mutually in contact. If the bottom of the vessel is metallic, and in order to prevent contact with those objects which may pass through the holes, the ladle is made to rest upon a porcelain or stoneware ring.

Experience has shown that this disposition is preferable to metallic sieves, especially those of copper or brass, which absorb nearly all the copper deposited.

During the operation, the articles should be frequently shaken up in the ladle. This shaking changes the points of contact of the objects, and brings each in turn to the surface.

It is well for small articles, to place the anode on top of the ladle, but without any connection with the objects



to be coppered. Fig. 78 represents a convenient form of anode for this purpose.

During the operation, the bath attacks and slowly dissolves the copper anode; but here theory is not quite in accord with practice, since this solution is not sufficiently rapid to compensate for the loss of metal, and to maintain the proper saturation of the bath. When the deposition

is found to be going on too slowly, we must bring up the bath by the addition of a certain quantity of acetate of copper and of cyanide of potassium (equal weights).

Some operators substitute the sulphate, or the cyanide, of copper, for the acetate of this metal. The first should be rejected on account of its too great acidity, which uselessly destroys part of the salts of the bath. The second is too expensive, and does not give more satisfactory results than the acetate, which is to be preferred on account of its comparative cheapness and its perfect neutrality. Moreover, the acetates of potassa, or soda, or ammonia, formed by double decomposition, are without any bad effects during the operation.

Carbonate of copper, recently precipitated and dissolved in just enough cyanide of potassium to discolor it, may also be employed. This mixture is added to worn-out baths to revivify them; but it is preferable not to wait until they are worn out, and to make up for the losses by adding, now and then, a small quantity of the double cyanide of potassium and copper already indicated.

When a bath has been too often recharged with salts, it becomes too dense, and its electric conductivity diminishes. The pieces plunged into it receive no deposit, or

Fig. 78.



only an imperfect one, although the relative quantities of copper salt and of dissolving agents are in suitable proportions. The working quality may, in such case, be restored by the addition of water.

When the anode has too large a surface, or remains immersed in non-working baths, the liquor becomes overloaded with copper, turns blue or green, and requires the addition of cyanide of potassium to the point of discoloration.

It happens sometimes that the anode becomes covered with a brownish or whitish coating preventing its solution; the bath then becomes gradually poorer in metal, and ceases to give a deposit. In this case, an addition must be made of a solution of acetate of copper in ammonia, until the blue coloration which it causes begins to disappear with difficulty. If too much is added, the excess must be corrected with cyanide of potassium. To sum up, an attentive and intelligent operator will always be able, with cyanide of potassium and salt of copper, to maintain the materials of his bath in a proper state of equilibrium.

Some operators copper silver articles before gilding them. This is done partly to give the deposit greater solidity, and partly to avoid the whitening at the angles, which otherwise soon shows itself as the result of wear and friction.

Large pieces of silverware may be coppered in any of the baths before mentioned. Very small articles, on the other hand, are simply threaded upon a zinc or iron wire, or placed in a perforated ladle with granules or cuttings of either of these metals. By plunging the whole for a few minutes in a very dilute, but very acid, solution of sulphate of copper, the zinc or the iron dissolves, taking the place of the copper in the solution, and the latter



is deposited as a uniform and adherent coating upon the silver, which acquires a magnificent pink color.

When the article thus coppered is intended to be gilded or silvered, it is quickly passed without drying or scratch-brushing, through the quicking bath, rinsed in cold water, and at once immersed in the depositing bath.

We append, in conclusion, a number of formulæ and methods from sundry reliable sources, which may be found useful.

The following method is that employed by Serin & Co., of Paris, for the electro-deposition of copper upon iron, viz.:—

*a. Preparation of the articles.* The articles are first immersed in dilute sulphuric acid, then washed in cold, followed by hot, water; they are then immersed in boiling alkali, from which they are removed and transferred to a bath of milk of lime, in which they are allowed to remain for several weeks.

*b. Preparation of the first copper bath.*

Water . . . . .	100 parts.
Cyanide of potassium . . . . .	4 to 4½ “

Dissolve in this, cyanide of copper, until a saturated solution is obtained.

*c. Treatment of the articles in the bath.* The articles are allowed to remain in this bath for about an hour, with the employment of a moderately strong current (sufficiently strong to manifest a lively evolution of gas). In this bath, the articles take on a thin copper coating, when they are ready for the subsequent operation.

*d. Preparation of the second copper bath.* Dissolve in water, with the aid of heat, so much sulphate of copper that the solution, when cold, shall register 24° Baumé. Dilute with water to 20° Baumé, and add enough sul-

phuric acid to bring the specific gravity of the solution to 22° Baumé. This solution forms the second copper bath.

*e. Treatment of the articles in the second copper bath.* The articles, thinly coppered in the first bath, are transferred to the second copper bath just described, through which the current has been directed before the articles are introduced. In this bath, the articles can be coated with a copper coating of great adhesion and of any desired thickness. When properly coated they are removed from the bath, washed in clean water, dried, and polished.

Instead of the first thin coating of copper here described, the articles may be first given a coating of lead by galvanic deposition, upon which they may be coppered in the second bath.

*f. Preparation of the lead bath.* Dissolve litharge in water containing 10 per cent. of caustic potassa. Anodes of lead plates are used to maintain the saturation of the bath. The galvanic current does not require to be strong.

L. Elsner's procedure for the electro-deposition of copper is as follows (Winckler, *Handbuch der Metallüberzüge*, 1881, p. 218): Dissolve 1 part of powered bitartrate of potassium in 10 parts of rain water, and add to this solution, freshly precipitated hydrated carbonate of copper (prepared by precipitating, in the cold, a dilute solution of sulphate of copper with a dilute solution of carbonate of sodium or potassium, and washing with water) until no more is taken up, that is, until the last portions added remain undissolved. The solution is then made decidedly alkaline by the addition of carbonate of potassium, filtered, and the clear liquid constitutes the copper bath. A current, of moderate strength only, is required, the copper anodes dissolving readily, and maintaining the metallic strength of the solution.

For electro-coppering cast iron, the same authority re-



commends a saturated aqueous solution of sulphate of sodium, to which as much hydrated carbonate of copper (or hydrated oxide of copper) is added as it will take up. The clear, dark blue solution which is filtered off from the undissolved residuum, rendered decidedly alkaline by the addition of carbonate of sodium, serves as the copper bath. Cast-iron objects are soon covered with a matt rose-colored deposit of copper.

Watt (*Electro-metallurgy*, 7th ed., p. 35) recommends the following formulæ for the galvanic deposition of copper on iron or zinc, viz. :—

1. Add to a solution of sulphate of copper, a solution of cyanide of potassium. Wash the greenish precipitate several times with cold water, and dissolve in cyanide of potassium.

2. Pour into a solution of sulphate of copper, a solution of ferrocyanide of potassium until no further precipitation takes place. Wash as above, and dissolve in cyanide of potassium. Work the solution hot.

3. Dissolve 8 ounces of sulphate of copper in 1 quart of hot water; when cold, gradually add liquid ammonia (sp. gr. .880), stirring after each addition, until the precipitate that at first forms is dissolved. Add cyanide of potassium until the blue color of the ammonio-sulphate of copper disappears; then add cyanide of potassium; and work the solution at a temperature of about 130° Fahr. Watt pronounces this "a very good solution for coppering."

Gore (*Electro-metallurgy*, 1877, p. 207) dissolves cyanide of copper to saturation in water containing about 2 pounds of cyanide of potassium to the gallon; then adds about four ounces more of the potassic salt per gallon, to form free cyanide. This solution is adapted for electro-coppering upon zinc, iron, etc., and should be used at a temperature of about 150° Fahr. ✓

Another formula recommended by the same authority as a good depositing solution for coating iron and steel by the battery process (*id.* p. 208) is the following, viz.: Dissolve ammoniuret of copper in a solution of cyanide of potassium. Nine hundred or 1000 parts of water, containing 80 parts of cyanide of potassium, dissolves 40 parts of the blue ammoniuret, and forms a colorless liquid.

Spencer's solution for the galvanic deposition of copper on iron is made by decomposing a solution of sulphate of copper in water, by the addition of a solution of the acetate, sulphate, or nitrate of ammonia. This bath is said to furnish upon iron a copper deposit of any desired thickness.

Under the head of GALVANOPLASTY proper we shall refer to some of the recent improvements introduced for obtaining copper on the commercial scale by galvanic precipitation, the continuous production of heavily coated steel wires for telegraphic and other purposes, and the like.

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## CHAPTER XI.

### ELECTRO-BRASSING.

BRASS deposits are much more frequently used in the arts than those of pure copper. Brass is preferred for those small articles of iron or zinc which are made in imitation of similar ones of brass, which are more expensive. (Wood-screws, hooks, rings for furniture and curtains, hooks and eyes for dresses, wires of all sizes for chaplets, etc. etc., are made of iron or zinc plated with brass, so as to resemble those of real brass.)



Moreover, all the manufacturers of *bronze composition*, lamps, clocks, chandeliers, statues, and other articles made of zinc or cheap alloys, begin by a brass deposit, before the bronze composition is applied. (For *bronzing* consult special chapter.)

Besides the fact that the bronzing operation is more easy and satisfactory upon a brass surface, there is also the advantage that, if, whether purposely or by constant use, the surface of the object becomes abraded, there appears the handsome yellow color of the underground, and the whole piece looks as if made of the more costly alloys of copper and zinc, or copper and tin.

The preliminary and finishing operations are the same for brass as for copper deposits. The disposition of the baths and apparatus is also similar; the formulæ alone are different.

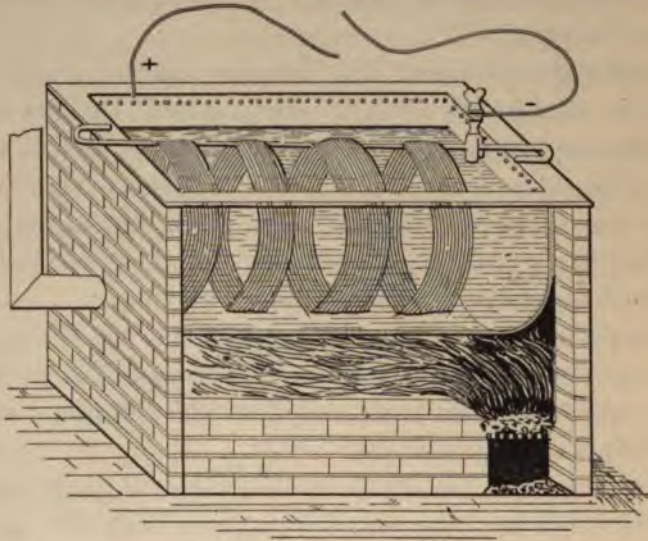
Heat is seldom employed in electro-brassing, although it is preferred by those who electro-plate, with this alloy, iron or zinc wire in coils. The best temperature for this class of work is found to be from 120° to 140° Fahr.; and the coils are allowed to dip into the bath one-half or two-thirds of their diameter only.

The bath is contained in a sheet-iron boiler (Fig. 79), heated either by direct fire, steam, or hot water. The inside is lined with brass sheets connected with the positive pole. A stout copper or brass rod, in the direction of the length of the boiler, rests upon the edges, and the contact of the two metals is prevented by interposed pieces of India-rubber tubing. The rod is connected with the negative pole by a binding screw.

The binding wire is removed from the coils, and the wires loosened and spread out as seen in Fig. 80. The two extremities are bent together, and, with a stronger wire, a triangular handle is formed which contains the

whole of a coil, and leaves a certain play necessary for the operation.

Fig. 79.

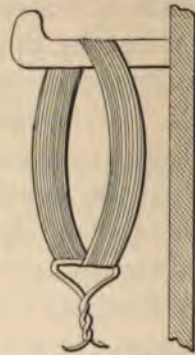


The iron wire, thus disposed, is cleaned by dipping into a pickle of diluted sulphuric acid, and suspended to

Fig. 80.



Fig. 81.



a stout, round peg fixed in the wall (Fig. 81), so that the coil may be made to rotate easily. After a scrubbing



with wet, sharp sand and a hard brush, the coil receives a primary deposit of pure copper in an apparatus similar to that just described. It is then carried to the brassing bath, and suspended therein from the horizontal rod. In this position, only a part of the coil at a time dips into the solution and receives the deposit, which, to be continuous, requires that the coil be turned, now and then, one-half or one-fourth of its circumference. Experience has demonstrated that, by dipping the coil entirely into the liquid, which is easily done by giving the proper bends (Fig. 82) to the supporting rod, the operation is not so successful. With this latter disposition, moreover, it is not so easy to spread the wires upon the rod.

Fig. 82.



The wires are washed, dried in sawdust, and then in a stove, and lastly passed through a draw-plate in order to impart to them the fine polish of true brass wire.

Copper and brass wires are also covered with brass electro-deposits, in order to give them various shades. The brass wires of Lyons and Germany, used for trimmings and epaulets, are thus prepared, either preparatory to gilding or silvering, or simply to arrive at special shades more pleasing than those of pure copper or pure brass. These wires, passed through the drawplate, are sold under the name of *false gold*. It is evident that the

composition of the brassing bath must be such as to give, with the battery, a deposit resembling gold.

*Formulae for Brassing Baths.*

Dissolve *together*, in 1000 parts of water, 25 parts of sulphate of copper, and 25 to 30 parts of sulphate of zinc;

Or,  $12\frac{1}{2}$  parts of acetate of copper, with  $12\frac{1}{2}$  to 15 parts of fused chloride of zinc;

To which add a solution of 100 parts of carbonate of soda, which immediately produces an abundant precipitate of the carbonates of copper and zinc, which is allowed to settle. When the precipitate has completely subsided, decant the supernatant liquor, and replace it by fresh water two or three times, after as many settlings.

Lastly, pour upon the precipitate 1000 parts of water containing in solution 100 parts of carbonate of soda and 50 parts of bisulphite of soda; and then, while stirring with a glass or wooden rod, add thereto cyanide of potassium until the liquid is perfectly clear, or at least until nothing but the grayish-black iron, often found in the cyanide, or the brown-red oxide of iron from the sulphate of zinc, remains in suspension. An additional quantity of from  $2\frac{1}{2}$  to 3 parts of ordinary cyanide improves the conducting power of the liquid.

Other formulæ, which have proved satisfactory in regular every-day work, are given herewith, viz.:—

*First Formula.*

COLD BRASSING BATH FOR ALL METALS.

Carbonate of copper (recently prepared)	. . .	10 parts
Carbonate of zinc (recently prepared)	. . .	10 "
Carbonate of soda (crystals)	. . .	20 "
Bisulphite of soda	. . .	20 "
Cyanide of potassium, pure	. . .	20 "
Arsenious acid (white arsenic)	. . .	$\frac{1}{5}$ part
Water	. . .	1000 parts



This bath is prepared as follows:—

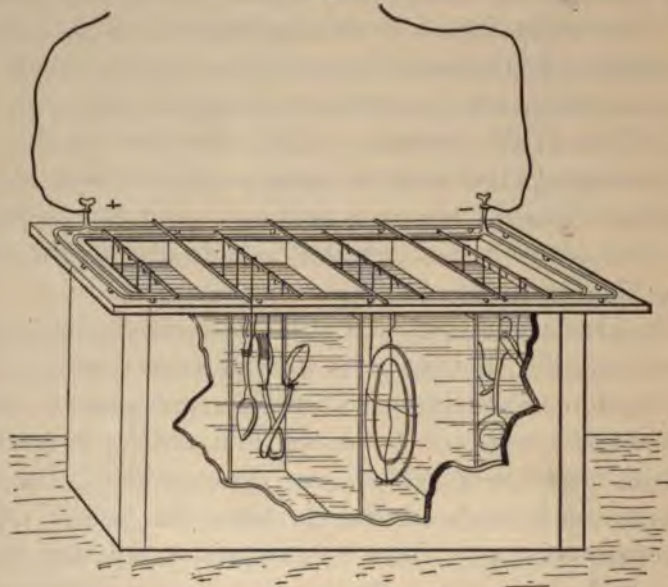
Dissolve in 200 parts of water, 15 parts of sulphate of copper, and 15 parts of crystallized sulphate of zinc, and add a solution of 40 parts of carbonate of soda in 100 parts of water. A greenish precipitate of mixed carbonates of copper and zinc is immediately formed, which is well stirred and allowed to deposit for several hours. The supernatant liquid, containing sulphate of soda, is of no value, and is drawn off, and replaced by 900 parts of water in which are dissolved the bisulphite and carbonate of soda of the formula. Lastly, dissolve together in the remaining 100 parts of warm water, the cyanide of potassium, and the arsenious acid, and pour this solution into that above named, which is rapidly decolorized, and forms the brassing-bath. Filter, if necessary.

The presence of arsenious acid causes the deposition of a brilliant alloy, but too great a proportion of it may impart a white or steel-gray color to the metal; and it often happens that with new baths the first articles immersed in them receive a deposit having these shades. The inconvenience is slight, however, since the yellow color soon predominates. Brass electro-platers say that arsenious acid cleans the baths, because it prevents deposits of a dull color, or rather because, being transformed into arsenic acid, it prevents the contamination of the deposits with the oxides of copper or zinc. The arsenious acid may be replaced by any of the soluble arsenites, as for example, that of potassa, soda, or ammonia, but in such case, the proportion given in the formula must be doubled. These baths, it may be added, act with greater regularity the older they are, and the more frequently they have been recharged with salts.

The baths for electro-brassing in the cold are generally kept in wooden tanks lined inside with gutta-percha,

which resists their action for a long time. The articles to be plated are suspended from copper or brass hooks to stout rods of the same metal, resting crosswise on the rim or flange of the tank, and communicating with the last zinc of the battery (Fig. 83), or with the negative

Fig. 83.



pole of the dynamo. The sides of the tank are also lined with one or several sheets of brass (united together), and connected with the last carbon, or copper, of the battery, or with the positive pole of the dynamo; or the vat is divided into several compartments by plates of brass similarly connected. The intensity of the current used is regulated by the surface of the articles to be electro-plated.

Theoretically speaking, such a bath should be maintained at a uniform degree of strength by the metal dissolved from the brass anodes, under the action of the electric current. But experience shows that this is not the



case, and that the proper equilibrium of the bath must be maintained by fresh additions from time to time of copper and zinc salts, and arsenious acid, dissolved in cyanide of potassium. It is quite impossible to state the necessary proportions of these additions for maintaining the bath in proper working order; and the intelligent operator must determine what is needful to be added from the rate of deposition, the color of the deposit, etc.

If the deposition be too slow, he will try whether the bath will take up salts of copper and zinc, without the addition of cyanide.

If the brass deposit has an earthy and ochreous appearance, and especially if the bath exhibits a bluish or greenish tint, he will add cyanide of potassium until complete decolorization takes place.

If the deposit be dull and unequal, a small quantity of arsenious acid, dissolved in cyanide, is needed.

If the deposit be too red, the operator will add some salt of zinc, alone, or dissolved in cyanide.

If the deposit be too white, or of a greenish-white color, he will add some salt of copper, either alone or dissolved in cyanide.

Lastly, when, after long use, the bath has become so overloaded with salts as to interpose too high a resistance for the free passage of the electric current, the liquid must be diluted with water until it works satisfactorily. The specific gravity of a brassing bath may vary, without inconvenience, from  $5^{\circ}$  to  $12^{\circ}$  of Baume's hydrometer.

It is well understood that the pieces, before electro-brassing, must be perfectly cleansed in the manner indicated in the proper place; and if, notwithstanding the proper care, the brass deposit be unsatisfactory, the objects must be removed from the bath, rinsed, scratch-brushed, and again placed in the bath, until the color and the

thickness of the deposit are satisfactory. They are then scratch-brushed anew, and, if necessary, rinsed in hot water, dried in warm white-wood sawdust, and put in the stove-room. The last three operations are indispensable for hollow pieces.

We give below several useful formulæ, for which Roseleur is authority, and which are based on the use of an impure cyanide of potassium.

*Second Formula.*

BRASSING BATH FOR WROUGHT AND CAST IRON, STEEL, AND TIN.

Dissolve together, in 800 parts of rain water—

Bisulphite of soda . . . . .	20 parts.
Cyanide of potassium (65 to 70 per cent. pure)	50 “
Carbonate of soda . . . . .	100 “

And to this add the following solution:—

Water . . . . .	200 parts.
Acetate of copper . . . . .	12.5 “
Protochloride of zinc (neutral) . . . . .	10 “

The two liquids become colorless by their admixture.

*Third Formula.*

BRASSING BATH FOR ZINC.

Distilled, or rain water . . . . .	200 parts.
Bisulphite of soda . . . . .	7 “
Cyanide of potassium (65 to 70 per cent. pure)	10 “

To which add the following solution:—

Water . . . . .	50 parts.
Acetate of copper . . . . .	3½ “
Chloride of zinc . . . . .	3½ “
Ammonia . . . . .	4 “

The filtered bath is colorless, and gives, under the action of the current, a brass deposit of a very fine shade, which may be made to vary from red to green, by in-



creasing, respectively, the proportion of copper or zinc. The anode is, of course, of brass.

The difficulty in electro-brassing, especially with small baths, lies in preserving the uniformity of the color of the deposit. It will be understood that the galvanic current, having to decompose simultaneously two salts, each offering a different resistance, must, according to its intensity, vary *ad infinitum* the composition and the color of the deposited alloy. It will be found in practice that a feeble current decomposes principally the copper salt without sensibly attacking that of zinc, the resulting deposit being reddish; on the other hand, a current of too great intensity decomposes the solution of zinc too rapidly, and deposits a white or bluish-white alloy.

These phenomena are most noticeable in newly prepared baths, and it is not uncommon to see one side of an object, that presented to the anode for example, covered with a fine brass deposit, while the opposite face has a reddish color. This is an indication that there is irregularity in the conducting power of the bath, which, however, corrects itself after being used for some time.

The inconvenience of a reddish deposit, due to a want of intensity in the current, may be remedied either by increasing the strength of the current, or by decreasing the number and the surfaces of the objects to be plated. On the contrary, the opposite inconvenience of white deposits will disappear by diminishing the strength of the current, or by increasing the extent of the surfaces to be covered.

The character of the deposit may also be modified by substituting for the brass anode, either a sheet of pure copper, or one of zinc, or by simply hooking one of these sheets to the brass anode.

A bath of pure copper will be transformed into one of

brass by the use of a zinc anode; and conversely, an electro-bath of brass will become one of copper in the presence of a copper anode.

The disposition of the baths for brass-plating will vary with the nature and the size of the objects to be plated; but it is always well to have all the articles suspended at about equal distances from the anode. With small articles, the bath may be subdivided by several anodes forming partitions, as in Fig. 83, page 136, so that each loaded rod will be located between two anodes, or in a separate bath of its own. These anodes should be removed when the bath is not in operation. Small articles which cannot be threaded upon a wire, like nails, wood-screws, etc., are plated in a perforated stoneware ladle, as explained in Chapter X.

In order that the electro-brassing of zinc and iron shall be sufficiently lasting, the deposit must not be too thin, and must be scratch-brushed, rinsed in water rendered slightly alkaline by quicklime, and thoroughly dried in a stove. Its lustre and color are thus enhanced. But, generally, and especially when the bronze lustre is to be imparted afterwards, an immersion of from 10 to 25 minutes in the brassing bath suffices.

The processes recommended for electro-brassing and bronzing by simple immersion are not altogether satisfactory. Nevertheless, a color resembling that of brass is given to small articles of iron or steel, by a long stirring in a suspended tub (see Fig. 26, page 57) containing the following solution:—

Water	. . . . .	1000 parts.
Sulphate of copper	. . . . .	4 to 5 "
Protochloride of tin (crystallized)	. . . . .	4 to 5 "

The shades may be modified by varying the proportions of the two salts.



In addition to the methods named above, which are those recommended by Roseleur, we append, for the information of our readers, a number of formulæ for electro-brassing which are approved by various authorities, and which will be found useful.

Dr. Emile Winckler (*Handbuch d. Metallüberzügen*, 227) recommends the following procedure for electro-brassing zinc, tin, copper, iron, and steel, viz.: Prepare a saturated solution in water (in separate vessels) of chloride of zinc,\* and of sulphate of copper. Prepare a separate solution of—

Cyanide of potassium . . . . .	100 parts.
Water . . . . .	1000 "

Add the cyanide solution to that of the sulphate of copper, in sufficient quantity to re-dissolve the cyanide of copper that will at first appear. The result should be a perfectly clear, grass-green solution. Into this, the solution of zinc chloride is gradually introduced, constantly stirring with a glass rod, until the solution exhibits a white turbidity.

This solution is diluted with 2000 parts of water, heated to boiling in an enamelled vessel of suitable size, then allowed to cool and filtered, when it is ready for use.

The bath is used at ordinary temperatures, with a brass anode, and the articles, properly cleansed, are allowed to

\* Winckler's formula calls for a clear solution of chloride of zinc, but he omits to inform the operator that to obtain this it will be necessary to add to the solution a few drops of hydrochloric acid, to dissolve the white precipitate of basic salt, which is invariably formed in dissolving this salt in water, or on diluting its concentrated solutions. The chloride of zinc of this formula may, however, be dispensed with, and the sulphate used in its place. As the sulphate yields a clear solution with water, it may, on this account, be found preferable by some operators.

remain in the bath until a sufficiently heavy coating of brass has been deposited. A deposit of the thickness of ordinary writing paper, will stand atmospheric exposure very well, assuming after long exposure the greenish discoloration characteristic of genuine bronzes.

De la Salzede dissolves—

Carbonate of potassium . . . . .	610 parts.
Chloride of copper (cupric chloride) . . . . .	25 “
Sulphate of zinc . . . . .	48 “
Nitrate of ammonium . . . . .	305 “
Cyanide of potassium . . . . .	12 “
in Water . . . . .	5000 “

When filtered, the above solution is ready for use. The bath is used with a moderate current and a brass anode. The deposited brass has a fine color, and, when a sufficiently thick coating has been obtained, the articles are removed from the bath, well rinsed in water, dried, and polished. Another formula of the same inventor has the following composition:—

Carbonate of potassium . . . . .	500 parts.
Cyanide of potassium . . . . .	50 “
Sulphate of zinc . . . . .	35 “
Chloride of copper . . . . .	15 “
Water . . . . .	5000 “

A bronzing solution is prepared by Salzede by substituting, for the sulphate of zinc of his first formula, 25 parts of chloride of tin. The second formula may be converted into a bronzing bath by substituting 12 parts of chloride of tin, in place of the zinc salt.

These baths are apt to work irregularly after some time, by reason of the more ready solution of the copper of the anode, by the cyanide. This difficulty, which is a common one with brassing baths, is referred to at some length later on, and certain suggested remedies are given.

Watt (*Electro-metallurgy*, 73 *et seq.*) recommends the following bath :—

Acetate of copper . . . . .	5 ounces.
Potassa (caustic) . . . . .	4½ pounds.
Sulphate of zinc . . . . .	10 ounces.
Aqua ammonia . . . . .	1 quart.
Cyanide of potassium . . . . .	8 ounces.

He dissolves the pulverized acetate of copper in one-half gallon of water, adds a pint of the ammonia, then dissolves the sulphate of zinc in one gallon of hot water, and adds to it the remaining portion of the ammonia, stirring well to insure its thorough mixture. The potassa is then dissolved in one gallon of water, and then the cyanide in the same quantity. In mixing these ingredients, he recommends the following order: add the copper solution to that of the zinc, and stir into it the solutions of potassa and cyanide. The mixture should be thoroughly stirred and allowed to digest for about an hour, with occasional stirring. Before using, it is to be diluted so as to make eight gallons of solution. This bath should be worked with a moderately strong current and a brass anode, which should be well cleaned before immersion. Should the bath be found to work slowly or irregularly, he advises the occasional addition of ammonia and a little cyanide. The addition of about an ounce of a solution of arsenious acid and strong cyanide from time to time is recommended as giving a brighter and less crystalline deposit.

Brunel, Bisson, and Gangain employ the following electro-brassing bath :—

Carbonate of potassium . . . . .	50 parts.
Chloride of copper . . . . .	2 “
Sulphate of zinc . . . . .	4 “
Nitrate of ammonium . . . . .	25 “
Distilled water . . . . .	500 “



The above solution is filtered, and is ready for use. The bath is used at the ordinary temperature with a brass anode. To convert it into a bronzing bath, tin salt is substituted for the sulphate of zinc of the above formula, and a bronze anode for that of brass.

Walters prefers to electrolyze a concentrated solution of cyanide of potassium with the use of a copper anode. When sufficient copper has been dissolved, the copper anode is removed, and one of zinc substituted and allowed to remain until an article at the cathode takes a deposit of the proper color.

Gore (*Electro-metallurgy*, 279) recommends as "a good solution for brassing by means of a separate current," the following solution:—

Aqua ammonia (strong)	. . .	9 to 10 parts.
Cyanide of potassium	. . .	16 to 20 "
Water	. . .	160 "

This liquid is saturated with brass by means of the current with an anode of brass, and is used at boiling temperature.

Morris & Johnson employ an electro-brassing bath prepared as follows. It may, by suitable modification of its constituents, be used for other alloys, and may be used either hot or cold.

Carbonate of ammonium	. . .	50 parts.
Cyanide of potassium	. . .	50 "
Cyanide of copper	. . .	6 "
Cyanide of zinc	. . .	3 "
Water (distilled)	. . .	400 "

By electrolyzing a solution of the two first-named ingredients, with a brass anode, a bath capable of giving a brass deposit will also be obtained, if the action of the current is continued until sufficient brass has been dissolved from the anode.



As before remarked, the above solution may be used cold, but the inventors prefer to operate at a temperature of 212° Fahr. When depositing, hydrogen is freely liberated at the cathode, and the brass coating may be made of any desired thickness. If the color of the deposited metal is too deep, indicating the deposition of too large a proportion of copper, the inventors recommend the addition of some carbonate of ammonium; if, on the contrary, zinc is too freely deposited, the addition of some cyanide of potassium is indicated.

If it be desired to obtain metallic deposits resembling various alloys (argentan, German-silver, etc.), it will be necessary to prepare a solution of carbonate of ammonium and cyanide of potassium, and to dissolve in this the cyanide of nickel, cyanide of zinc, and cyanide of copper in suitable proportions, corresponding to the alloy required, and to submit the objects in this to the action of the current, using a German-silver or other corresponding anode.

Bacco's procedure, which is affirmed to produce, upon zinc articles, an adherent coating of brass that will even stand burnishing, and which may be obtained either by simple immersion, or by galvanic means, is as follows: He prepares a solution of equal parts of sulphate of copper and sulphate of zinc, in water, and adds thereto a sufficient quantity of solution of cyanide of potassium to dissolve the precipitate that is formed. To the resulting solution  $\frac{1}{10}$  to  $\frac{1}{8}$  of aqua ammonia is added, and it is then diluted to 8° Baumé with water, when it is ready for use.

For a light colored brass deposit the relative proportions of metallic salts will be—

Sulphate of zinc . . . . .	2 parts.
Sulphate of copper . . . . .	1 part.

The zinc objects, previously cleansed by scouring with pumice powder and water, or with muriatic acid and fine sand, and then rinsed in water, are at once suspended in the above described bath, and allowed to remain for 24 hours. They are thereupon taken out and washed with water, whereupon the deposit should appear as bright as though polished.

By omitting the zinc salt in the above formula, and following the same method, articles of zinc may be coppered by simple immersion.

These copper or brass deposits are very adherent, and may be polished on the buffing wheel, or burnished. If this solution is worked with the current, copper or brass deposits of any desired thickness may be obtained. The copper- or brass-coated articles may be silvered or gilded.

If, instead of the sulphate of zinc of the formula, 2 parts of chloride of tin, and 1 of chloride of copper be substituted, the resulting metallic deposit will have the appearance of bronze. In this case, a bronze anode must be employed, while, it is scarcely necessary to mention, for brassing, a brass anode will be used.

Newton employs for his electro-brassing solution a mixture of the chloride of zinc with the chloride of ammonium, sodium, or potassium, dissolved in water; or a solution of the acetate of zinc with the acetate of ammonium, sodium, or potassium. This solution, he combines with a suitable proportion of the corresponding salt of copper; *i. e.*, with the chloride of zinc, he uses the chloride of copper, etc.

The same inventor prepares a bronzing solution by dissolving the double tartrate of copper and potassium, and the double tartrate of tin and potassium, in suitable proportions, either with or without the addition of caustic potassa. For depositing an alloy of copper, tin, and zinc,



he employs a bath consisting of the double cyanide of copper and potassium in combination with zincate and stannate of potassium. The last-named substances are made by fusion of oxide of zinc and of tin, respectively, with caustic potassa.

For electro-bronzing, Ruolz dissolves in 5000 parts of water sufficient cyanide of potassium to make a solution of the density of 4° Baumé at the ordinary temperature. In this he dissolves, at a temperature of from 125° to 150° Fahr., 30 parts of dry cyanide of copper, and 10 parts of oxide of tin. The resulting solution should be quite clear before using.

Dr. Elsner's electro-bronzing solution is made by dissolving 60 parts of sulphate of copper in 1000 parts of water, and adding thereto  $7\frac{1}{2}$  to 10 parts of chloride of zinc dissolved in caustic potassa. This solution bronzes cast-iron statuettes quite satisfactorily. The bath is worked with the current, at ordinary temperatures, using a bronze anode. Cast-iron objects receive a matt yellowish-brown deposit. When the deposit is sufficiently heavy, the articles are removed from the bath, rinsed, dried, and polished or burnished.

The fact has been mentioned above, in connection with this subject, that a current of too great intensity decomposes principally the zinc of the solution, depositing a grayish zinc coating, while, on the other hand, a feeble current affects principally the copper of the bath, yielding a reddish deposit. Hess claims to overcome this difficulty by his method of procedure, which is as follows: He prepares a solution (Japing, *Die Electrolyse, etc.*, 182) of—

Bicarbonate of sodium	. . . . .	84 parts.
Chloride of ammonium	. . . . .	54 "
Cyanide of potassium	. . . . .	13 "
Water	. . . . .	2000 "

The depositing vat is lined with sheets of brass, which serve as the anode. To charge the solution, he electrolyses the bath, using a brass plate for the cathode. When the current has passed for about an hour, it is in condition to use. A bath thus prepared will, according to Hess, dissolve alloys of all proportions, so that every variety of copper-zinc alloy, each with its characteristic color, may be reproduced in it.

Watt (*Electro-metallurgy*, 83), referring to the difficulty of keeping brassing solutions in proper working condition, attributes the cause to the fact that the copper of the anode is more readily attacked by the solution, while the zinc, being liable to be converted into an almost insoluble salt, either remains on the anode in the form of a white mass, or falls to the bottom of the bath, but a small portion of it entering the solution; consequently, the bath, instead of depositing the yellow alloy, deposits only, or chiefly, copper. To correct this difficulty, he recommends the addition of some concentrated zinc solution; or, of strong aqua ammonia in large quantity, which will dissolve the zinc precipitate from the anode, and from the bottom of the bath, and restore the solution to good working condition. At the time of adding the ammonia, he recommends the addition also of a little additional cyanide. The above suggestion may be modified by separating the clear liquid from the precipitated zinc salt, treating this with ammonia and cyanide, as above, until it has dissolved, and adding this solution to the bulk of the solution, which will then be found to work properly. Where it is practicable, this last plan is the preferable one.

The following practical hints from the same author will be found useful to remember; viz., Iron, lead, zinc, tin, and alloys of lead, etc. will not all receive an equally



good coating of brass if placed in the bath at the same time. . . . In immersing in the bath, two different metals, as cast iron and zinc for instance, the zinc would receive the deposit at once, whilst the iron would not receive the smallest amount of deposit. Even cast and wrought iron require to be coated in different baths. Iron and zinc require different degrees of battery power to effect a good deposit upon them. A battery which would coat zinc well would not cause the least deposit to take place upon cast iron. Cast iron requires a solution containing a greater percentage of metal than zinc or its alloys, while zinc will receive a good deposit when but little metal is in the bath. . . . Wrought-iron work does not require so much metal in the bath as cast iron. Lead requires a bath richer in metals than zinc or its alloys. It does not receive the deposit as favorably as zinc, but pewter receives it tolerably well.

In another place we shall refer to certain methods in vogue for imparting the appearance of bronze, etc., to metallic surfaces by mechanical or chemical means.

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## CHAPTER XII.

TINNING—TINNING BY SIMPLE IMMERSION—ELECTRO-TINNING  
—TINNING BY CONTACT WITH ANOTHER METAL—TINNED  
CAST IRON.

### *Tinning.*

It has already been said that, as is the case with copper and brass deposits, tinning is often the complement of the cleansing process for certain metals, like wrought and cast iron, upon which the more precious

metals are to be deposited. We might, therefore, confine ourselves to the tinning of cast iron; but, as the tinning of a multitude of different articles is, at the present time, an important industry, we believe that a description of all the operations and processes will be found instructive and useful.

Tinning by the wet way is effected by three distinct methods;—

1. BY EXCHANGE, that is to say, by the solution in a stannic bath, of a small quantity of the metal immersed in it, which displaces an equivalent proportion of the tin, and which deposits itself in the form of an adherent layer upon the other metal. This process does not give sufficiently lasting results, and is but a kind of whitening of the object, like that obtained with silver and gold by simple immersion, which will be described further on.

2. BY THE GALVANIC WAY, that is to say, by the decomposition of certain tin solutions by means of the galvanic current. This mode of operation is similar to that already described for copper and brass deposits.

3. BY THE METHOD OF CONTACT, OR OF DOUBLE AFFINITY; which means that, by immersing at the same time, in a tin solution, two different metals kept in contact with each other, zinc and iron for instance, the zinc, instead of becoming tinned as by the first method, will dissolve and take the place of the tin, which, in its turn, will be deposited in a uniform and adherent coating upon the iron.

*Tinning Bath (for Iron) by Simple Immersion.*

This process is of little importance as a means of protecting iron against oxidation, since the layer of tin is a mere film. However, it may be useful as a complement of the cleansing process and as a preparation for a thicker

coating of tin to be subsequently applied by one of the other processes to be described.

For the preparation of this bath, dissolve, with the aid of heat, in a large enamelled cast-iron kettle, in 2000 parts of water:—

Ammonia-alum . . . . .	30 parts.
Protochloride of tin (fused) . . . . .	1 part.

As soon as the solution boils, the objects of iron, previously cleansed and rinsed in cold water, are steeped in it. They are immediately covered with a film of tin of a fine white color and dead lustre, and may be rendered bright by tumbling.

As it becomes spent the bath is maintained at the proper strength by small additions, from time to time, of fused protochloride of tin.

This bath is also very convenient for a preliminary tinning of zinc; but, as for iron, the coating is too thin to be resistant. When the objects thus tinned, or whitened, present considerable surface, they are brightened by scratch-brushing.

For tinning zinc by simple immersion, the ammonia-alum may be replaced by any other alum, and even by the sulphate of aluminium; though experience proves that, for wrought and cast iron and steel, this substitution is objectionable.

If it is desired, with the above solution, to tin other metals than zinc or iron, we must have recourse to the battery. Roseleur, however, prefers, for this purpose, certain special solutions, the description of which will follow.

More recently the following modified formula has been proposed, especially for small objects, viz.:—

Ammonia-alum . . . . .	50 parts.
Protochloride of tin . . . . .	3 “
Water . . . . .	1000 “



The articles are immersed in this bath at a boiling temperature. Tin salt should be added, from time to time, as the solution becomes weakened.

According to Roseleur, zinc may be tinned with a thin coating, by the simple immersion process, by the use of a bath composed of 5 parts of pyrophosphate of sodium and 1 part of protochloride of tin, dissolved in 300 parts of distilled water. This bath will be referred to in another place.

A method of immersion tinning, described by Roseleur as "whitening" by tin, which has been practised from time immemorial, for obtaining a thin coating of tin upon pins, nails, and other small articles of brass and copper, consists of disposing the articles in a copper trough in layers between sheets of tin, in such a manner that each layer of the articles shall be between two plates of tin; then covering the charge with a saturated solution of cream of tartar, and boiling.

This process, it will be observed, is adapted only for articles of brass or copper. Articles of iron and steel may be treated in the same manner, however, if given a previous coating of copper, by one or the other of the methods previously described. The addition of a small quantity of protochloride of tin to the solution may facilitate its operation. Instead of sheets of tin, grain tin may be used, arranged in layers upon copper or brass gauze, alternating with the articles to be coated. The process is only adapted for small articles, and the tinning takes place rapidly.

Lüdersdorff employs for simple immersion tinning of zinc wares (Winckler's *Handb. d. Metallüberzügen*, 267) a bath composed of—

Cream of tartar (bitartrate of potassium)	. . . . .	2 parts.
Chloride of tin (stannic chloride)	. . . . .	2 "
Water	. . . . .	4 to 5 "



This mixture is heated to about 170° Fah., to promote its solution. Lüdersdorff prefers stannic chloride to the stannous salt, for the reason that the latter deposits the metal in the form of a black powder in the zinc, whenever the bath acquires a certain degree of concentration. To coat zinc articles with the above-named bath, they are either simply immersed in it for several hours, at the end of which time they will be found to have taken on a grayish appearance, when they are to be removed, scoured, without previously drying, with a mixture of fine sand and clay, until they exhibit the proper lustre, when the operation is complete; or, instead of immersing the articles in the bath, they may be scoured with it. To do this, sufficient fine sand is added to the liquid, to form a thin mush, with which the articles are scoured or brushed. We shall refer again to this process in connection with tinning by contact with another metal.

The zinc articles must, before tinning, be thoroughly freed from oxide, for which purpose Lüdersdorff recommends a pickle composed of—

Nitric acid of 36° B. . . . .	2 parts.
Sulphuric acid (conc.) . . . . .	1 part.
Diluted with water . . . . .	3 parts.

The zinc articles are dipped into this pickle for a few seconds, then passed at once through several wash waters, and finally dried in saw-dust. If the surface does not appear perfectly white and brilliant, the operation must be repeated. For large objects of zinc, which cannot be well cleansed in this powerful acid dip, Lüdersdorff recommends ammonio-potassic tartrate, which, he alleges, will dissolve the grayish film of oxide from the zinc, without attacking the metal. The articles must be left for some time in contact with this solution, when they may be removed and washed in water.

The ammonio-potassic tartrate may be prepared by heating to about 170° Fah., in a suitable vessel, 1 part of bitartrate of potassium (cream of tartar) dissolved in 4 parts of water, and adding to this, in small portions at a time, coarsely powdered carbonate of ammonium, with constant stirring, until a fresh portion of the ammonium salt fails to cause any effervescence.

According to Gore (*Electro-Metallurgy*, 265), clean articles of copper, brass, or bronze, in contact with cuttings of tin, in a boiling solution of peroxide of tin in caustic potash, become coated in a few minutes with a beautiful layer of metal.

#### *Electro-Tinning.*

Electro-deposits of tin may be obtained with a variety of tin solutions; and the results are more or less satisfactory, and the methods more or less practical, as regards the facility of the operation, its cost, the strength and the beauty of the tinning. There is, however, but little demand for electro-tinned articles, and consequently but little industrial importance is attached to these processes.

The bath, which Roseleur recommends as uniting in the highest degree all the advantages desired by the operator, is composed of—

Rain (or distilled) water . . . . .	5000 parts.
Pyrophosphate of sodium (or potassium) . . . . .	50 “
Protochloride of tin (stannous chloride) crystallized . . . . .	6 “

Or, preferably, 5 parts of the tin salt fused, in order to have it free from an excess of acid.

The water is put into a tank entirely lined with plates or anodes of tin, united together and connected with the positive pole (carbon or copper) of the battery. The pyrophosphate of sodium, or potassium, is next introduced and stirred in, and when-dissolved, the protochloride of tin is placed in a sieve of copper half immersed in the solu-



tion. A milky-white precipitate immediately forms, which disappears by continued agitation. When the liquid has become clear and colorless, or only slightly yellow, the tinning bath is ready, and we have only to dispose upon transverse metallic rods, connected with the negative pole, the previously cleansed objects to be tinned.

The anodes alone will not suffice to keep the bath saturated, and when the deposit takes place slowly, it becomes necessary to add, in small portions at a time, a mixture of equal parts of tin salt and pyrophosphate. The solution of these salts should always be made with the aid of the sieve, since, if fragments of protochloride of tin were to fall to the bottom of the bath, they would become covered with a difficultly-soluble crust preventing their solution.

The tinning thus produced upon any kind of metal, and with equal facility, is quite resistant, and has a white color and dead lustre resembling electro-deposited silver. A bright lustre will be obtained with the scratch-brush, or the burnisher. The reduction of these baths requires quite an intense current, and, as above indicated, a large surface of anode.

T. Fearn has patented, in England, a number of solutions for the deposition of tin by the galvanic method. Of these, the first two of those about to be described, appear to be best adapted for the purpose. Fearn's process is reported by Gore to be in use in Birmingham, Eng., by the Electro-Stannous Company."

The inventor dissolves 150 pounds of sal-ammoniac in 100 gallons of water, and pours into it 200 fluidounces of solution of tin salt (stannous chloride), containing 3 ounces of metallic tin to the gallon. The mixture is well stirred. It is worked at a temperature of 70° Fah., with a current of moderate intensity with a tin anode, which it dissolves freely.

Another electro-tinning bath of the same inventor is prepared by dissolving 400 ounces of tartrate of potassium in 50 gallons of water, and in another 50 gallons of water 1200 ounces of solid caustic potassa; 600 fluidounces of the tin salt solution of above-named strength, are then gradually added, with stirring, to the tartrate solution; and, finally, the potassa solution is poured into the mixture, and the whole thoroughly agitated until the precipitate dissolves and a clear solution results. This solution may be worked in the cold, and yields, on metal surfaces, a thick deposit of tin, without requiring alternate deposition and scratch-brushing. The anode does not suffice to keep the bath saturated, more tin being deposited than is dissolved in a given time, so that to keep up its strength, occasional additions of the oxide, or other compound of the metal, must be made.

Another of Fearn's electro-tinning baths is made by dissolving 56 pounds of sal-ammoniac in 60 gallons of water, and 20 pounds of pyrophosphate of sodium in 40 gallons of water. To this last solution are added 100 fluidounces of tin salt solution of above-named strength. The mixture is stirred until the resulting precipitate is dissolved, and the sal-ammoniac solution is added, with stirring, to the mixture. This bath is directed to be worked at a temperature of 100° to 110° Fah., with a moderate current and a tin anode. Its metallic strength must be maintained by occasional additions of oxide, or other compound of tin. Cast-iron articles require to be coppered previous to being tinned in these baths.

Joseph Steele effects the electro-deposition of tin upon zinc, iron, steel, copper, and brass, with a moderately strong solution of oxide of tin in a mixture of soda (of commerce) and caustic potash dissolved in water. To this he adds a small quantity of cyanide of potassium and



acetate of zinc. The bath is worked at 75° Fah., with a tin anode.

Dr. Elsner (Japing, *Die Electrolyse*, 264) prepares an electro-tinning bath by dissolving—

Chloride of tin (stannic chloride) . . .	30 parts.
Water . . . . .	1250 “

and adding thereto a concentrated aqueous solution of caustic potassa, until the white precipitate of hydrated oxide of tin that is formed at first is completely dissolved. The bath is used at ordinary temperatures with a moderate current and a tin anode.

For electro-tinning hollow-ware (kitchen utensils), Winckler (*Handb. d. Metallüberzügen*, 266) employs a bath composed of—

Protochloride of tin (stannous chloride) . . .	8 parts.
Perchloride of tin (stannic chloride) . . .	2 “
Bitartrate of potassium . . . . .	16 “

dissolved in water. By simply heating the articles, the tin coating assumes the proper lustre.

For coating lead with tin by galvanic means, Munro precipitates a solution of tin salt with carbonate of sodium solution, and dissolves the precipitate in dilute sulphuric acid. The sulphate of tin thus formed constitutes the bath, in which the lead articles are suspended in the usual manner, a plate of tin serving as the anode.

For the same purpose (electro-tinning lead) Alfred Cox recommends a bath prepared by precipitating a concentrated solution of commercial tin salt with phosphate of sodium. The well-washed precipitate is dissolved in concentrated solution of caustic soda, to which about 5 per cent. of ammonia has been added. The resulting solution, diluted with water, constitutes the electro-tinning bath.

Numerous other methods for electro-tinning have been recommended, but this method of depositing tin, as above remarked, possesses no industrial importance, because of the ease, rapidity, and cheapness with which articles of iron and copper are coated with tin by simple immersion in a bath of the metal in a melted state. This method of tinning, which is exclusively adopted for tinning sheet-iron, and largely, also, for tinning cast-iron hollow-ware (kitchen utensils), will be described in a separate chapter.

*Tinning by Contact with another Metal.*

A bath suitable for tinning may vary greatly in its composition; however, we give below two formulæ which may be depended on to give rapid and reliable results. Roseleur expresses his preference for the second formula.

*First Formula.*

Distilled water . . . . .	3000 parts.
Bitartrate of potassium (cream of tartar) . . . . .	30 "
Protochloride of tin (stannous chloride) . . . . .	3 "

The powdered cream of tartar is dissolved in 2000 parts of warm water, and the tin salt in 1000 parts of cold water. The mixed solutions form a clear liquid of strongly acid reaction, which constitutes the bath.

*Second Formula.*

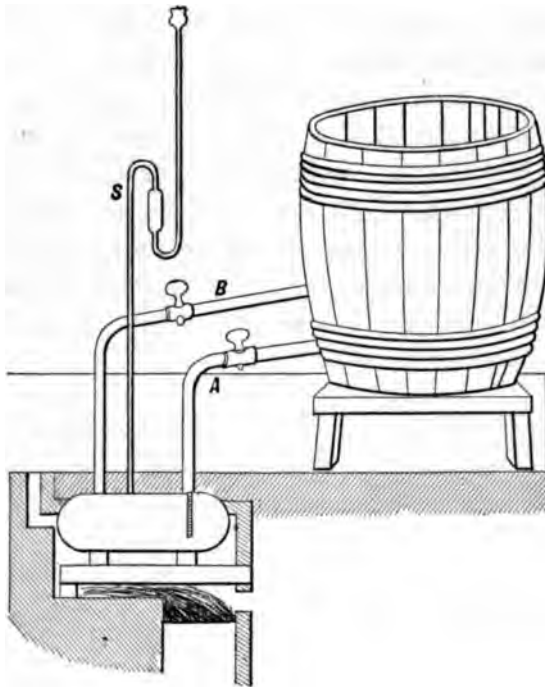
Distilled water . . . . .	3000 parts.
Pyrophosphate of potassa (or soda) . . . . .	60 "
Protochloride of tin, crystallized ( <i>i. e.</i> , acid) . . . . .	6 "
Or, the same, fused ( <i>i. e.</i> , neutral) . . . . .	4 "

The whole is dissolved at the same time upon a metallic sieve, and, after stirring, there results a clear liquid which constitutes the bath.

These solutions may be kept in a cask open at the top. This cask or tank (Fig. 84) receives at its lower part two

superposed tubes communicating with a small boiler built below the level of the bottom of the tank. The tube *A*, starting from the bottom of the tank, reaches nearly to the bottom of the boiler; on the other hand,

Fig. 84.



the upper tube *B*, distant three or four inches from the bottom of the tank, communicates with the top of the boiler; lastly, a third tube *S*, open above, is provided, to act as a safety-valve, and prevent an explosion, should there occur an obstruction in either of the other tubes.

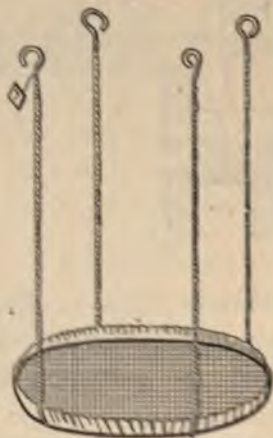
It will be readily understood that, with such a disposition, and with the boiler and tank filled with liquid, as soon as heat is applied, the expanded and lighter liquid will rise through the pipe *B*, while the colder and denser



liquid will enter the boiler through the pipe *A*. A continual circulation is thus established, which is not only satisfactory as a means of heating, but also keeps up a constant agitation of the contents of the bath, and mixes the impoverished lighter portions with the richer and denser ones. A small quantity of water, or mercury, is introduced into the upper branch of the tube *S*, to prevent the escape of the steam.

Large pieces, like cast-iron kitchen utensils, are simply cleansed and rinsed, and dropped into the bath with a few fragments of zinc. It is, however, preferable to use spirals of zinc, since, having fewer points of contact with the articles to be tinned, they lessen the risk of spotting them. On an average, the surface presented by the zinc introduced into the bath should be the thirtieth of that of the tinned articles.

Fig. 85.



If, on the other hand, we wish to tin very small objects, such as pins, nails, hooks, etc., we dispose them in layers, say, about an inch thick, upon perforated trays of zinc, which allow of the circulation of the liquid, and



which are provided with a rim to prevent the objects from falling off. These trays (Fig. 85) are suspended in the bath from chains, one of which carries a numbered tag, by which each one may be identified and removed from the bath in its proper order.

From time to time, the surfaces of these zinc trays must be scraped and cleaned to remove the white incrustation which forms upon them, and which prevents metallic contact with the articles to be tinned.

The length of the operation may vary from one to three hours. Then all the objects are removed, and 25 parts of pyrophosphate, and as much of fused protochloride of tin, are introduced into the bath.

During the time the solution of these added salts is taking place, the large articles are scratch-brushed, and the small ones moved about with a suitable fork in order to change the points of contact. The objects are then again steeped in the bath for at least two hours. These two immersions, and this length of time, are necessary for good tinning. Finally the large pieces are again scratch-brushed, and the small ones rendered bright by tumbling by one of the methods previously described. The operation is ended by drying them in dry and warm sawdust.

Should it be observed that the tin deposit is gray and dull, although abundant, the bath should be recharged once or twice, with the crystallized protochloride of tin. If, on the contrary, the deposit is very white but blistered and without adherence or thickness, the acid salt must be replaced by the fused one. In this latter case, the proportion of tin salt may be diminished, and that of the pyrophosphate may be increased.

As much of the success of the operation depends upon the quality of the pyrophosphate, we shall indicate, in

the brief treatise on chemistry at the end of this work, the process of obtaining it in satisfactory form.

When this tinning bath has been worked for a long time, the liquid should be decanted to separate the pyrophosphate of zinc that has formed. And when, after several years, the bath is entirely spent, from the profound alteration of its salts, it should be put aside in suitable vats provided for the purpose and called preserving vats, so called because it is customary to temporarily preserve in them, after cleaning, the articles to be tinned.

Zinc is well tinned in a similar bath, but the proportions should be modified as follows:—

Distilled water . . . . .	300 parts.
Pyrophosphate of sodium . . . . .	5 “
Protochloride of tin (fused) . . . . .	1 part.

With this, a thin coating of tin may be obtained by simple immersion, as noticed under that heading, and one of any thickness by the aid of the battery.

F. Weil's process (*Chemical News*, xiii. 2) consists in preparing a solution of a tin salt in strong alkali (soda or potassa), in which he immerses the articles in contact with zinc. This bath is used hot, and may be used for tinning on copper, and also on iron and steel. In order to obtain a heavier deposit free from zinc, with which that above named is apt to be contaminated, the same inventor recommends placing in the vessel containing the tin solution, a porous cell containing the alkaline lixivium and the metallic zinc. The article to be tinned is suspended in the outer liquid, and connected with the zinc in the porous cell by means of a conducting wire.

Heillier (*Moniteur Scient.*, July 15, 1869) employs a solution made by dissolving 1 part stannous chloride in 10 parts of water, to which he adds a solution of 2 parts caustic soda in 20 of water. The solution is used hot,

the articles to be tinned being placed on a perforated plate of block tin in the hot solution, and moved about with a rod of zinc until sufficiently coated.

Another method of general utility consists in immersing the well-cleansed metallic articles in a bath composed of—

Bicarbonate of potassium . . . . .	3 parts.
Protochloride of tin (stannous chloride) . . . . .	2 “
Water . . . . .	1000 “

Fragments of zinc are then introduced into the bath, and the articles receive a very uniform coating of tin.

To tin articles of zinc, Hess (Winckler, *Handb. d. Metallüberzügen*) allows them to remain for a quarter to a half hour, in a boiling solution, composed of—

Phosphate of sodium . . . . .	50 parts.
Sal-ammoniac . . . . .	50 “
Bicarbonate of sodium . . . . .	25 “
Tin salt (stannous chloride) . . . . .	25 “
Water . . . . .	1000 “

In this bath, some fragments of pure zinc are likewise placed.

Prof. Fz. Stolba (*Dingler's Polytechnisches Journal*, cxcviii. 308) uses, for tinning, a 5 or 10 per cent. solution of tin salt (stannous chloride) to which a small pinch of cream of tartar (potass. bitartrate) has been added. The well-cleansed article is first rubbed with this solution, and then with zinc powder; then washed and polished.

Urquhart (*Electro-Plating*, 207) recommends the operator to prepare a saturated solution of the double chloride of tin and sodium in water, and to dilute this with twice its bulk of water. The articles to be tinned should be placed in a tray or basket of zinc and immersed in this solution, or otherwise immersed in contact with zinc.



## CHAPTER XIII.

GILDING—GILDING BY SIMPLE IMMERSION—PREPARATION OF  
SIMPLE IMMERSION GILDING BATHS—COLORING PROCESS.

*Gilding.*

GILDING, in the arts, may be executed by two very distinct methods: The wet and the dry way.

The first method appears to be the only one needed in this work, but the recent demands of the trade, which often requires the two kinds of gilding upon the same piece, render it necessary for us to give some information upon what are called the "old processes."

Gilding by the wet way is effected either by means of simple chemical reactions, and receives then the name of *immersion-gilding*; or with the aid of electricity, when it is called *gilding by the battery*, *electro-gilding*, or *gold electroplating*.

Gilding by dipping, or simple immersion, has great analogy with the old processes called gilding by stirring, with the rag, with the cork, etc., according to the mode of operation, all of which result in producing mere films of gold without either firmness or lasting properties.

Electro-gilding, on the contrary, corresponds with the old process of gilding by fire, or mercury. The thickness of the deposit is entirely in the control of the operator; but it must be admitted that, notwithstanding certain advantages possessed by the method, electro-gilding is, even at the present day, far inferior to fire-gilding in respect to firmness, the preservation of the subjacent sur-



faces, and especially the power of resistance to the action of the noxious gases. This criticism, however, does not prevent us from acknowledging the very great improvements made in the art of electro-gilding of late years by the labors of many intelligent industrials; and we may express the hope that the products of both processes will soon be equal in quality.

*Simple-Immersion Gilding.*

This mode of gilding is practised upon trinkets made of copper, brass, bronze, or German-silver.

The baths employed contain the gold in the form of a double salt, and should fulfil the following conditions:—

The solution must possess little stability, that is to say, it should decompose and yield up its gold under feeble influences, and it should dissolve the copper plunged into it in quantity equivalent to that of the deposited gold, thus forming a new double salt in which the copper takes the place of the gold.

When, as is more commonly the case, the articles have been previously amalgamated, it is mercury, instead of copper, which is substituted for gold in the solution.

In order to explain, we should say that if, in a bath of double pyrophosphate of potassium and gold, we dip a well-cleansed piece of copper, this metal will be coated with a thin coating of gold, and will restore to the liquid an equivalent quantity of copper, so that the former salt will be transformed into a double pyrophosphate of potassium and copper.

*Preparation of Baths for Immersion-Gilding.*

The best of these baths is composed of—

Distilled water . . . . .	1000 parts.
Pyrophosphate of potassium* or sodium . . . . .	80 “
Hydrocyanic acid of 8 per cent. (prussic acid) . . . . .	$\frac{1}{2}$ part.
Chloride of gold (crystallized) . . . . .	2 parts.

This quantity of chloride represents one part of pure gold treated with aqua regia, as will be described later.

To prepare this bath, place nine hundred parts of distilled water in a porcelain dish or capsule, or in an enamelled cast-iron kettle, and add in small portions, stirring with a glass rod all the while, the eighty parts of pyrophosphate; apply heat to complete the solution, then filter, and allow to cool.

Distilled or rain water is necessary, because the lime-salts contained in ordinary water decompose a portion of the pyrophosphate; and, if this latter salt were added all at once to the liquid, it would require a long time to dissolve.

While the above solution is filtering, the chloride of gold is prepared, by introducing into a small glass flask—

Pure gold (finely laminated) . . . . .	1 part.
Hydrochloric acid, pure . . . . .	$2\frac{1}{2}$ parts.
Nitric acid, pure . . . . .	$1\frac{1}{2}$ “

The flask is gently heated, and, after a few seconds, effervescence takes place, and abundant nitrous vapors

\* As the pyrophosphate of potassium does not crystallize, its composition is often variable, being either too much or too little basic. The pyrophosphate of sodium is most generally employed in the arts, and is obtained by fusing, at a white heat, the ordinary crystallized phosphate of sodium. The pyrophosphate of sodium may be obtained in the form of crystals, which is a proof of a definite composition.

are given off. In a few minutes, the gold has entirely disappeared, and there remains a reddish-yellow liquid.

The flask is then placed upon a sheet of wire-gauze supported upon a tripod, and heated over the gas or alcohol lamp until the excess of the acids is evaporated. Too much acidity, be it observed, may cause great irregularities in the working of the bath, and even prevent its action altogether.

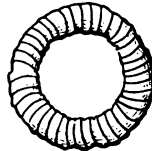
Care should be taken to avoid too rapid heating, which may cause violent "bumping," and the loss of some of the gold by spurting out of the flask. <sup>^</sup>

The heating should be discontinued when vapors are no longer evolved from the flask, and when the liquid has become of an oily consistency and of a deep hyacinth-red color. The flask is then removed from the fire by means of wooden pincers, and set to cool upon a ring of

Fig. 86.



Fig. 87.



plaited straw (Figs. 86 and 87). Should it be necessary to perform this operation more rapidly, the flask may be held by the neck between the wooden pincers, and heated over the naked flame. But this operation must be done carefully, and the liquid kept in constant agitation to prevent the reduction of a portion of the gold.

The well-prepared chloride of gold, when cold, forms a saffron-yellow crystalline mass. If the color is red, it has been too strongly evaporated, and in this condition will answer very well for electro-baths; but if intended

✓  
pic



to be used for immersion baths, it should be again evaporated with a small addition of the two acids.

It frequently happens from carelessness, that the preparation is burned; that is to say, the perchloride of gold, by a too protracted or intense heating, has been decomposed and has passed to the state of an insoluble subchloride, or even to that of metallic gold. The treatment must then be begun afresh with aqua regia, *i. e.* the indicated mixture of pure nitric and hydrochloric acids.

When the chloride of gold has cooled and crystallized, it is dissolved in the flask with a little distilled water, the solution is thrown upon a paper filter placed in a glass funnel, and filtered into a clean bottle (Figs. 88, 89, 90).

Fig. 88.



Fig. 89.

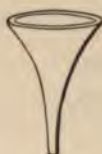


Fig. 90.



To facilitate this operation, a fold of paper should be placed in the neck of the bottle, to allow the escape of the air in the flask. The object of this filtration is to separate a small quantity of silver which is always found in the commercial gold. This separation is based on the fact that the chloride of gold is very soluble, while that of silver is perfectly insoluble in water. The flask and filter are thoroughly rinsed with the unemployed tenth part of water, so as to introduce all the gold into the bath.

The filtered solution of chloride of gold is poured into



the cooled one of pyrophosphate, and the whole is stirred with a glass rod. Lastly, the  $\frac{1}{5}$  part of hydrocyanic acid is added, and the bath is brought up nearly to the boiling point for use.

If the solution of pyrophosphate be still tepid, it is preferable to add the prussic acid before the chloride of gold.

Hydrocyanic (or prussic) acid is not absolutely necessary for the success of the gilding, and many operators do not use it at all; but, then, the bath is too easily decomposed, and the gold is precipitated too rapidly upon the objects immersed in it.

At the moment when the solutions are mixed in the cold, the liquid is yellow or greenish-yellow; but it must become colorless on increasing the temperature. Nevertheless, it sometimes happens that the liquid becomes currant-red or wine-lees-violet in color, which is an indication that there is a want of hydrocyanic acid, which must be added drop by drop, until the liquid becomes colorless. An excess of this acid, however, is objectionable because the deposit of gold is rendered too thin, and may cease entirely, in which case the bath cannot be decomposed except with the aid of the battery. At all events, there is a very simple method of keeping these baths in good working order, which consists in adding prussic acid gradually to those too rich in gold; and conversely, correcting the excess of prussic acid with a small proportion of chloride of gold, until the gilding is produced without difficulty and of the proper shade.

Prepared in the above-described manner, the bath will produce a very fine gilding upon well-cleansed articles, which must also have been passed through a very diluted solution of nitrate of mercury (quicking solution), without which the deposit of gold will be reddish and streaked, and will not cover the soldered portions.

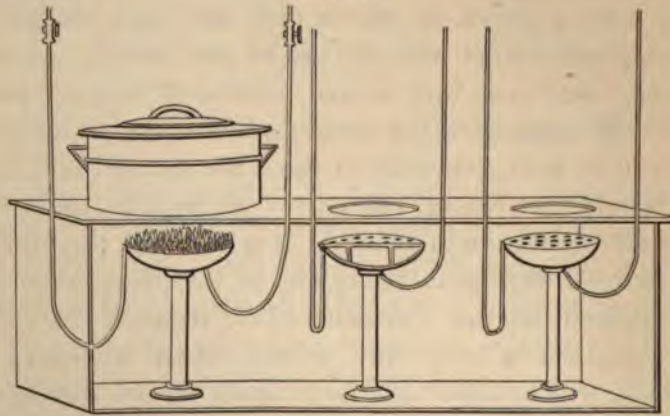
The articles to be gilded must be constantly agitated in the bath, and are supported by a hook or in a stone-ware ladle perforated with holes, or in baskets of brass gauze, according to their shape or size. (See Figs. 1 to 9 of this work.)

Important as are the minute precautions here indicated, they are far from being observed by gilders well conversant with this kind of work. For the preparation of their baths, they are satisfied with dissolving the pyrophosphate in ordinary water, and adding at the same time the prussic acid. Their gold is dissolved as above described, and its solution, without previous filtration, is added to that (more or less hot) of the pyrophosphate.

Gilders by the immersion process usually employ three baths, disposed in close proximity to each other, and heated upon the same furnace, either by charcoal or gas.\*

\* The gas furnace, which is the most convenient and economical one (Fig. 91), is made of a sheet-iron box provided on top with three

Fig. 91.



holes intended to receive the bottoms of three kettles. Inside, and under each kettle, is a Bunsen burner composed of five or six jets burning with a blue flame. These jets are often replaced by a species



The first bath is one that has been nearly deprived of gold by a previous operation, but is used for removing any acid which may possibly remain upon the articles to be gilded. The second bath still contains some gold, but not enough to give a sufficiently rich and dark gilding. By commencing the gilding in this, the gold remaining in it is utilized, while at the same time the strength of the third bath, in which the gilding is finished, is advantageously husbanded.

It need hardly be said, that the fresh bath of to-day becomes the second of to-morrow, and so forth.

This method of operating allows of much more gilding with a given quantity of gold, than with one bath alone. It explains, likewise, why it is that well-organized works having a number of baths at work at one time are able to produce a cheaper and finer gilding than their confrères whose arrangements are not so practical.

The gilding is done in a few seconds, and the finishing operations consist in rinsing in fresh water, drying in dry and warm sawdust, and, if necessary, burnishing.

A good sawdust should be free from resinous and other impurities, and should be that from white woods, of which that from fir, poplar, and linden is especially to be recommended. That of oak and walnut blackens the gilding; and that of boxwood, although often employed, is not sufficiently absorbent.

After drying very small articles in sawdust, the latter

of rose-jet burner, inside of which the mixture of gas and air takes place. This apparatus has two separate stopcocks, one connected with a small central jet, and the other with the rose burner. When both cocks are open, the gas is lighted at all the apertures, and the baths are rapidly heated up to the point of ebullition. The cock of the rose burner is then turned off, and the heat of the central jet is sufficient to keep up the proper temperature.

substance is removed by sieves of various numbers, or by winnowing.

*Coloring Process.*

It happens sometimes, that, through neglect of some of the precautions above indicated, the gilding is dull and irregular in tone. We must then have recourse to coloring, which is conducted as follows:—

Fuse together in their water of crystallization, and at about 212° Fahr., equal parts of—

Sulphate of iron (copperas).

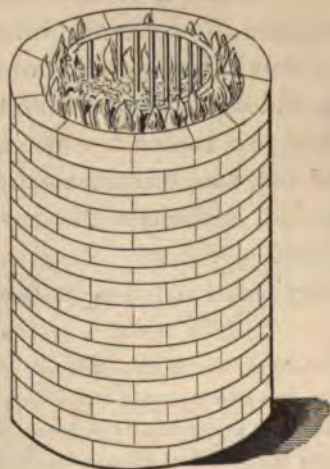
Sulphate of zinc (white vitriol).

Sulphate of aluminium and potassium (potash alum).

Nitrate of potassium (saltpetre).

Smear the imperfectly gilded articles with the mixture, so that all parts are well covered, and place them in the centre of a cylindrical furnace (Fig. 92) in which the

Fig. 92.



fuel (charcoal) is disposed in the annular space between the furnace walls and the cylindrical and vertical grate.

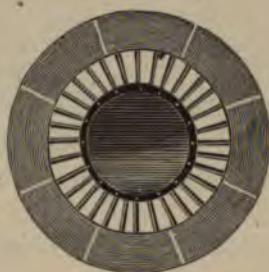


The central portion, into which the heat radiates, receives the objects. Fig. 93 represents a vertical section, and Fig. 94, a plan, of this apparatus.

Fig. 93.



Fig. 94.



The salts begin to dry, then to fuse, and the mass acquires the dull appearance of yellowish clay.

When the moistened finger is presented to one of the pieces and a slight hissing sound is heard, it is evidence that they have been sufficiently heated, and all the articles are then removed, and quickly immersed in a very diluted solution of sulphuric acid, where the external coating of salts which covers the gilding at once dissolves, leaving this of a warm and uniform shade of color.

This process will evidently only answer the purpose when all parts of the copper articles have been entirely covered with gold by the first operation. If they are not, the ungilt portions will show themselves by a red coloration, and the articles must then be "stripped" of their gold, cleansed, and gilded anew. We shall shortly indicate the processes by which these results are arrived at without injury to the copper or its alloys.

At the present time, the majority of gilders by immersion, gild also with the battery; and, when the first gild-

ing is imperfect, instead of coloring by the process just described, they place the articles for a few moments into the electro-bath, which is preferably worked hot, and the composition of which will be given further on.

## CHAPTER XIV.

ORMOLU—COLORED GOLDS—GREEN AND WHITE GILDING—  
GILDING SILVER BY SIMPLE IMMERSION.

### *Simple-Immersion Gilding (continued).*

WE have said that, generally, immersion gilding is especially resorted to for false jewelry. There is, however, an easy method of obtaining by this process results rivaling those obtainable by the battery, and which consists in gilding several times, by dipping, those objects which require a good plating. The secret is, that before each immersion, the article is "quicked," *i. e.*, passed through the solution of nitrate of mercury. By this operation, a coating of mercury is deposited at each operation, and dissolving in the bath of pyrophosphate, is each time replaced by a fresh coating of gold.

This method is constantly applied to the plating of large pieces, such as clocks, chandeliers, ornamental bronzes, etc., which are usually gilded by the battery. Executed by this method immersion gilding, as compared with electro-gilding, is superior in richness of tone, brilliancy, lustre, and especially in having no tendency to scale off, as the deposit obtained by this system consists of pure gold only, whereas, by the galvanic process, a subsalt of this metal is often deposited.



It is easy to satisfy one's self that the coating of gold increases in depth with each successive quicking and immersion, by observing the varying intensity with which nitric acid attacks the objects after each such operation. Roseleur affirms that he has succeeded in gilding copper in this manner with such solidity that it would resist the action of concentrated acids for several hours.

A strong gilding by immersion, like that by the battery, may be scratch-brushed and given the color known as ormolu; but in this case the latter operation is done in the cold.

*Ormolu.*

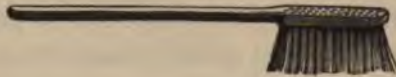
This operation consists in applying, by means of a brush or pencil to the objects, gilded and scratch-brushed, a thin magma of nitrate of potassium, alum, and hematite, which have been intimately mixed and ground under the muller, with the addition of a little vinegar, and of a solution of saffron, or annotto, or other coloring substance, according to the depth of yellow or red desired.

If the gilding on which the operation is performed, is heavy, the objects are heated until the coating of the magma curls at the touch of a wet finger. On the other hand, if the gilding is a mere film of gold, with which we are here occupied, the mixture is simply allowed to remain upon the articles for a few minutes; after which in both cases, the articles are rapidly washed in warm water holding in suspension a certain quantity of the materials for ormolu coloring.

Without using any other water, the articles are rapidly dried, when they appear of a darker shade. We must then equalize the color, that is to say, remove the portions too much colored by striking them vertically with the long bristles of a hand brush (Fig. 95).

Ormolu coloring is practised, of course, only after burnishing, if the whole or a part of the article requires it.

Fig. 95.



If the tint of ormolu does not appear satisfactory, whether from too great or too small a proportion of the substances employed, it is easy to begin the operation anew, after washing off the ormolu in a diluted solution of sulphuric acid.

We shall give, in the chapter on CHEMICAL PRODUCTS, the manner of preparing various shades of ormolu.

#### *Colored Golds.*

A greater variety can scarcely be imagined than the different tints and colors presented by the gilded articles found in the trade. They vary from the red of rose copper, to a pale white, similar to that of silver. Hence, the various denominations employed in the arts, to designate them, *i. e.*, yellow gold, virgin gold, red gold, pink gold, new gold, blossom gold, green gold, and white gold.

The last two shades, very much sought for, are easily obtained by simple immersion. The mode of obtaining the other shades will be described under *Electro-Gilding*.

#### *Green and White Gilding.*

These shades, which may be graduated at will, are obtained by adding drop by drop, and until the desired shade is arrived at, a solution of nitrate of silver to the bath of double pyrophosphate of sodium and gold, of which we have given the formula.

The solution of nitrate of silver is prepared by dissolv-



ing, in 100 parts of distilled water, ten parts of crystallized nitrate of silver, or, preferably, the fused nitrate commonly called lunar caustic.

The pyrophosphate dissolves silver but slightly; nevertheless, it absorbs it in sufficient quantity for whitening the gilding to the point of making it appear like silver.

It is always to be recommended, before gilding green or white, to yellow-gild the objects in the ordinary bath, then to pass them rapidly through the mercurial solution, and, lastly, to dip them into the gold bath containing the nitrate of silver.

The bath, to which the silver solution has been added, parts quite rapidly with its silver upon the first articles placed in it. To maintain the constancy of the shade it is, therefore, necessary to add a few drops of the silver solution as often as may be found needful.

#### *Gilding Silver by Simple Immersion.*

Although gilding by immersion is generally confined to copper and its alloys, it is also possible to gild silver in the following manner:—

The silver articles, previously cleansed and scratch-brushed, are boiled for about half an hour in the gold bath of pyrophosphate, to which have been added a few drops of sulphurous acid, or, preferably, hydrocyanic acid in excess of the quantity prescribed for the normal bath. The last-named acid dissolves a small proportion of silver, and allows an *equivalent* of gold to deposit in its place. The first named, *i. e.*, sulphurous acid, acts as a reducing agent upon the gold solution, and causes the metal to deposit upon the silver, in virtue of the chemical affinity between metals, which is especially manifested when one of them is in the nascent state, *i. e.*, just being disengaged from a combination. This gilding is very fine, but light.

... and thicker by  
... silver with a rod of  
... however, we introduce  
... by the contact of two  
... solution.

## CHAPTER XV.

... (CONTINUED).

### *Glass, or Crystal.*

... baths of pyrophosphates  
... employed for gilding glass, crystal,  
... and porcelain.  
... as follows:—  
... first in an agate mortar and then  
... ground plate glass, some well-neu-  
... with rectified essence of lavender,  
... which is then applied with a  
... upon the glass, porcelain, or  
... which it is desired to decorate. After  
... up to a dark red. At this tem-  
... is partially decomposed, and the  
... reduces the platinum to the metallic  
... appears with a perfect lustre. After  
... through aqua fortis, which will  
... platinum, but will destroy the impurities  
... its surface. Rinse the object in plenty  
... into the gold bath, after wrapping with  
... brass wire, having numerous points of  
... the platinum places.  
... minutes, the platinum will be entirely cov-

ered with a fine film of gold possessing the same adherence and polish. A rubbing of the gilding with a chamois skin finishes the operation. This method, it will be noticed, dispenses with burnishing, which is always costly, and often impracticable in the deeply indented parts.

If the gilding be too red, add to the bath a few drops of a solution of double cyanide of potassium and silver (liquid for silver electroplating).

This method succeeds much better than the employment of baths requiring the use of the battery; the gilding has a bright instead of a dead lustre, and its adherence is more perfect.

At the present time, the process of bright gilding invented by Dutertre has been generally substituted for that just described. It consists in applying with a brush or pencil, to the objects to be gilded, an intimate mixture of sulphide of gold and various essences, which are then submitted to an incipient red heat. The resulting gilding has the appearance of burnished gold, is more or less firm and lasting, and is applied to a multitude of small porcelain articles, the indented surfaces of which render impossible the employment of the burnisher.

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## CHAPTER XVI.

### SIMPLE-IMMERSION GILDING (CONCLUSION).

#### *Simple-Immersion Gilding with Bicarbonate.*

WE have described in great detail the pyrophosphate gilding bath because it appears to us preferable to all others. Nevertheless, it is possible to gild, by simple immersion, with other substances, and especially with the bicarbonates

of potassium or sodium, which, until recently, were extolled by a few rule-of-thumb practical men. This simply proves that they were not acquainted with, or did not know how to use, the pyrophosphates.

The bicarbonate bath is prepared by mixing in a cast-iron kettle, turned clean and smooth inside on the lathe, and gilded by protracted ebullition therein, of old or nearly spent gilding-baths—

Water . . . . .	1600 parts.
Bicarbonate of potassium or sodium (preferably, of potassium) . . . . .	900 “
Pure gold (to be transformed into chloride) . . . . .	12* “

The whole is boiled for at least two hours, fresh water being added to replace that lost by evaporation. A part of the gold, in the form of a violet-black powder, will be found to have been precipitated, and the bath will require to be cooled and decanted. It is again boiled, and the gilding is proceeded with, in the same manner as previously indicated, except that the mercurial solution should be more diluted than is customary with the pyrophosphate baths.

The operation should be arrested when about half of the gold in the bath has been deposited. The remainder goes to the spent liquors from which the gold is subsequently regained.

If we now compare the formulæ of these two baths, and consider the dilution of the one and the concentration of the other; the rapidity of operation in the first, and the loss of time occasioned by the second; the facility of using all the gold dissolved by the pyrophosphate, and the impossibility of utilizing a great proportion of that in the bicarbonate; we must acknowledge that there is no possible

\* This weight is that of the metallic gold, and not that of the chloride resulting from the treatment with *aqua regia*.



doubt as to which to choose, especially when the quality and the fineness of the products are at least equal. We may add in conclusion, that, at the present time, we know of no gilder employing the above formula, which we have simply recorded as a matter of history.

*Immersion-Gilding—Diluted Bath.*

Roseleur concludes his list of formulæ for simple immersion gilding, with one, which, on account of the facility with which it may be worked and the great variety of articles for which it may be used, is often employed, notwithstanding the slight durability of the results it furnishes.

This bath should be employed only as a complement to the cleansing process, and as a preliminary operation to a more resistant electro-gilding in a cyanide bath. It is composed of—

Water . . . . .	1000 parts.
Bicarbonate of potassium . . . . .	20 “
Caustic potassa . . . . .	108 “
Cyanide of potassium . . . . .	9 “
Gold . . . . .	1 part.

The whole is brought up to the point of ebullition, and a pale gilding, a mere blush, is obtained even upon imperfectly cleansed articles, and without employing nitrate of mercury.

It is possible, to repeat four or five times, the addition of a small proportion of chloride of gold to this bath, without the addition of other substances. Afterwards, it is maintained at the proper strength by additions of gold and salts in the above proportions, and it lasts for an almost indefinite period.

Such a bath will gild about 4000 parts by weight of small trinkets for each part (by weight) of gold consumed,

whereas a bath of pyrophosphates will gild only about 1000 parts by weight of small articles per unit of gold extracted from the bath.

The gilders of large bronze pieces use this bath for cleansing them before they are taken to the electro-bath, and on this account it is called the *cleansing or preparing bath*.

The following processes for immersion-gilding, from various authorities, may be found useful:—

Gore (*Electro-Metallurgy*, 129) notices a solution for simple-immersion gilding, at one time extensively used by the Messrs. Elkington. It is prepared by converting one part of gold into neutral terchloride (by the method previously described), dissolving it in a small quantity of water, and adding to it, gradually, thirty-one parts of bicarbonate of potassium. This liquid is then mixed with a solution of thirty parts of the bicarbonate dissolved in two hundred parts of water, and boiled for two hours. The solution, which is yellow at first, becomes green, and is then ready for use. Trinkets of brass or copper, previously cleansed, are immersed in this solution for about half a minute. The bath is used hot. Articles of German-silver, silver, or platinum, must be immersed in contact with wires of copper or zinc.

A similar solution is made by converting five Troy-ounces of gold into chloride, dissolving this in four gallons of distilled water, adding twenty pounds of pure bicarbonate of potassium, and boiling the mixture for several hours. It is used warm, and articles to be gilded are immersed from a few seconds to one minute.

A solution for gilding articles of silver, described by this and other authors, is prepared by dissolving equal parts by weight of corrosive sublimate and sal-ammoniac



in nitric acid, adding some grain gold to it, and evaporating the liquid to half its bulk. The hot solution is applied to the surface of the silver article.

C. D. Braun's solution for gilding zinc (*Chem. News*, xxix. 230; Gore, *Electro-Metallurgy*, 129) is prepared by dissolving sulphide of gold in a solution of sulphide of ammonium, excluded from the atmosphere.

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## CHAPTER XVII.

### GILDING WITH GOLD AMALGAM.

THE older processes admit of the gilding of small copper articles with a thin and adherent coating. One of these ancient methods which we shall now describe, gives results very analogous to those obtained by dipping, just explained.

This operation of gilding with gold amalgam, which is a modification of the method of fire-gilding, which will be shortly described, is performed as follows:—

In the centre of a charcoal stove place a crucible holding a small quantity of pure, dry mercury, and when the temperature has reached about 212° Fah., add thereto one-half its weight of gold. Stir with an iron rod, and when the amalgam has acquired the consistency of butter, throw it into cold water, and keep it there for use.

After cleansing the articles to be gilded in aqua fortis, place them in a stoneware pan, and sprinkle them with a very weak solution of nitrate of mercury, taking care to keep the articles in motion all the while, in order to change the positions of their surfaces and cause them to become covered uniformly with a white coating of mercury.

At this point, add to the mass the required quantity of amalgam, and continue to move the articles briskly about. The amalgam spreads rapidly, and after a few minutes will be found to have attached itself uniformly to the surface of the articles. Then rinse in cold water, and transfer the contents of the stoneware pan into a large and deep copper ladle, perforated with numerous small holes, and having a long handle which allows the operator to impart a shaking motion to its contents.

The ladle and its contents are then kept over a live charcoal fire, and the articles are constantly shaken in order to distribute the heat as much as possible. The mercury of the amalgam is soon volatilized, and the gold remains adherent to the articles.

If, instead of a yellow gilding, a red one be desired, the *waxing* process is now resorted to, which operation consists in pouring upon the articles, still in the ladle and upon the fire, an intimate and fluid mixture of—

Oil . . . . .	25 parts.
Yellow wax . . . . .	25 "
Acetate of copper . . . . .	10 "
Hematite . . . . .	40 "

The articles impregnated with this mixture are constantly agitated. It speedily takes fire and is allowed to burn out, at which instant the whole is thrown into a very diluted solution of sulphuric acid. The waxing is, of course, done only after the complete volatilization of the mercury.

After coming out of the pickle, the gilding has the appearance of ochreous clay, and must be scratch-brushed. Small articles are polished by tumbling along with a lot of copper beads, or the waste from the same, moistened with vinegar-water. The gilded articles and the copper granules, rolling over each other, become polished



by mutual attrition. Lastly, rinsing, and drying in saw-dust, and, if necessary, burnishing, complete the operation.

Gilding by stirring and amalgam may give good results; but most generally the quantity of gold deposited is so slight that it is not rare to find the film of gold in the acid solution used for quenching, and that the finished articles have nothing to enhance their value but the red from the waxing, enhanced by the bright lustre obtained by the polishing operation. Such copper articles, however, are with difficulty oxidized, as if they had been penetrated by the fatty substances of the waxing composition. Roseleur affirms that he has examined jewelry, claimed to have been gilded by this process, and the *gilding of which had been found very fine*; and was unable to find a trace of gold. The entire quantity of the gold employed must therefore have been left in the acid pickle, which was thrown away.

He adds, furthermore, that he assisted in executing a very fine gilding by this procedure, which *succeeded remarkably well*, where the gold by mischance fell into the fire instead of getting into the crucible with the mercury, where it was afterwards found intact.

Each operator has his own method of waxing, and varies its composition. That given above succeeds well.

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## CHAPTER XVIII.

### GILDING BY FRICTION.

WE will not dismiss the methods of thin gilding, without mentioning a very simple, and often very useful, process of gilding silver. It was formerly, and is even at the

present time, used for gilding the interior of snuff-boxes, and similar articles.

This process is variously termed *gilding with the rag, with the thumb, with the cork.*

The procedure is as follows:—

Dissolve pure gold, finely laminated, in a mixture of—

Nitric acid . . . . .	5 parts.
Chloride of ammonium (sal ammoniac) . . . . .	2 “
Nitrate of potassium (saltpetre) . . . . .	$\frac{1}{2}$ part.

Heat carefully upon a gentle fire; the nitric acid decomposes the chloride of ammonium, the liberated hydrochloric acid combining with the nitric, thus forming *aqua regia* which dissolves the gold. The nitrate of potassa remains mixed with the chloride of gold, and, as we shall soon see, performs a useful office.

When all the gold has disappeared, pour the cooled contents of the flask into a flat-bottomed stoneware pan. Into this liquid, dispose one upon the other, and in sufficient quantity, squares of pure linen cloth, and pat them with a glass rod, in order that they shall become equally impregnated with the chloride of gold. Each square of cloth is then taken with wooden pincers, well drained and spread for drying in a dark closet. When the desiccation is nearly complete, each piece of cloth, supported upon glass rods, is held over a charcoal fire until it ignites. The combustion is accelerated by the presence of the nitrate of potassa, and is finished upon a marble slab. Grind the ashes under a muller, collect, and keep them between the folds of a sheet of parchment around which a wet cloth has been folded. The ashes remain there for a week, but every day they are stirred in order to have an equal wetting by the dampness which penetrates through the parchment.

The powder is then ready to use and it is sufficient to

mix it upon a slab with a few drops of water, and to rub with this paste, the previously well-cleaned surfaces of the silver to be gilded. The smooth surfaces are rubbed with the thumb, the fillets or grooves with a fine cork cut to the proper shape, and the corners or angles with a stick of soft wood, such as linden or poplar. Lastly, the articles are burnished. This gilding is very thin, but quite resistant, especially after the action of the burnishing tool, which, crushing the minute particles of gold, has imbedded them, as it were, into the pores of the silver. If a red shade be desired instead of a yellow one, a small proportion of pure copper is added to the gold to be dissolved in aqua regia.

By the action of the fire during the combustion of the cloth, a part of the perchloride of gold is reduced to metallic gold, and the remainder transformed into subchloride. The presence of the latter salt in the mixture appears to aid the adherence of the deposit, since the subchloride of gold, in contact with silver, causes a decomposition whereby the chloride of silver is formed, and the gold is deposited in the nascent state, *i. e.*, in the best condition for the combination to take place.

We are perfectly satisfied that gilding by friction will succeed just as well by using the ashes immediately after the burning of the cloth impregnated with perchloride of gold ; but we have preferred to describe the operation precisely as Roseleur states he has seen it performed, with all its quasi-mysterious accompaniments.

## CHAPTER XIX.

## GILDING WITH THE BRUSH, OR WITH SHELL GOLD.

THIS method consists in the application to the surfaces to be gilded, of a paste, charged with gold powder, and its durability is no greater than that of the size employed. It is applied only on very small surfaces to make slight repairs or to cover defective places which do not require the gilding anew of finished articles.

The gold powder is simply mixed with gum-water, applied with a brush upon the parts to be covered, and allowed to dry.

The gold powder is prepared by the attrition under the muller of the cuttings of gold beater's foil, and in order to prevent them from being blown away, a certain quantity of white honey is added. When it is considered that the powder is fine enough, the paste is put into water, by which the honey is dissolved. After several washings, settlings, and decantations, the powder is allowed to dry. When in a hurry, the washing may be performed upon a paper filter. The dry powder is again ground with a little gummy or mucilaginous water, and the resulting paste spread upon a small porcelain cup, or more generally upon the inside of a mussel-shell (Fig. 96).

Fig. 96.



If a powder of green gold be desired, silver foil is mixed with the gold cuttings. An addition of rose-copper foil produces a red gold. For this purpose, however, it is preferable to use foils laminated from alloys made for the purpose.



We may anticipate, by stating that a similar method is employed for the preparation of a silver powder for touching up slight defects in articles not exposed to friction.

Every gilder should have at hand a complete stock of these various powders, which will save him a great deal of tedious work.

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## CHAPTER XX.

### ELECTRO-GILDING, OR GOLD ELECTRO-PLATING.

#### *Electro-Gilding.*

GILDING by the battery possesses two decided merits: first the advantage of being easily applied to all the usual metals; and second, of producing a deposit, the thickness of which is entirely at the command of the operator.

It is not always necessary in electro-gilding to use a battery, for it will be remembered that the contact of two heterogeneous metals, immersed in an electrolyte, especially if this be an acid or saline liquid, is sufficient to produce the phenomenon of an electric current. Electro-gilding, therefore, will take place whenever contact is established between an electro-negative and an electro-positive body jointly immersed in a suitable solution containing gold.

We have already stated that, in gilding silver by immersion, the gold deposition is caused by the contact of copper or zinc with the silver, which performs the function of the positive element of a feeble battery, the negative element of which is represented by the silver. We shall see, further on, that it is sufficient to plunge the articles, attached to zinc wires, into electro-gilding baths

in order that the operation shall take place in the same manner as with the battery.

In a general way, therefore, it is correct to define as electro-gilding, or electro-deposition, the deposit obtained by an electric current, whatever be its mode of production. It is customary, however, to confine the term to methods and formulæ which require generators of electricity separated from the baths, with which we shall here concern ourselves.

Electro-gilding may be done with the aid of heat, or in the cold. The latter method is especially employed for large articles, such as clocks, chandeliers, etc., which would require the heating of great volumes of liquid.

Hot electro-gilding, on the other hand, is admirably adapted to the great majority of cases, where small articles, such as forks, spoons, knives, snuff-boxes, etc., are to be gilded.

Let us here say that hot gilding offers several advantages over the cold method. The deposits are smoother and cleaner, the color is deeper, and the articles, removed from the bath, may not require coloring. It will be useful, here, to correct the mistaken idea, very generally entertained, and which is due to the facility with which pleasing but not durable deposits with very little gold may be obtained in hot baths, namely, that *gildings made by the hot method are less resistant than those obtained in the cold way.*

We affirm, on the contrary, that *for equal quantities of gold deposited, hot gilding is much more durable than cold.* This will be understood, when we consider that electro-deposits are nothing else than a species of network, the meshes of which are more or less close. Is it not plausible then, that with a cold bath and upon a cold article, the network should remain what it was, at the

time of the deposit; whereas, a cold surface plunged into a hot bath would expand by the heat and present to the deposit a larger surface, which, contracting on cooling, would, at the same time, condense the meshes of the gold network deposited?

Another proof of the superiority of hot over cold gilding is the fact that we cannot gild by the latter method either steel, tin, or lead, which may be gilded in hot baths. The removal of any greasy impurities or oxides which may remain on the surface of the articles, is likewise aided by hot baths, and thus the success of the operation is facilitated.

To sum up: The want of durability is not due to the use of hot baths, but to the thinness and beauty of the deposit which it is possible to obtain by the hot method, and with which too many gilders content themselves.

*Cold Electro-gilding Baths.*

The proportions and the nature of the salts employed may vary greatly; but the three formulæ given below, are in general use and give satisfactory results.

*First Formula.*

BATH WITH FULMINATE OF GOLD.

Water (preferably distilled) . . . . .	1000 parts.
Cyanide of potassium (ordinary 70 per cent.)	30 "
Gold . . . . .	10 "
Aqua ammonia . . . . .	50 "

This bath is prepared as follows:—

1. Heat, in a glass flask, the 10 parts of gold with 25 parts of pure hydrochloric acid, with the addition of 12.5 parts of pure nitric acid. When the gold is dissolved, continue the heat in order to expel the excess of acids, and until the color of the syrupy liquid is dark red, nearly black. Remove then from the fire, and dissolve the

brown-yellow crystalline mass, formed on cooling, in a quart or two of water, and pour into a large porcelain dish.

Add to this liquid, the 50 parts of ammonia specified in the formula, which immediately produces an abundant yellowish precipitate of fulminate of gold (called also aurate of ammonium, or ammoniuret of gold). Throw the whole upon filtering paper, and save the wash-waters, which are slightly tinged with yellow and still contain traces of gold. Wash the precipitate remaining upon the filter several times with cold water, until it no longer smells of ammonia.

The fulminate of gold should not be dried, as in that condition it is *highly explosive*, and detonates with violence by a slight shock, or friction.

2. Dissolve in the depositing vat, and in the 1000 parts of water, the 30 parts of ordinary cyanide of potassium. Filter, if necessary, and add the moist fulminate of gold, which rapidly dissolves on stirring, and forms a clear liquid, which is the gilding bath. The ammonia should be expelled by boiling for about one hour; and when cool, the solution is ready for use.

For a newly prepared, cold electro-gilding bath, Roseleur prefers the ordinary cyanide of potassium, which, containing some free potassa, renders the liquid a better conductor of electricity. On the other hand, for the subsequent maintenance of its strength, he recommends the pure cyanide, which possesses the advantage of having a uniform composition, and does not load the solution with foreign salts.

The gold solution for maintaining the metallic strength of the bath is prepared as follows: Transform the gold into fulminate, as indicated above, and suspend the product in water (100 parts of water for each 10 parts of gold),



then add cyanide of potassium until the liquid is colorless. If a sufficiency of water has not been used with the fulminate, the liquid will be dark red, and will not be decolorized by an excess of cyanide; nevertheless, there is no inconvenience in introducing this liquid into the impoverished bath.

*Second Formula.*

BATH OF DOUBLE CYANIDE OF GOLD AND POTASSIUM.

Water (preferably distilled) . . . . .	1000 parts.
Cyanide of potassium, pure . . . . .	20 "
Or ordinary cyanide, according to strength	30 to 40 "
Gold . . . . .	10 "

For the preparation of the bath, proceed as follows:—

1. Convert the gold into neutral chloride, as in the preceding formula, and, when cold and crystallized, dissolve it in 200 parts of water. Filter if necessary.

2. Dissolve the cyanide in the remaining 800 parts of water, filter if necessary, and mix the two solutions, which become colorless.

If possible, it is recommended to boil this bath for about half an hour before using it, by which treatment it becomes a better conductor of electricity, and the gilding is more uniform.

Its strength is maintained by additions of neutral chloride of gold and pure cyanide of potassium (from 1 to 1.5 parts of pure cyanide to each part of gold used).

These two baths may be diluted with an equal or double volume of water; the gilding will remain fine, but the amount of gold deposited in a given time is proportionately less.

*Third Formula.*

BATH OF FERROCYANIDE OF GOLD.

Ferrocyanide of potassium (yellow prussiate of potassa)	20 parts.
Carbonate of potassium, pure	15 "
Chloride of ammonium (sal ammoniac)	3 "
Gold (to be transformed into chloride)	1½ "
Water	1000 "

Boil together all the salts, with the exception of the chloride of gold, separate the precipitate of carbonate of iron by filtration, add then the chloride of gold dissolved in a little water, and allow the bath to cool of.

It is scarcely necessary to say that any salt of gold, and the oxide, or even the finely comminuted metal, may take the place of the chloride of gold; but this latter is preferable on account of the facility of its preparation, and its solubility.\*

A few operators prefer the fulminate of gold prepared as in the first formula.

The addition of a little hydrocyanic (prussic) acid produces a brighter, but thinner, gilding.

The indicated cyanides may be replaced by the cyanides or ferrocyanides of other, earthy or alkaline, bases, provided they are soluble; such are the cyanides of sodium, calcium, and ammonium.

\* The use of the cyanide of gold, extolled by certain manufacturers of chemical products, has nothing to recommend it, except that it enables them to sell at a very high price a product which contains but a small proportion of metal. Any salt of gold will be transformed into cyanide in the presence of cyanide of potassium, and it is entirely useless to pay a high price for a product which may readily be made by each one for himself. Roseleur affirms that the small proportion of chloride of potassium resulting from the transformation of the chloride of gold into cyanide does not interfere with the proper working of the baths. From this opinion we must dissent.

Ebermeyer (*Dingler's Jour.*, cxxiv. 631) proposes a bath of very similar constitution, with the addition of a small quantity of cyanide of potassium, to aid its conductivity, and four parts of gold to the one thousand of solution, for gilding copper wire. He prefers, however, to use the bath at a temperature of from 100° to 125° Fah.

Cold gilding baths are generally kept in vessels of stoneware, earthenware, or porcelain; but for baths of large dimensions, wooden troughs lined with gutta percha are used.

The interior walls of this bath are partly covered by an anode of gold entirely immersed in the bath and supported on the edges by small wires of platinum, and connected by a metallic conductor to the positive pole of the battery, Fig. 97. The articles to be gilded are suspended, by means of metallic slinging wires, to a movable frame of clean brass rods connected with the negative pole.

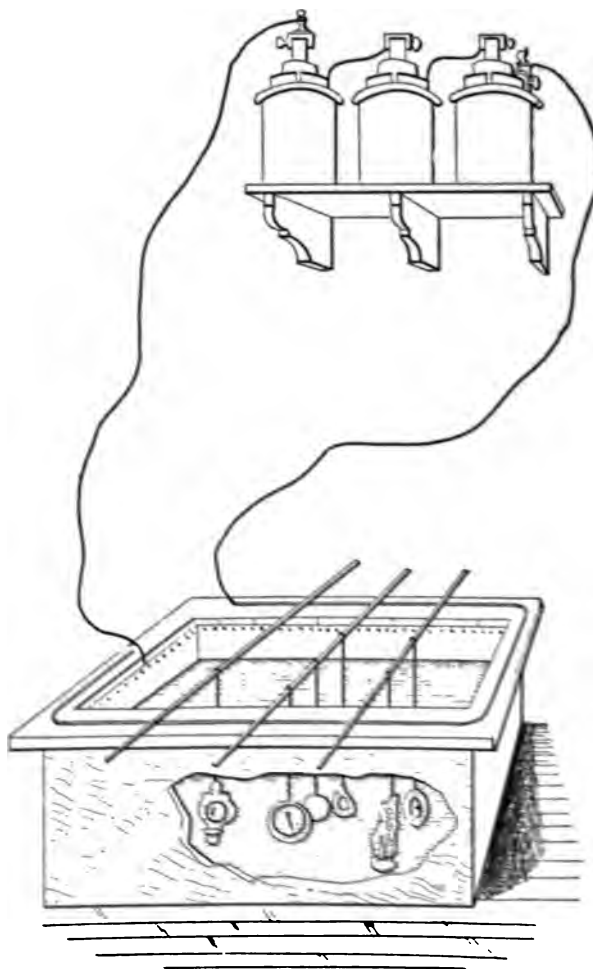
The deposit of gold is often pure yellow, but it has sometimes a dull and earthy-gray color. In the latter case it must be scratch-brushed a long time and with the greatest care, and then treated to ormolu coloring.

The object of the gold anode is not only to aid the electrical conductivity of the bath, but also to maintain its metallic strength. Theoretically, as much gold should be dissolved from the anode as there is gold deposited upon the other pole; but in practice this is not the case, and it is found necessary to add now and then either the oxide or the chloride of gold, and also a certain proportion of cyanide of potassium, to make up for that transformed into carbonate of potassium and cyanate of ammonium.

Ebermeyer (*Ding. Jour.*, cxxiv. 631) has made a series of experiments to determine whether it was possible to ascertain, from the loss of weight of a gold anode, the quantity of gold precipitated upon the cathode (*i. e.*, the

article receiving the deposit). He concludes that this cannot be done; that, in a gold bath containing much

Fig. 97.



gold, the anode is only slightly attacked: but, when the bath becomes poor in gold, the anode is more strongly attacked. So long, therefore, as such baths still contain



gold in notable quantity, he concludes, the operator may dispense entirely with the gold anode, and work with one of platinum. On this point, it will be observed, Ebermeyer coincides with Roseleur.

The proportion of the cyanide should be about double that of the chloride of gold added. By observing the color of the bath and the shade of the deposit, however, it may be readily determined if the proportion of the chloride of gold is too great, in which case a larger quantity of the solvent should be added, and *vice versa*.

If gold predominates, the deposit is quite black or dark red; on the other hand, when the cyanide is in excess, the gilding takes place very slowly and has a grayish look, and it will often happen that pieces already gilded will lose their gold, instead of receiving additions of new metal.

Some gilders, in order not to increase the density of their baths by the addition of fresh salts, add a little hydrocyanic acid, which, displacing the carbonic acid of the carbonates, forms new cyanides. This process is costly, and encourages the employment of one of the most poisonous substances. It will be preferable to add some water with the new salts, or to substitute for the cyanide of potassium, which is transformed by decomposition into soluble carbonate, the cyanide of calcium, which, reacting upon the carbonate of potassium in the bath, forms a soluble cyanide of potassium and an insoluble carbonate of calcium which separates by precipitation. The cyanide of ammonium may also be employed, and will, by double decomposition, produce a volatile salt, the carbonate of ammonium.

Notwithstanding these inconveniences, the cyanide of potassium is nearly always employed, because its preparation is more simple and less costly.

When the bath is not in use the gold anode must always

be removed from it, otherwise it will continue to be dissolved, and the bath will become charged with too much metal.

If the anode is only partly immersed in the bath, it will be rapidly cut at the level of the liquid; and for this reason Roseleur recommends the employment of anodes of platinum, which are not acted upon.\*

Cold electro-gilding, in opposition to the hot method, should be done slowly; and the operator should frequently examine the pieces in the bath, in order to scratch-brush those receiving an irregular deposit, or which exhibit dark spots.

As it is not possible to constantly alter the surface of the anode, to correspond with that of the articles, the intensity of the current should be often changed. With too high intensity, the deposit is black or more or less red; with a current of the right intensity, it is yellow. With a weak current those portions only that face the anode become covered with gold; it is therefore advisable to move the objects about frequently, in order that the deposit shall be regular. With freshly prepared baths, it often happens that surfaces already gilded will lose their gold by changing their positions; thus, for instance, if the interior of a snuff-box is gilded when opposite the gold anode, it may be ungilded by presenting the exterior to the anode. When this action takes place, it is positive evidence either that the bath contains too much cyanide of potassium, and consequently too little gold, or that the electric current is too weak.

\* It is a phenomenon worthy of remark, that the solutions of cyanides, even without the action of the electric current, rapidly dissolve, in the cold, or at a moderate temperature, all the metals except platinum; and that at the boiling point, they have scarcely any action upon the metals.



When the deposit obtained in these baths is defective in color, although the quantity of deposited gold may be sufficient, the proper shade or tone may be imparted by one of the following methods:—

1. The gilded article is steeped in a solution of nitrate of mercury, until its color has become white. It is then heated to volatilize the mercury, and lastly scratch-brushed.

2. Dip the article in strong sulphuric acid, then heat it until abundant white fumes are disengaged, and immerse it, still hot, in a weak pickle of sulphuric acid. In this case, the acid has destroyed the organic impurities which may exist in the deposit, and reduces to the metallic state the subsalts of gold.

3. Smear the gilded article with a thick magma of powdered borax and water, or with biphosphate of calcium, of the consistency of honey, and heat until *igneous* fusion takes place. Then plunge the article into diluted sulphuric acid, which dissolves the borax or the biphosphate and leaves the gold with its natural bright lustre.

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## CHAPTER XXI.

ELECTRO-GILDING IN HOT BATHS—GREEN GOLD—WHITE GOLD  
—RED GOLD—PINK (OR NEW) GOLD.

### *Electro-Gilding in Hot Baths.*

WE have already stated that this mode of gilding is more regular in operation, more rapidly executed, and exhibits greater richness of coloring, than that obtained with cold baths.

The composition of the baths may be greatly varied;

the four following formulæ, however, are especially recommended by Roseleur.

These formulæ are set down in the order of their value, the first one being the most highly esteemed.

*First Formula.*

Phosphate of sodium (crystallized)	. . . . .	60 parts.
Bisulphite of sodium	. . . . .	10 "
Cyanide of potassium, pure	. . . . .	1 part.
Gold* (to be transformed into chloride)	. . . . .	1 "
Rain (or distilled) water	. . . . .	1000 parts.

This formula is equally satisfactory for the rapid electro-gilding of silver, bronze, copper, German-silver, and other alloys rich in copper. On the other hand, for gilding wrought and cast iron and steel, directly, that is to say, without a previous coating of copper, the formula should be modified as follows:—

Distilled water	. . . . .	1000 parts.
Phosphate of sodium	. . . . .	50 "
Bisulphite of sodium	. . . . .	12½ "
Cyanide of potassium (pure)	. . . . .	½ part.
Gold	. . . . .	1 "

If, on the contrary, we wish to gild zinc, tin, lead, antimony, or the alloys of these metals, it is always preferable to give them a previous coating of copper, or, at least, to begin the gilding in a hot gold electro-bath, nearly spent,

\* It should be well understood, once for all, unless the contrary is expressly stated, that the proportion of gold indicated in all these formulæ is that of the metal employed, and not that of the resulting salt. It is not necessary, therefore, to consider the weight of the chloride when the gold has been dissolved in aqua regia. For the information of those who buy the chloride of gold already prepared, we will say that 10 parts of metallic gold correspond to about 18 parts of neutral chloride, or to 20 or 22 parts of acid chloride, such as is sold by chemical dealers.



and to scratch-brush the articles carefully. The gilding is completed in a fresh hot bath, with quite an energetic current.

PREPARATION OF THE HOT ELECTRO-GILDING BATH BY THE PRECEDING FORMULA.

We proceed as follows:—

1. Into a porcelain dish, or an enamelled cast-iron kettle, heated over a charcoal furnace, introduce 800 parts of rain (or distilled) water, and stir into it the 60 parts of crystallized phosphate of sodium. When the salt is entirely dissolved, remove the vessel from the fire, filter if necessary, and allow the solution to cool off.

2. Introduce into a glass flask, 1 part of finely laminated gold, with  $1\frac{1}{2}$  parts of pure nitric acid and  $2\frac{1}{2}$  parts of pure hydrochloric acid. Heat slowly until all the gold has dissolved, and then more rapidly to expel the excess of acid. There should remain in the flask a syrupy liquid of a blackish-red color. Then remove the flask from the fire, and allow the contents to cool, when it should form a brown-red crystalline mass.

3. Dissolve in a porcelain dish, in 100 parts of water, 10 parts of bisulphite of sodium and from  $\frac{1}{2}$  to 1 part (according to circumstances) of pure cyanide of potassium.

4. Then dissolve the neutral chloride of gold in the remaining 100 parts of water, and pour it slowly (stirring all the while with a glass rod), into the *cold* solution of phosphate of sodium. This mixture acquires a greenish-yellow tinge; and without losing time, pour into the mixture the solutions of bisulphite and of cyanide. The resulting liquid soon becomes colorless, and the gilding bath is ready.

If, instead of allowing the solution of phosphate of sodium to cool off, the chloride of gold were poured into

it while hot, there would be danger of a partial reduction of the gold, in the form of a brownish-red powder.

To sum up, the proper preparation of this bath requires :—

1. The solution of 60 parts of phosphate of sodium in 800 parts of water, which should be allowed to *cool off* ;
2. The solution, in 100 parts of water, of the chloride resulting from the treatment of 1 part of gold with aqua regia, and its gradual mixture with the former solution ;
3. The solution in the remaining 100 parts of water, of 10 parts of bisulphite of sodium, and 1 part of pure cyanide, and the mixture of this last solution with the preceding ones.

Roseleur deprecates the practice of many gilders in substituting ordinary for distilled water, then dissolving all the salts together except the chloride of gold, and adding the last to the liquid while the latter is still hot. This method is certainly more rapid, but always produces turbid baths, the working of which is uncertain.

The hot electro-gilding baths are kept in porcelain dishes for those of small dimensions, but, with large volumes, enamelled cast-iron kettles are employed. They are worked at a temperature which may vary from 110° to 175° Fah.

Small articles, like brooches, bracelets, and trinkets in general, are kept in the right hand with the conducting wire, and immersed and constantly agitated in the bath. The left hand holds the anode of platinum wire, which is steeped more or less in the liquor, according to the surface of the articles to be gilded.

Large pieces are suspended from one or more brass rods, and immersed in the bath along with the platinum anode and are allowed to remain motionless.



The gilding is very rapid, and a sufficient thickness is obtained after an immersion of a few minutes.

The shade of the gold deposit is modified by dipping the platinum anode more or less into the liquid. If it dips but a little, relatively to the surface of the articles, the gilding is pale; by immersing it more and more, the shade will become deeper and deeper, until it is decidedly red.

Generally, the gilders of trinkets nearly exhaust their baths; and as soon as they cease to give satisfactory results make a new one, and keep the old bath for colored golds, as shall be explained further on, or for beginning the gilding of articles which are scratch-brushed and then finished in a fresh bath. On the contrary, those who gild large pieces maintain the strength of their baths by successive additions of chloride of gold, or, what is better, of equal parts of fulminate of gold and pure cyanide of potassium. In this manner baths may be made to last a long time, but they are open to the inconvenience of furnishing a red or green gilding, after having served to gild many articles of copper or of silver.

As a general rule, it is preferable to replace an impoverished bath by a fresh one, instead of keeping up its strength by additions of metal.

Articles of copper, or its alloys, should be perfectly cleansed, and, according to the judgment of the operator, will be passed, or not, through a *very diluted* solution of nitrate of mercury. Silver requires to be well cleansed by dipping, and perfectly scratch-brushed. For this latter metal, the gilding should be strong, in order to prevent the corners and parts in relief from soon becoming white from wear; and, when practicable, a good precaution will be to give it a preliminary coating of copper or brass, or at least a first gilding in an old bath.



*Second Formula for Hot Gilding.*

Phosphate of sodium . . . . .	40 parts.
Bisulphite of sodium . . . . .	10 "
Bicarbonate of potassium . . . . .	5 "
Caustic potassa . . . . .	5 "
Cyanide of potassium . . . . .	1½ part.
Gold . . . . .	1½ "
Rain (or distilled) water . . . . .	1000 parts.

All the substances except the chloride of gold may be dissolved together, and if necessary filtered; then the solution of the chloride of gold is added. This bath is used at a temperature of from 110° to 140° Fah., and produces a very fine gilding, but it requires quite an intense electric current. It is not adapted for the direct gilding of iron or steel.

*Third Formula for Hot Gilding.*

Ferrocyanide of potassium . . . . .	15 parts.
Carbonate of potassium (pure) . . . . .	5 "
Chloride of ammonium . . . . .	2 "
Gold . . . . .	1 part.
Water . . . . .	500 parts.

The first three salts are dissolved in hot water, and the solution is filtered; after cooling, the gold solution is added, and the whole brought again to a boil for half an hour, taking care to replace the evaporated water.

*Fourth Formula for Hot Gilding.*

Cyanide of potassium (pure) . . . . .	5 parts.
Gold . . . . .	1 part.
Water . . . . .	300 parts.

Dissolve the chloride of gold in the whole of the water, and add the cyanide little by little. This rapidly dissolves and forms a completely colorless liquid.

Of this bath, Roseleur remarks, it may be employed

almost without regard to temperature, and its simple formula should render it preferable to all others, were it not that it is variable in its operation. This bath, he adds, is especially open to the objection of ungilding one face of the object while the other face is being gilded, or of producing a red gilding at the bottom and a yellow one at the top of an object. This inconvenience, and others not enumerated, he concludes, may be made to disappear, though only imperfectly, by a prolonged ebullition.

The first formula alone is recommended by this authority for the direct gilding of wrought iron, polished cast iron, and steel. The gilding obtained upon these metals with the other formulæ above named he does not consider to be so good.

For gilding polished steel without the interposition of copper, Roseleur recommends the operator to diminish by one-half the proportion of cyanide indicated in the first formula; his proportions would therefore be  $\frac{1}{2}$  part of cyanide to 1 of gold.

The articles of steel, after cleansing by alkalies, are rapidly passed through a very diluted solution of hydrochloric acid, wiped off when practicable, and immersed in a very hot bath with an intense galvanic current at the beginning, which is gradually diminished afterwards by progressively withdrawing the platinum anode.

Small articles of steel, such as pens, watch-hands, etc., are threaded upon a thin brass wire, and separated one from the other by glass beads. After cleansing, they are suspended in a boiling bath, then rinsed, and dried in hot and dry sawdust.

Steel that has been tempered blue, is at once discolored by its passage through very dilute hydrochloric acid (say  $\frac{1}{16}$  acid).

The practice of the William Rogers Manufacturing



Company, of Hartford, Conn., is to deposit gold and silver direct on iron and steel. In the gilding of Britannia metal, German-silver, etc., as the practice of this establishment is to use the gilding solution hot, these compositions are first coppered or silvered in a cold bath in the usual way, as the hot alkaline solution would oxidize these metals and the gilding would be without adherence.

The proportions of the double cyanide gilding bath, as above remarked, are varied very much in practice without affecting the quality of the work, as will appear from the following statements derived from various authoritative sources. Gore (*Electro-Metallurgy*, 131) recommends as a very good proportion :—

## GORE'S ELECTRO-GILDING BATH.

## I.

Cyanide of potassium	. . . . .	16 parts.
Gold	. . . . .	1 part.
Water	. . . . .	160 parts.

Or,

## II.

Cyanide of potassium	. . . . .	7 to 8 parts.
Cyanide of gold	. . . . .	1 part.
(Corresponding to gold about $\frac{1}{2}$ part.)		
Water	. . . . .	100 parts.

Or,

## III.

Cyanide of potassium	. . . . .	32 parts.
Gold	. . . . .	4 "
Water	. . . . .	160 "

The same author states that the proportion of gold in the electro-gilding solutions used in large establishments, varies as much as from  $\frac{1}{2}$  ounce to 50 Troy ounces to the gallon.

We may add that the gilding solution used by the



Wm. Rogers Manufacturing Company, of Hartford, contains considerably less than  $\frac{1}{2}$  ounce gold to the gallon.

Napier (*Electro-Metallurgy* (1876), p. 168) recommends for general work a gilding solution containing from one-half to one ounce of gold, but adds that for gilding small articles, "a weaker solution will do."

Urquhart (*Electro-Plating*, 174) on this point has the following: "The proportions of gold and potassium cyanide to the gallon of solution vary according to the class or kind of work to be done in it. A fourth of an ounce of gold will be found to work; half an ounce will afford a better deposit in less time; and one ounce is sufficient for all ordinary work. The current needed for the richer solutions is small. Rich solutions admit of the complete art of electro-gilding being practised, and the various shades of color being given to the articles; while the weak solutions are only fitted for practically one color of gilding."

Watt (*Electro-Metallurgy*, 59) remarks that "some gilders use five or six pennyweights of gold to the quart of solution, others as much as eight or ten pennyweights; but I have generally found that a solution containing less gold will give better results than one richer in metal, independent of the advantage in point of economy. I have observed that a bath containing five or six pennyweights of gold to the quart of water, and the necessary proportion of cyanide, and worked in several united cells of Smee's battery, has required a much larger surface of anode to be exposed to a given surface of negative electrode (that is, the article to be gilt), than would be required to gild an article in a solution containing one and a half pennyweights to the quart of solution, worked with a single cell of constant battery. Hence I infer that the weaker solution is the better conductor of the two."

Napier (*Electro-Metallurgy*, 168) calls attention to the

fact that the temperature at which the bath is worked has a decided influence on the color of the deposited gold, as well as on the current required. The hotter the solution the less current is required. "Generally," he adds, "three or four pairs of plates are used for gilding, and the solution is kept at 130° to 150° Fahr.; but one pair will answer if the solution is heated to 200° Fahr.

For gilding German-silver, Watt prefers to work the bath at a lower temperature than usual with hot baths, to weaken the solution, and to expose a smaller surface of anode. The bath, he directs, should be so weak that the German-silver will not deposit the gold *per se* (that is without the battery); for gilding iron and steel goods, he directs that the bath should be weaker than for any other metal; and for this purpose, recommends the following, with which Gore substantially agrees:—

*Watt's Formula for Gilding Iron and Steel.*

Ordinary gilding solution (containing, say, one ounce of gold to the gallon)	. . . . .	4 parts.
Cyanide of potassium, about	. . . . .	16 "
Water	. . . . .	20 "

This solution would contain between 3 and 4 dwts. of gold to the gallon. It should not be worked so hot as the ordinary solution, and with weak current, and small anode surface, and deposition must take place at first very slowly. He prefers also to give articles of iron or steel a preliminary coat of copper or brass before gilding.

Gore, on the other hand, in his directions as to gilding, conforms very nearly to the usual American practice, in omitting the preparatory coppering of iron and steel. Respecting other base metals, he recommends (*Electro-Metallurgy*, 142) before gilding that articles composed of antimony, lead, tin or zinc, Britannia-metal, pewter, type-

metal, etc., should receive a film of copper or brass in a cyanide solution.

In this connection, it may be observed that all authorities on this subject, with the single exception of Roseleur, agree in the statement that no solution has been found to work so well for electro-gilding as the simple cyanide of gold, dissolved in a solution of cyanide of potassium, or the double cyanide of gold and potassium dissolved in water.

It is possible that the inconveniences attendant upon its use, as reported by Roseleur, may be due to the method of preparing it. For it will be observed, Roseleur, in this and several other formulæ recommended by him, adds the chloride of gold directly to the potassium cyanide solution, without first converting the gold into cyanide. The additional labor required to do this is very slight, but many electro-gilders follow the same careless method. The result is that there is formed in the gilding bath a quantity of chloride of potassium which is the equivalent of the gold chloride decomposed by the cyanide; and careful observers, who have studied this subject, do not hesitate to affirm that the presence of this foreign salt often seriously interferes with the successful working of the bath, when everything else may be in perfect order. It is worthy of notice also, that Roseleur in his directions for preparing the usual cyanide bath for electro-plating (silvering) calls attention to the practice followed by some operators of adding their chloride or nitrate of silver directly to the cyanide, and deprecates the practice as objectionable on the same grounds that we base our objection to his analogous mode of preparing the electro-gilding bath. It is certainly safer, and will be found more satisfactory by the operator, to first convert the chloride of gold into cyanide by the gradual addition, drop by drop, of cyanide of potassium, with constant stirring, and allowing the precipitate



always to subside before adding a fresh quantity, and ceasing to add any more cyanide when the addition of a drop or two ceases to cause any more precipitation. The resulting cyanide of gold should be carefully washed by decantation, first pouring off the supernatant liquid, and then washing and decanting several times with fresh water. These wash waters should be kept to save any traces of gold they may contain. The washed gold cyanide should then be dissolved in the quantity of cyanide of potassium named in the formula; and the result will be a gilding bath free from useless and possibly injurious ingredients.

The double cyanide gilding bath may also be prepared by electrolysis. For this purpose prepare a solution of cyanide of potassium of the desired degree of concentration, and, employing a sheet or plate of gold for an anode, and a plate of platinum or gold as the cathode, pass the current through the solution for an hour or two, keeping the temperature at about 150° Fah. When the bath is supposed to contain enough gold, its condition is tested occasionally, to ascertain the fact, by disconnecting the gold or platinum cathode, and substituting a well cleansed article, say of German-silver, in its place for about a minute. When the appearance of the article tested indicates a satisfactory deposit of gold, the bath is in proper working condition, and may be used at once, with the same current and anode. By this method, however, the bath must necessarily contain free potassa, equivalent in quantity to the amount of gold converted into cyanide, which, in time, will absorb carbonic acid from the atmosphere, and thus introduce the carbonate of potassium into the bath. This fault may be avoided, by adding to the bath when freshly prepared a small quantity of hydrocyanic acid, which will convert the free potassa into cyanide of potassium; or, after the bath has been exposed to the atmosphere long enough

to convert all the potassa into carbonate, by adding a small quantity of the cyanide of calcium, which will form, by double decomposition, insoluble carbonate of calcium (which falls to the bottom as an inert powder) and cyanide of potassium. The preparation of the cyanide gilding bath by electrolysis is rarely practised on the large scale, where the method of preparation by chemical means is adopted. It is, however, well adapted for the wants of amateurs and others operating on a small scale, and it has the advantage of insuring the operator against the loss of any of his gold, which, if he is inexperienced, might occur by the use of the chemical methods of preparing the bath.

#### GENERAL OBSERVATIONS UPON HOT ELECTRO-GILDING.

Hot, as well as cold baths, may be used in a more concentrated condition, that is to say, the quantity of water may be diminished without changing the proportions of the salts and of the gold. Roseleur finds it preferable, in practice, to use diluted solutions, which deliver the metal in smaller quantity in a given time, but with a better aggregation of its molecules.

Instead of suspending the articles in a state of immobility in the hot baths, they should, as far as practicable, be kept in constant agitation. By this artifice fresh portions of the liquid are constantly brought in contact with the objects, and the gilding acquires a uniform color.

Where it is desired to gild only the inside of an article, as for instance, a silver cream-ewer, sugar-bowl, mug, etc., the gilding is most conveniently done (after proper cleansing) by connecting the handle, or other convenient part of the exterior, with the negative wire, carefully suspending a gold anode in the centre of the vessel, then filling the vessel up to the upper edge with the gilding solution, and passing the current until a sufficient deposit has been



obtained. The extreme edge, the lips of jugs, and other parts of irregular outline at the upper portion of these vessels, which cannot be reached, may be gilded either by guiding the current through a rag wetted with the gilding solution and laid on the part, or by suspending the article in a little gilding solution, so that the unguilded extremity may be immersed, after having protected, by stopping-off varnish, those parts of the exterior that may also dip into the solution.

Copper or brass goods that have mountings, pewter-soldered, may give trouble from the indisposition of the solder to receive a proper deposit. In this case, the simplest mode of procedure is that recommended by Watt, namely, to moisten the soldered places with a drop of acidified sulphate of copper (or concentrated solution of silver) and touch the same with a piece of steel, when the moistened parts at once receive a bright coating of copper (or silver), which may be strengthened, if necessary, by repeating the operation. Thus coated, the soldered spots at once accept the gilding.

Roseleur prefers to use as the anode in hot electro-gilding, a foil or a wire of platinum in place of one of gold, for the reasons that it is not dissolved, and is more handy for regulating the intensity of the current, by immersing it more or less deeply into the liquid. With the same bath and current, this anode will effect the deposit of gold with three different shades: a pale color, with the anode dipping but slightly; a yellow color, when the immersion is greater; and a red gold, if the whole anode is immersed. These various shades are simply due to different modes of aggregation of the gold molecules, and the phenomenon becomes more striking when we operate with baths containing alloys. Thus, for instance, in a bath of pink gold, composed of gold, copper, and silver,



we may at will, and by increasing or diminishing the length of the platinum anode in the liquid, impart to the deposit a white, yellow, or red shade, since the various metals require for their reduction different degrees of intensity in the galvanic current.

Therefore, with hot electro-gilding baths, and especially with small articles, a skilful operator with his right hand will keep them constantly moving in the liquid, while the left is employed in changing the position of the platinum anode, so as to suit the surface and the nature of the articles, and obtain the desired shade.

All the hot electro-gilding baths may be maintained at normal strength by successive additions of chloride of gold, with a proper proportion of the other salts; but it will soon be noticed that, with the increasing density of the liquid, the results become inferior, and that it is better to use up the bath entirely and prepare a fresh one.

When a bath becomes exhausted, the gilding is reddish in tint, if much copper has been gilded in it, and green in the case of silver articles. It may be used then for giving a preparatory coating to objects which are finished in a fresh bath.

Electro-gilding, either by the cold or hot method, may present many different colorations, due sometimes, as already said, to different modes of molecular aggregation, but oftener, to the alloying of other metals with the gold. Thus green, or white golds, result from the simultaneous deposition of gold and silver in various proportions; red gold, from an alloy of copper and gold; and pink gold, from the combination of gold, silver, and copper.

#### *Green and White Gilding.*

To obtain these shades, it is sufficient to add to one of the above baths a solution of the double cyanide of

silver and potassium, or a diluted solution of nitrate of silver until the desired shade is obtained. The tints will vary from a leek-green to a very pale whitish-yellow. This kind of gilding, mingled upon the same articles with red, yellow, or pink gold, produces splendid effects of contrast, especially upon chased parts, where the green gold assumes a velvety lustre.

#### *Red Gilding*

is obtained by mixing, in suitable proportions, the electro-copper bath, already described, with one of the baths for electro-gilding. We may also use for this purpose an old bath in which many copper articles have been gilded, with a quite intense current. Yellow gilding may be made to pass to red, by heating it after smearing it with a paste of acetate of copper, cream of tartar, and common salt, called *green for red* by old gilders (see this term in the chapter on CHEMICAL PRODUCTS at the end of this work). The heated piece is plunged into a weak solution of sulphuric acid, and afterwards carefully scratch-brushed.

#### *Pink Gilding.*

This species of gilding requires many precautions, and is the most difficult to obtain, not only on account of the different tendencies of the various metals to decompose under the influence of the current, but also because the jewellers disagree as to what should be called the proper shade. The gilder should expect trouble on that account, since he will have to vary the shade for each customer, some preferring a gilding slightly yellower, and others redder, or whiter. Roseleur holds that pink gilding, to be perfect, should present at the same time the red, yellow, and white shades, in such a manner that a practised eye



will distinguish them. It is impossible to describe the effect produced by these mixed tints, which can be remembered only after having been seen.

Some time ago, the various shades of pink were obtained by gilding in the following bath at different temperatures, and with currents of variable intensity, the articles already yellow-gilded by battery, or by immersion. This bath was composed of—

New silvering bath	. . . . .	1 part.
Hot gilding bath (new)	. . . . .	25 parts.
New coppering bath	. . . . .	15 “

This formula has no regularity in its working, and may give to a first batch of articles a white color, to the second a red, and to the third a dull, dark shade.

At the present time the following methods are used:—

The articles are first yellow-gilded by the formula of the immersion bath of pyrophosphate, or by that of the hot electro-bath. Then, without drying, but keeping them in fresh water, they are made into small lots or packages weighing about 1 or 2 ounces each, which are lightly passed through the quicking bath, and then red gilded, hot, either in an old and nearly spent electro-bath in which a great deal of copper has already been gilded, or in a new bath composed of ten parts of hot electro-gilding bath (first formula, Chapter XXI. p. 200), and three to four parts of the electro-coppering solution (first formula, Chapter X. p. 118).

According as the electric current is more or less intense, so will the gilding be more or less red. For imparting to it the pale tint of many articles gilded by the use of amalgam (see Chapter XVII.), the red gilding is passed through a boiling and nearly spent bath of pyrophosphate, to which has been added one-tenth, or a twentieth, or a thirtieth of its volume of a silver bath, or simply a



few drops of a concentrated solution of nitrate of silver. A few gilders simply pass their red gilding through a cold bath for silvering by dipping. In whatever manner we operate, a blush of silver is deposited upon, and whitens, more or less, the red gilding.

This gilding should be scratch-brushed, or, preferably, burnished, and it then imitates gilding by mercury or jeweller's alloy. It may be chased, but then the lustre soon disappears, on account of the large proportion of copper it contains.

In case of failure to obtain the proper pink gilding, which often happens, it is sufficient to plunge the articles for a few seconds into a mixture composed of five parts of sulphuric acid to one of nitric acid. The copper and silver are dissolved, and the yellow gilding reappears, upon which the operation may be begun anew.

#### ADDITIONAL FORMULÆ.

Günther recommends (Winckler, *Handb. d. Metall-überzügen*, 175) the following baths for electro-gilding, viz:—

For yellow gold, he prepares a neutral chloride of gold, in the usual manner, and prepares a bath having the following proportions:—

Chloride of gold . . . . .	25 parts.
Ferrocyanide of potassium (fused) . . . . .	60 to 80 “
Water . . . . .	3000 “

This is boiled about a quarter of an hour, and then diluted to double its volume with water, boiled again, allowed to cool, and filtered.

For red gold, he proposes the addition of some metallic copper to the acid mixture used in dissolving the gold; the bath is then prepared as above; or he adds to the

gilding bath, prepared as above, a sufficient quantity of a solution composed of—

Cyanide of copper . . . . .	4 parts.
Cyanide of potassium . . . . .	9 “
Water . . . . .	400 “

For green gold, he adds a small quantity of silver to the acid mixture while the gold is dissolving; or uses, as an addition to the bath prepared as above, a suitable quantity of a solution composed of—

Cyanide of silver . . . . .	4 parts.
Ferrocyanide of potassium . . . . .	40 “
Water . . . . .	600 “

Briant prepares a gilding solution by treating a warm solution of chloride of gold with an excess of magnesia, by which the gold is precipitated as oxide. The precipitate is filtered, washed, and digested with water containing about 8 per cent. of nitric acid, which dissolves out the magnesia, leaving the gold oxide, which should be repeatedly washed until it shows no acid reaction when tested with test paper. He dissolves the oxide, resulting from the treatment of  $3\frac{1}{2}$  parts of gold in the manner just described, in a solution composed of—

Water . . . . .	400 parts.
Ferrocyanide of potassium . . . . .	40 “
Caustic potassa . . . . .	10 “

This solution is boiled for 20 minutes, and the small amount of precipitated iron is removed by filtration. The resulting golden-yellow liquid forms the gilding bath, and may be used either hot or cold.

Elsner's solution (Winckler, *Handb. d. Metallüberzügen*) is prepared in substantially the same manner.

Braun (Winckler, *Handb. d. Metallüberzügen*, 172) prepares a hot electro-gilding bath with fulminate of gold resembling the first formula for “cold electro-gilding

baths" (Chapter XX. page 191), but more dilute. He prefers to use it at a temperature of from 100° to 140° Fahr., and with a moderately strong current. His directions for preparing the bath are substantially as follows: He prepares a neutral chloride of gold in the usual manner, and adds to the solution common salt, in the proportion of 3 parts of salt to each 10 parts of gold; then evaporates to dryness, and cautiously fuses the resulting double chloride to drive off the excess of acid. The fused salt on cooling is dissolved in distilled water, and treated with ammonia in excess, whereby gold fulminate is precipitated. This is filtered and washed with water until the last portions of the wash water are tasteless. The *still moist* fulminate of gold is then dissolved in cyanide of potassium, and the solution diluted with water, so that the liquid shall contain in 1000 parts 15 parts of gold. The liquid is now boiled until all the ammonia has been driven off (that is, until it no longer smells of ammonia), and is then further diluted with water, so that 2000 parts of solution shall contain 15 parts of gold. Braun uses this bath chiefly for electro-gilding articles of German-silver; it is affirmed to produce a fine dead gilding.

Gore notices (*Electro-metallurgy*, 138) that a very rich dead gilding may be obtained in a cyanide solution by adding a little *wet* aurate of ammonia (*i. e.*, fulminate of gold) to the liquid, just before gilding; and a clear, bright yellow gilding by adding to an ordinary cyanide gilding solution a small quantity of caustic soda; and that copper and brass trinkets that require to have a "dead" gilded appearance, may be dipped for this purpose before gilding in a mixture of equal parts of sulphuric and nitric acids, to which a little common salt has been added.

For a half-dead and dead gilding, Messrs. Christoffe & Co., of Paris, employ a cyanide solution, in combination



with the Elkington bath. The solution is worked at a temperature of from 65° to 85° Fahr. with a gold anode. For half-dead effect (Winckler, *Handb. d. Metallüberzügen*, 174), they convert 31 parts of gold into chloride, add thereto 1960 parts cyanide of potassium solution (of 25° B.), and 840 parts of caustic potassa solution of same density; the mixture is then boiled until the solution marks 35° B.

This solution is mixed with the Elkington bath, composed of 150 parts gold chloride, 9000 parts bicarbonate of potassium, and 30,000 parts of water, boiled for two hours. The articles to be gilded are not previously coppered.

For dead gilding, they dissolve 31 parts of *moist fulminate* of gold in 1000 parts of distilled water, containing 250 parts of cyanide of potassium, and add thereto 4500 parts of a ferrocyanide of potassium solution of 30° B. strength. The resulting solution is boiled for about half an hour, and is then ready. It may be worked either cold or warm, and the articles are not previously coppered.

Becquerel recommends (Gore, *Electro-Metallurgy*, 133) a solution made of 1 part of gold chloride, and 10 of ferrocyanide of potassium in 100 parts of water, to which, after filtering, to remove separated iron, 100 parts of a saturated solution of ferrocyanide of potassium is added, after which an equal or double volume of water is also added. The color of the gilding will depend on the concentration of the bath; the best effect is had with the most dilute baths, and with those most free from iron. Washing the articles in diluted sulphuric acid, and rubbing gently with a piece of linen cloth brightens the gilding.

Levol (*Id.* 133) dissolves neutral gold chloride in water, and adds enough of an aqueous solution of sulpho-cyanide of potassium to redissolve the precipitate at first formed.

A slight acidity must be maintained by occasional additions of a few drops of hydrochloric acid when required.

Fizeau (*Id.* 133) dissolves 1 part dry chloride of gold in 160 parts of distilled water, and adds, little by little, carbonate of potassium solution until the solution begins to become cloudy, when it is ready for use. Another of his formulæ is a solution of 1 part of gold chloride and 4 of hyposulphite of sodium in 1000 parts of distilled water.

Spencer has proposed the use of the bromide and iodide of gold for electro-gilding baths. His process is substantially as follows:—

He prepares a saturated solution of bromide of gold by adding gold leaf to bromine, until it will dissolve no more. This solution may be used as it is, but to obtain a thick deposit, he recommends the addition of two parts of a saturated solution of acetate of ammonium to one part of the bromide solution. Where this solution is to be used to gild alloys that will receive a gold deposit by simple immersion in it, he advises the addition to the bath of an excess of carbonate and bicarbonate of sodium.

In an analogous way Spencer prepares and employs a solution containing iodide of gold.

Jacobi's formula is—

Ferrocyanide of potassium . . . . .	12 parts.
Caustic potassa . . . . .	3 "
Gold . . . . .	1 part.
Water . . . . .	120 parts.

The gold is converted into chloride, dissolved in the aqueous solution containing the other ingredients, and the resulting liquid forms the gilding bath.

Hansen's patented process for electro-gilding, plating, or coppering upon glass or porcelain, which presents some differences to those described in Chapter XV., consists (Elsner, *Chem.-Techn. Mittheil.*, 1876-1877) in preparing two



solutions: one of sulphur in oil of lavender, which is concentrated until it has a thick syrupy consistence; and another, of chloride of gold or platinum, in sulphuric ether. He mixes these two solutions, and by gentle heating, evaporates, until the resulting mass has become pasty. This mixture is suitably laid on the glass or porcelain surface with a brush, to form the intended decoration, and the article is heated in a muffle, for the purpose of driving off the sulphur and other volatile and decomposable substances—the gold or platinum being left behind in the metallic state, firmly adherent to the surface of the object. Thus prepared, the metallized surface of the article may be plated with a coating of gold, silver, or copper of any desired thickness by galvanic means. For this purpose Hansen gives the composition of electro-baths of these respective metals which he prefers to use. It will be unnecessary to reproduce them, as any of the formulæ named in this work will serve the purpose.

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## CHAPTER XXII.

### GILDING WATCH MOVEMENTS, AND OTHER SMALL ARTICLES FOR WATCHMAKERS.

IN the gilding of watch movements, and other small articles for watchmakers, gold is seldom directly applied upon the copper. In the majority of cases, there is a preliminary operation, called *graining*, by which a very agreeable grained, and slightly dead appearance, is given to the articles. If one carefully examines the interior of a watch, the peculiar stippled matt lustre of the parts will be at once noticed.



V This peculiar bright-matt lustre, as Roseleur terms it, is totally different from what we have already mentioned. For instance, it does not resemble the dead lustre obtained by slow and thick electro-deposits of gold, silver, or copper, which is coarser and duller than that of watch movements. Neither does it resemble the dead lustre obtained with acids, which is the result of a multitude of small holes formed by the action of these agents; whereas the grained dead lustre is formed by the juxtaposition, upon a previously smooth surface, of an infinite number of granules of greater or less size, and *always in relief*.

The graining may be produced by different methods, and upon gold, platinum, and silver; and since the latter metal is that preferred, we shall describe the process as applied to it.

This species of gilding requires the following successive operations:—

1. *Preparation of the Pieces.*—Coming from the hands of the watchmaker, they still retain the marks of the file, which are obliterated by a rubbing upon a wet stone, and lastly upon an oilstone.

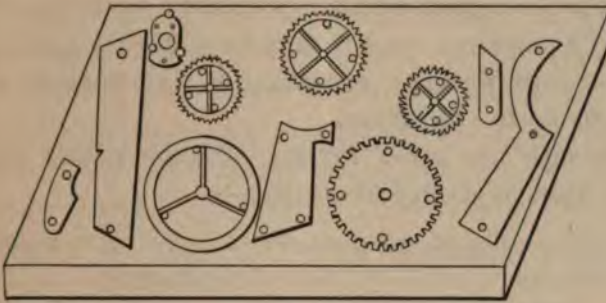
2. The oil or grease is next removed by boiling the pieces, for a few minutes, in an alkaline solution, made of one hundred parts of water and ten of caustic soda or potassa, and rinsing them in clean water, which should wet them entirely if all the oil has been removed. In going through this operation, the articles are threaded upon a brass wire.

3. A few gilders then cleanse them rapidly in the acid mixture for a bright lustre; others simply dry them carefully in white sawdust.

4.  *Holding the Pieces.*—The pieces thus prepared are fastened, by means of brass pins with flat heads, upon the smooth side of a block of cork (Fig. 98). A few

operators have lately substituted gutta-percha for cork, but this method does not appear to have given good results, since, so far as I know, it has not become popular.

Fig. 98.



5. The parts thus held upon the cork are thoroughly rubbed over with a brush, entirely free from fatty matters, and charged with a paste of water and of the finest pumice-stone powder. The brush is made to move in circles, in order not to abrade one side more than the other. The whole is then thoroughly rinsed in clean water, and no particles of pumice dust should remain upon the pieces, or the cork.

6. Afterwards the pieces are plunged, cork and all, into a weak quicking solution, which very slightly whitens the copper, and is composed of—

Water	. . . . .	10,000 parts.
Nitrate of mercury	. . . . .	2 "
Sulphuric acid	. . . . .	4 "

The pieces are simply passed through the solution, and then rinsed. This operation, which too many gilders neglect, gives strength to the graining which, without it, possesses no adherence, especially when the movements are made of German-silver, dignified by the name of



nickel by watchmakers, or when the false cases contain tin in their composition.

7. *Graining*.—In this state, the parts are ready for the graining, that is to say, a light silvering obtained by a peculiar procedure.

There are a great number of formulæ for preparing the graining powders; and it may be said that each gilder has his own formula, according to the fineness of the grain he desires to obtain.

Herewith are given several formulæ which may be relied upon to give good results:—

Silver, in impalpable powder* . . . . .	3 parts.
Bitartrate of potassium (cream of tartar), finely pulverized and passed through a silk sieve . . . . .	30 "
Chloride of sodium (common salt), pulverized and sifted as above . . . . .	100 "

\* The silver powder is obtained by immersing cleansed copper plates in a *very diluted* solution of nitrate of silver made with distilled water. The more dilute the solution is, the finer will be the state of division of the silver, which will be deposited upon the copper as a species of moss, and the more easily may it be detached. The operation is generally conducted as follows: In a suitable vessel of glass or porcelain, 2 parts of crystallized nitrate of silver are dissolved in 1000 of distilled water, and five or six bands of cleansed copper about  $\frac{3}{4}$  of an inch wide are plunged into it. These bands should be long enough to allow of a portion being above the liquid.

The whole is kept for twenty-four hours in a dark place, and the liquid is now and then stirred with the copper bands. This motion is sufficient to loosen the deposited silver, and present fresh copper surfaces to the action of the liquid.

When no more silver becomes attached to the copper, the operation is at an end, and there remains a blue solution of nitrate of copper.

The silver powder is washed either by decantation, or upon a filter, until no trace of the copper solution remains. Lastly, another washing is had with distilled water, and the silver powder is dried. Great care is required in this operation to avoid contact with hard bodies, which may render the powder compact, and produce a sort of cohesion



*Second formula.*

Silver powder . . . . .	3 parts.
Cream of tartar . . . . .	12 to 15 "
Common salt (white and clean) . . . . .	40 "

*Third formula.*

Silver powder . . . . .	3 parts.
Cream of tartar . . . . .	10 "
Common salt (white and clean) . . . . .	100 "

All of these substances should be as pure as possible, and perfectly dry. Cream of tartar is generally dry; but common salt often needs, before or after it has been pulverized, a thorough desiccation, by gentle heating in a porcelain or silver dish, and stirring with a glass rod, or a silver spoon.

The mixture of the three substances must be thorough, and should be effected at a moderate heat, long protracted.

The graining is the coarser, according as there is more common salt in the mixture; and conversely, it is the finer and more condensed as the proportion of cream of tartar is greater, but it is then more difficult to scratch-brush.

8. *The Graining proper.*—This operation is effected as follows: A thin paste of one of the above mixtures, with

of the molecules which injures it for the subsequent operation of graining.

At the present time, the majority of operators, instead of preparing their graining silver, prefer buying the Nuremberg powder, which is produced by grinding a mixture of honey and silver foil with a muller, upon a ground glass plate until the proper comminution is obtained. The silver is separated by dissolving the honey in boiling water, and washing the deposited metal on a filter, until there is no remaining trace of honey. The silver is then carefully dried at a gentle heat.

This silver, like bronze powders, is sold in small packages weighing about an ounce.

water, is spread by means of a spatula upon the articles attached to the cork. The cork itself is placed upon a platter, holding it with the left hand. An oval brush (Fig. 99), with close bristles is held in the right hand,

Fig. 99.



with which the pieces are brushed in every direction, turning both the brush and the sheet of cork all the while. A fresh quantity of the paste is added two or three times, and

used in the manner indicated. The more the brush and the cork are rotated, the rounder becomes the grain, which is a good quality; and the more paste added, the larger the grain.

Watchmakers generally require a fine grain, circular at its base, pointed at its apex, and close, that is to say, a multitude of juxtaposed, diminutive cones. Sometimes, however, a larger grain may make a better appearance; but this will depend on the nature and the size of the articles.

9. When the desired grain is obtained, the pieces are washed and then scratch-brushed, with brushes of very fine brass wire. (Fig. 100.) As these wires are very stiff and springy, they will, when cut,

Fig. 100.



bind and turn in every direction, and no work can be done with them. It is therefore absolutely necessary to anneal them more or less upon an even fire. An intelligent worker will always have three scratch-brushes, annealed to different degrees: one which is *half soft*, or half annealed, for the first operation of uncovering the grain; one *harder*, or little annealed, for bringing up the lustre; and one *very soft*, or fully annealed, used before gilding for removing the scratches which may have been made

by the preceding tool, and for scratch-brushing after gilding. Of course, the scratch-brushing operation, like the graining proper, should be done by giving a rotary motion between the fingers both to the tool and the cork. After a good scratch-brushing, the grain, seen through a magnifier, should be regular, homogeneous, and with a uniform lustre all over. Decoctions of liquorice, soapwort, or Panama wood, are employed in this operation.

It frequently happens that the same piece is composed of both copper and steel, and this latter metal requires to be preserved against the action of the cleansing acids and of the graining mixture, by applying a stopping-off varnish.

The operation consists in covering the pinions and other parts of steel with a fatty composition, which is sufficiently hard to resist the tearing action of the bristle and wire brushes, and sufficiently insoluble in the alkalies of the gilding bath to remain unaffected.

The formula of this composition is as follows:—

Yellow wax . . . . .	6 parts.
Translucent resin . . . . .	10 “
Red sealing-wax (extra fine) . . . . .	4 “
Impalpable peroxide of iron (English polishing rouge) . . . . .	3 “

The resin and sealing-wax are melted together in a porcelain dish upon a water-bath, whereupon the yellow wax is added. When the whole is thoroughly fluid, the rouge is gradually added, and stirred into the mass with a wooden or glass rod. The heat is then removed, but the stirring should be continued until the mixture becomes solid, otherwise all the oxide of iron will fall to the bottom of the dish.

Flat parts which are to receive this varnish are slightly



heated, and then covered with the above mixture, which melts and is easily spread. For covering steel pinions, which generally form cylindrical projections upon the face of the wheels, a species of stylus of brass or copper is employed, having a wooden handle. (Fig. 101.)

The metallic extremity of this tool is heated over an alcohol lamp, and a small quantity of varnish is taken up with it. The composition soon melts, and, by turning the tool around the steel pinion, this becomes coated. Before fastening the pinion upon the cork, a small cavity is dug in the latter, in which the pinion rests. The remainder of the operation is conducted as with the other parts of the watch movements. Nevertheless, it is prudent to use a scratch-brush with long wires, as their flexibility prevents the removal of the composition. When, *after* gild-

ing, the varnish is to be removed, the parts are plunged into warm oil, or into tepid benzine or turpentine, then into a very hot soap water, or alkaline solution, and lastly rinsed in fresh water. Scratch-brushing, and drying in warm sawdust of white wood, terminate the operation.

The pinions are cleaned out and polished by passing between them small pieces of very soft white wood, the friction of which is sufficient to restore to the steel its primitive lustre.

The gilding of those parts composed of copper and steel requires the greatest care, since the slightest rust will destroy their future usefulness. Should some gold have become deposited upon the steel, it should be removed by rubbing with a stick of wood and impalpable pumice dust, putty powder, or rouge.

10. *Gilding*.—After the series of preparations above described, we come at last to the gilding, which may be



Fig. 101.

effected by one of the processes already indicated. Hot baths, of course, should not be employed for those pieces covered with the varnish. The following is a minute description of this process as employed at Besançon, and which, according to Roseleur, gives good results.

Four parts of finely laminated and pure gold, first heated to redness in order to destroy any organic matter that may be present, are dissolved in a glass flask in a mixture of six parts of pure nitric acid, and twelve of pure hydrochloric acid. When the gold is dissolved, and the excess of acids has been evaporated, leaving in the flask a dark-red, nearly syrupy liquid, the whole is removed from the fire and allowed to cool. The chloride of gold is then dissolved in fifty or sixty parts of distilled water, and poured into a large glass vessel. It is then diluted with about five hundred parts of distilled water, and an excess of pure ammonia is added, which precipitates the gold in the state of a yellowish powder of fulminate of gold, *which is highly explosive when dry*. A sufficient quantity of ammonia has been added, when a new quantity of this reagent, being added to the supernatant liquid, does not produce any turbidity, or precipitate. The clear liquid is decanted and saved. The precipitate is then collected upon a small filter, previously wetted with distilled water, and there washed with distilled water until all ammoniacal odor has disappeared. The filter, with its contents, is then transferred to a glass or porcelain vessel containing a solution of twelve parts of cyanide of potassium in one thousand of water, which rapidly dissolves the gold and leaves the filter. The solution is filtered anew, boiled for fifteen to twenty minutes, filtered again, and left to cool. The bath obtained is excellent for gilding the most delicate watch works, under



the influence of an electric current regulated to suit the surfaces to be gilded.

This bath, or these baths, since every gilder possesses several of them of various stages of freshness, are generally kept in flat bottomed glass or porcelain vessels, holding about a gallon, and having a depth of four or five inches. The articles to be gilded are suspended in the bath from metallic holders, connected with the negative electrode, and of a shape appropriate to the nature and form of the articles. One, or several, platinum wires are used for anodes, and are disposed in the centre or about the circumference of the bath.

The current used should be constant but of very moderate intensity.

The slower the rate of deposition, the finer and more adherent the gilding will be. When the operator judges that the coating is sufficient, the articles are removed from the bath, washed in clean water, and fixed again upon the cork block, in order to proceed to the last scratch-brushing with a decoction of liquorice, the bark of Panama wood, horse-chestnut, or soapwort.

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## CHAPTER XXIII.

### GILDING FINE WIRE.

FINE wire of gold, or silver, or of gilded or silvered copper, is much used in the manufacture of metallic fringes and lace for epaulets, and other purposes.

Formerly, as Roseleur explains, the copper or silver wire was gilded with amalgam, that is to say, with the aid of fire and mercury. A cylindrical rod of copper or



Silver, of variable dimensions, was well cleansed, and then covered with the aid of mercury, either with gold-foil, or with gold amalgam. The whole was heated over a clear charcoal fire, in order to volatilize the mercury; and then passed through draw plates of steel, for the large numbers, and of ruby, corundum, or diamond for the smaller numbers. This process was open to the disadvantage of leaving parts of the wire uncovered with gold, because of the irregularity of the coating of the latter metal.

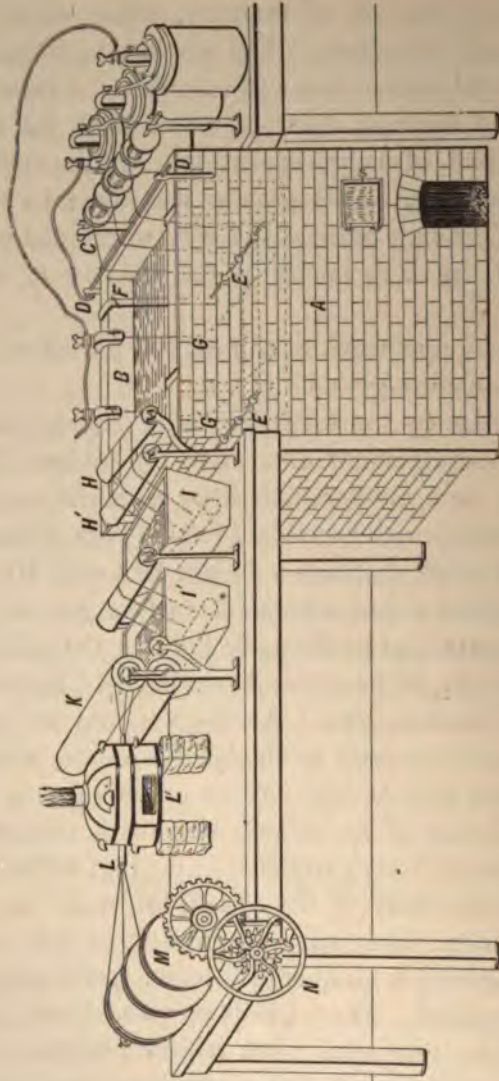
At the present time, nearly all the gilded wire manufactured is electro-gilded.

We explain in the following, after Roseleur's suggestions, the arrangement of a bath for gilding fine wire, relying for being understood upon a careful examination of the perspective and sectional views (Figs. 102 and 104).

Upon a brick furnace A (Figs. 102 and 104), which may be heated either with solid fuel or gas, is placed a cast-iron enamelled kettle B, for holding the gilding bath. This kettle should be about 3 feet long,  $1\frac{1}{2}$  feet wide, and from 6 to 7 inches deep. As the fire may be lighted or not, it is not necessary to change the kettle, whether the bath be used cold or hot. If we employ gas as fuel, the burner is made of an elliptic ring with numerous jets (twenty-five or thirty) attached to it (Fig. 103).

At one extremity of the apparatus, near the battery, are two wooden uprights, C, supporting an iron rod, upon which are strung a number of wooden spools carrying the wire to be gilded. These spools may turn freely upon the rod, and the unwound wire, before plunging into the bath, is passed over a copper or brass tension bar, D, connected with the negative pole of the battery, thus establishing the required metallic connection between the wire and this pole.

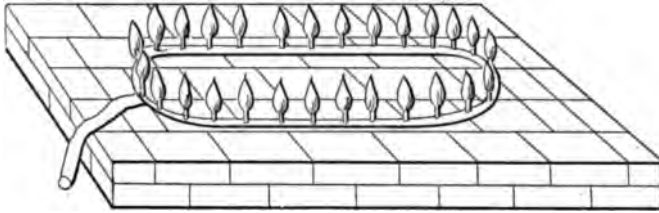
Fig. 102.



The wire penetrates the bath to about two-thirds of its depth, and is kept stretched by a system of small grooved pulleys E, E of glass, porcelain, or ivory, revolv-

ing freely upon glass or ivory axes, themselves maintained near the bottom by supports secured to the rim of the kettle.

Fig. 103.



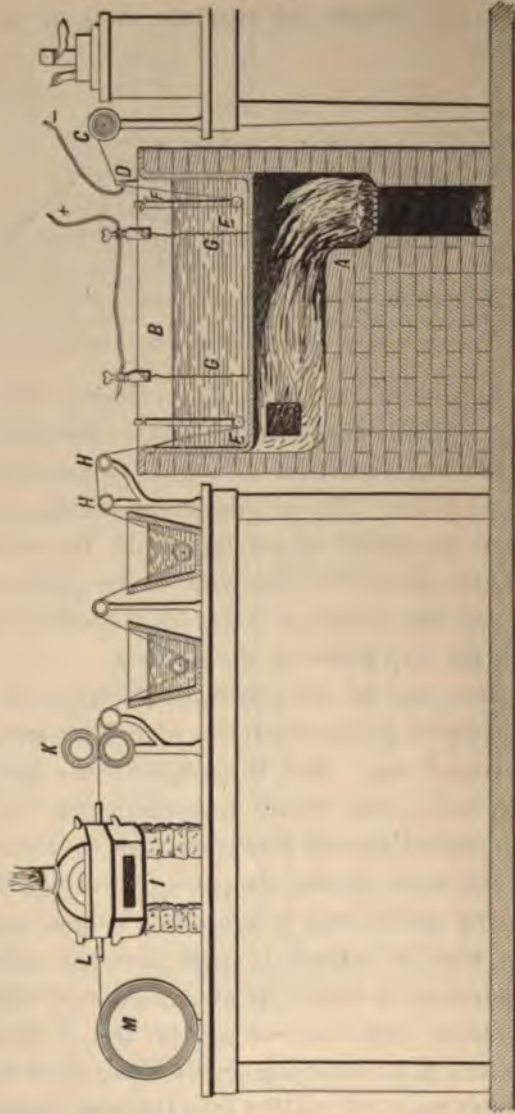
At the bottom of the bath, and crossing the path of wire to be gilded, are two or more platinum wires, *b, c, d, e, f, g*, the vertical branches of which communicate with the positive pole. These platinum anodes must, of course, have no point of contact with the wire to be gilded. Thus, therefore, the wire to be gilded, on the one hand, and the platinum wires on the other, represent in the bath the two poles of the battery.

At the other end of the apparatus, a series of wooden spools, *m*, is placed, upon which the wire, after having been gilded, is wound up. But these spools are fast upon a square iron axis, and which communicates by gearing with a hand-wheel moved slowly enough to insure a good gilding to the wire, during its passage through the bath.

After being gilded and before being wound upon these spools, the wire is caused to pass through other parts of the apparatus, in which it is rinsed and dried in a suitable manner; thus, as seen in Fig. 104, it reaches two wooden rollers, *h, h*, revolving freely upon their axes, and is carried over grooved rollers into the first trough, filled with a weak solution of cyanide of potassium, which cleans and brightens the gilding. By a similar disposition, it passes into the second trough, filled with fresh water fre-



Fig. 104.



quently renewed, which removes the salts it has carried with it. From these it is passed between the drying rollers, κ, which are covered with several layers

of calico, and revolved by gearing in opposite directions. As a last precaution, before being finally wound on the spools, the wire is completely dried by passing it through a large flat tube, L, maintained at a dull red heat in the furnace I.

In a bath of the size indicated above, twenty coils may be gilded at the same time. The copper wire to be gilded is generally silvered beforehand, and passed once through a draw-plate, in order to avoid the cleansing process before gilding.

The more intense the current, or the slower the rate of passage of the wire through the bath, the greater will be the quantity of gold deposited; and to make no mistakes, it will be well to weigh the bobbins before and after the operation. For this purpose, the extreme spools for paying out and winding should be of the same weight.

This process of gilding requires constant supervision, either for uniting the broken ends, the severed parts of which may touch the anodes and stop the operation; or for regulating the intensity of the current, which, if too powerful or too weak, will produce, correspondingly, a red or green gilding.

The baths of double cyanide of gold and potassium are employed cold or slightly tepid (Chapter XX.).

On the other hand, the baths with phosphate and biphosphate of sodium are used for hot electro-gilding, and their concentration should be double, *i. e.*, the proportion of water should be one-half of that indicated (Chapter XXI.).

As the platinum anodes do not make up for the metallic loss of the bath, it is necessary to add frequently new portions of metal and of solvents, in the manner already indicated.

Pure gold wire is often gilded, in order to impart to it a more uniform, and a deeper shade.

After being gilded, the wire is passed through the draw-plate or rollers, according as we desire to have it round or flat. With the draw-plate it is diminished by about one-fourth or one-half of a number, simply to remove the dulness of the deposit, and bring up the lustre. When the gilded wire is flattened between rollers, its surface is bright or dull, according to the condition of the surface of the rollers.

It is evident that silvering, or any other metallic electro-deposit, may be effected upon fine wire in a similar manner.

## CHAPTER XXIV.

### “STOPPING-OFF” VARNISHES.

WHEN we desire to obtain upon the same object gildings of several colors, we employ “stopping-off” varnishes. Thus, after having gilded an article of a uniform color (red, or green, for instance), it is covered with a fatty varnish (made drying by the addition of chromate of lead), at those places which we desire to preserve from, or to resist the action of, the new bath. By thus “stopping-off,” and using successive baths, we are enabled to obtain five or six different shades upon the same object.

The “stopping-off” varnishes are applied with a brush or pencil, and should be thoroughly dried in a stove before the object is introduced into another solution. These varnishes may be colored with various oxides, or colored salts, in order to facilitate their use upon those places which should be sharply delineated; chromate of lead



and artificial ultramarine blue, are well suited for the purpose. The "stopping-off" varnishes are also employed for protecting the reverse parts of articles which are intended to receive the gilding only on one side. When the operation is finished, the varnish is easily removed by a washing, first with essence of turpentine, and then with alcohol. These liquids may be advantageously replaced by gasoline, benzine, or benzole. The latter substance is a product of the distillation of coal-tar, and dissolves, even in the cold, nearly all fatty and resinous bodies. It is sufficient, when we have used benzole, to wash the article in boiling water, and then to dry it in warm sawdust, from which it comes out perfectly clean. Such is not always the case with rectified turpentine, and it is prudent, where this has been used, to plunge the object afterwards into a hot lye of caustic potash, then to rinse and dry it in warm sawdust. We describe these varnishes more fully in another chapter.

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## CHAPTER XXV.

DEAD-GILDING—FIRE-GILDING—GILDING, PARTLY DEAD, PARTLY BRIGHT (DEMI-MATT).

### *Dead-Gilding.*

IN addition to the several processes previously indicated, dead-lustre gilding may be obtained by a number of different methods.

1. By the slow deposit of a large quantity of gold. This gilding is very durable, but is dull and earthy in appearance. Moreover it is too costly for the arts.

2. By acids; that is to say, by giving a dead lustre to

the metallic surface, before gilding, and by the processes indicated in the cleansing operations. This method is employed only for small articles, or when gilding by immersion. Varnishers, however, use it for bronze articles, or large embossed work.

3. With frosted silver, *i. e.*, by depositing upon the object to be gilded, a coating of frosted silver (by processes soon to be described), and then gilding in a good bath. Unfortunately, this method is somewhat expensive, and the burnished parts are greenish. Moreover the intermediary coat of silver is easily affected by sulphurous gases, and the gilding is thus blackened.

4. By copper, *i. e.*, by depositing in a solution of sulphate of copper, decomposed by the current, a galvanoplastic coat of this metal which possesses a pink, dead lustre. The piece is then rapidly passed through the acid mixture for bright dipping, then through quicking solution, and finally gilded in a good bath. When the dead lustre obtained in the galvanoplastic bath is perfect, the subsequent use of the acids may be dispensed with, and the article is simply plunged into the quicking solution before gilding. This last mode of operation is generally preferred by gilders. This gilding is very handsome in lustre and color. The burnished parts will be red, if vinegar or soap-water be employed; and of a fine yellow color, if the burnish be wetted with saliva, a decoction of flaxseed, of soapwort, or of marshmallow root. We shall indicate further on the best conditions for obtaining a fine dead lustre with copper.

If the deposit of gold be of insufficient thickness, it will blacken sooner or later, by the oxidization of the intermediary coat of copper.

5. Lastly, dead lustre may be effected with the aid of mercury. This is the old process of gilding by fire, which

we shall now describe. It furnishes the most durable products, but the method is costly.

### *Fire-Gilding.*

Although we have chosen this chapter on dead-lustre gilding for describing the method of fire-gilding, it should not be forgotten that we may also produce a bright lustre by the same means. Before the introduction of the galvanic processes into the arts, there were nearly as many sorts of gildings as at the present time; but their cost was greater, the operations were more difficult, and the workman was constantly exposed to the deleterious vapors of mercury. We must also acknowledge that the products were, and still are, superior in respect to durability, if not in appearance to those obtained by electro-deposition.

Fire-gilding may furnish gilding with a bright or a dead lustre, scratch-brushed, ormolued, and also with different shades. We indicate in the following, the different modes of operation.

The amalgam of gold is prepared in the manner described in the process of gilding with amalgam (Chapter XVII.). only a little less mercury is used, in order to obtain an amalgam about as hard as wax. This amalgam is crystalline, and a certain crackling sound is heard when we press the crystals between the fingers. A stock of amalgam is generally prepared in advance, and it is divided into small pellets of nearly equal size, the value of which is ascertained from their number, and from the total weight of gold employed. Thus, if 100 grains of gold has been used, and the resulting amalgam has been divided into ten equal pellets, each one will contain 10 grains of the precious metal. These pellets are kept in water, but they should not remain too long without being used, because the phenomenon of *liquation* takes place,



and the different parts do not present the same composition. In a word, the mercury separates from its combination with the gold.

When using the amalgam, it is spread with the finger upon a flat, hard stone, called the *gilding stone*, and having dipped a scratch-brush of stout brass wire into quickening solution until it becomes completely white, it is then touched to the amalgam, a portion of which it carries away. The object, previously well cleansed, is scratch-brushed in every direction, and the brush is frequently dipped in a very dilute quickening solution in order to facilitate the regular spreading of the amalgam.

This operation requires great care to obtain a uniform coating upon the hollows and elevations.

When the back part of a piece does not require gilding, a portion beyond the edge should be gilded, in order that the naked copper shall cause no injury in the subsequent operations.

When the article is uniformly covered with the amalgam, it is heated over a charcoal furnace without draft, resting upon a cast-iron plate.\* The entire attention of the operator is now required for watching the process. With his left hand covered with a thick glove of buckskin, he turns the piece in every direction upon the fire, and, as the mercury disappears, with his right hand he strikes the article in every direction with a brush, with long handle and bristles (Fig. 93), in order to equalize the gilding, and to work the remaining amalgam upon those parts which appear to require it.

\* M. Dreyer has his gilding furnace which allows the workman to watch the operation from behind a glass frame, to avoid the risk of inhaling the mercury vapors. His care and diligence, and carelessness that his apparatus should become poisonous, and in these workshops a simple hood is used, and the workman remains constantly exposed to the fumes of mercury, the effects of which are most pernicious.

When all of the mercury has volatilized, the gilding has a dull greenish-yellow color, and the operator

Fig. 105.



then examines whether the coating of gold is continuous. Should a few uncovered places appear, a fresh quantity of amalgam is added, and the operation is repeated.

The next operation is scratch-brushing, which leaves the piece with a pale-green color, after which another heating is necessary for arriving at the desired shade. The re-heating should be sufficient for expelling any remaining mercury, and to produce a fine orange-yellow gilding.

We may now proceed to one of two distinct operations, according as we desire a bright or a dead surface. In the first case, we submit the object, with the aid of heat, to the ormolu process already described. In the second, the object is firmly fixed to an iron rod, with wire of the same metal (Fig. 106), and smeared with a hot paste for dead gilding, composed of nitrate of potassium (saltpetre), chloride of sodium (common salt), and the double sulphate of aluminium and potassium (potash alum). The whole is heated over a brisk charcoal fire, without draft, and moved about until the mixture becomes dry and begins to fuse, when the article is immediately plunged into a barrel, or cask, half filled with water, in the side of which a square opening has been made by two saw-cuts.

Fig. 106.



The covering of salts is immediately dissolved, and the dead lustre appears in all its beauty. This operation,

without being very difficult, requires a certain amount of practice, and is usually intrusted to a skilful workman.

The gilding must be strong to stand the dead lustre process, especially when (as is often the case) the first trial is not successful.

An object may possess the right kind of dead lustre, and still be covered with red lines left by the iron wire. These disappear by plunging the object into a not-too-diluted solution of nitric acid. Pure hydrochloric acid is preferable.

Fine gilders do not employ pure gold; that which they use is previously alloyed with a certain proportion of copper or silver. With the latter metal the gilding is green. Red gilding is either obtained with a dark ormolu or with the *green-for-red*, previously mentioned. (See the chapter on CHEMICAL PRODUCTS.)

*Gilding with a partly Dead, partly Bright Lustre.*

During the past twenty years, mixtures of bright gilding by the wet way, and dead gilding by fire, upon the same article, have been much in vogue.

In order to arrive at these results, operate as follows:—

Gild with the amalgam those parts which are intended to have a dead lustre, and heat, scratch-brush, and reheat to the orange-yellow color as directed. Then, with the current, give a sufficiently strong gold deposit to the whole, without regard to the parts already fire-gilded, scratch-brush all the surfaces carefully, and smear the electro-gilded portions, first with a thin mixture of water, glue, and Spanish-white, and afterwards with a thick paste of yellow clay. After drying, cover the fire-gilded portions with the paste for dead gilding, and proceed as has previously been explained. The Spanish-white, etc., are dissolved in a dilute solution of hydrochloric acid. The



size is intended to preserve from the heat the electro-gilded portions, which are again wire-brushed with all the care necessary for not scratching the dead lustre. The operation is finished by burnishing.

This method, which is generally followed, is open to several objections, among which is the production of red spots on those places which have been heated too much, or where the coating of gold was not thick enough. It is easier and safer to proceed as follows:—

Gild with the amalgam, and in the manner above described, dead-lustre those portions which are to receive it, and preserve them entirely with “stopping-off” varnish. After thorough drying, cleanse the object by dipping in acids, in the usual manner, and gild in the electro-bath. The varnish will not be affected by these acids and solutions. When the desired shade is obtained, remove the varnish with benzole, which, without friction and without injury to either the shade or the velvety appearance of the dead lustre, rapidly dissolves it. Wash in a hot solution of cyanide of potassium, then in boiling water, and allow to dry in the air.

The varnish coating may also be removed by allowing the object to remain for a variable length of time in concentrated sulphuric acid of 66° Baumé, which has no action whatever upon the gilding. In this case, the washing with cyanide is unnecessary, and pure water is sufficient.

Gilding with a dead lustre, whatever be the process employed, is adapted only to those objects which will never be subjected to friction. Even contact with the fingers injures it.

A new freshness is imparted to old dead gildings by a washing in caustic lye, and then in a dilute solution of nitric, or sulphuric acid. This process is sufficient to re-

move the greasy spots, dust, and smoke, but, evidently, will not remedy scratches. In the latter case, the objects must be scratch-brushed, and then heated with the dead-lustre composition.

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## CHAPTER XXVI.

### DEAD-GILDING ZINC.

THERE is, at the present time, no artistic bronze, whatever be its finish, and its elegance of shape, which may not be reproduced in zinc (dignified with the name of *Bronze composition*) with an accuracy which often deceives the most practised eye. Most of our stores are filled with clocks, chandeliers, cups, and other *articles de luxe*, made of zinc only. Many such articles are simply bronzed to imitate similar objects of real copper, brass, or bronze; but others rival in their gilding the finest fire-gilt products, with dead lustre, scratch-brushed, or burnished.

Gilded zinc, especially with dead lustre, is, at the present day, manufactured in France on such a large scale, that it will be serviceable to devote an entire chapter to the manner of executing it.

The first operation consists in stopping with tin solder all the holes and the small fissures which may exist in the object of zinc, and, at the same time removing, with appropriate tools, the seams, burrs, rough spots, etc.

Afterwards, the piece is cleansed by passing it, for a few seconds only, through a boiling solution of 100 parts of water and 5 or 6 parts of caustic potassa or soda. Too long a sojourn in this caustic lye will destroy the



polish of the zinc, as the metal begins to dissolve. After this cleansing, the object is rinsed in fresh water. It is then steeped for half a minute in a pickle composed of 10 parts of sulphuric acid, and 100 parts of water, and lastly rinsed in cold, or preferably, boiling water.

Thus prepared, the object is immersed either in a cold or warm, electro-bath for coppering or brassing, for a few moments, or until it has been covered with a thin metallic film, which is deposited very uniformly if the object has on it no tin solder, and has been perfectly cleansed.

On the contrary, the deposit is black and dull on those parts which have been soldered, or imperfectly cleansed. In the latter case, the article is thoroughly scratch-brushed, and dipped again into the electro-bath for a half hour or an hour, until the deposit is sufficiently thick. Most gilders use a warm bath for the preliminary coating, scratch-brush, and complete the deposit in a cold bath.

If a bright gilding be desired, the article may be rinsed in fresh water, and then conveyed to an electro-gilding bath.

On the other hand, if we desire a dead-lustre gilding, equal in appearance to the best fire-gilding, we proceed by either of the following methods:—

*First Method.—With Silver.*

An electro-silvering bath is prepared by dissolving in 1000 parts of water 15 parts of fused nitrate of silver, and adding 25 parts of pure cyanide of potassium, which, at first, produces an abundant precipitate, which soon dissolves. The filtered liquid is the silver bath, into which the zinc article, previously coated with copper or brass, is immersed. Under the influence of a properly adjusted electric current, the silver deposited is of a very



handsome frosted (dead-lustre) appearance, and perfectly white. The object is then rapidly and thoroughly rinsed, and immersed in an electro-gilding bath, of which we shall give the formula.

The dead-gilding obtained by this process is very fine and satiny, but is soon altered and darkened by the sulphuretted-hydrogen in the atmosphere (and from which coal gas is not entirely free), which sulphurizes the silver through the thin film of gold.

This process is seldom employed at the present day, and the following one is preferred, and rightly so, since it is more durable and more economical:—

*Second Method.—By Galvanoplastic Processes.*

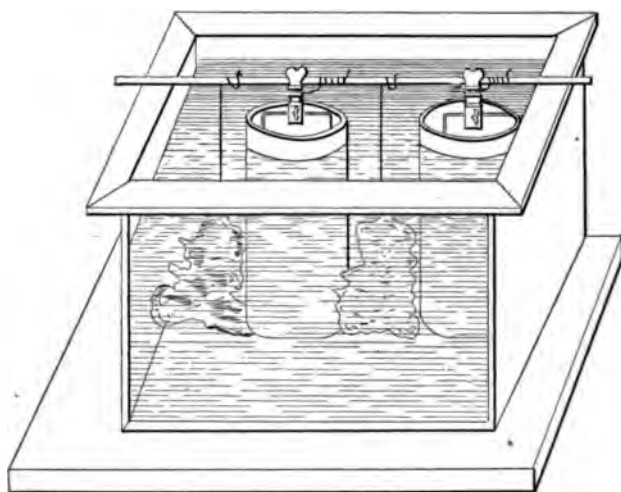
Add to a suitable quantity of water, one-tenth of its volume of sulphuric acid, and dissolve in this acid liquid, as much sulphate of copper (blue-vitriol) as it will take up at the ordinary temperature. This solution will then mark from 20° to 24° Baumé, and should be diluted with enough water to reduce its density to 16° or 18°.

This electro-bath is generally contained in large vessels of stoneware, slate, wood, or gutta-percha; and porous cells are immersed in it, which are filled with a weak solution of sulphuric acid and of amalgamating salts. Plates, or cylinders, of zinc are placed in these cells, and are connected with one, or several brass rods, which rest upon the sides of the trough, and support the articles which are to be treated. (Fig. 107.) The articles of zinc, previously coated with copper or brass, are then suspended to the rods, and remain in the solution of sulphate of copper until they have acquired a satisfactory dead lustre.

It is prudent, a few seconds after the articles have been immersed in the bath, to take them out, and examine

them carefully. Indeed, should the previous coating of copper or brass be insufficient to resist the corroding action of the acid solution of sulphate of copper, there is produced a muddy and dark deposit,

Fig. 107.



which is easily removed with the finger. And should this occur, the objects must be scratch-brushed and placed again in the former alkaline coppering or brassing baths, in order to increase the deposit which should protect the zinc in the galvanoplastic bath.

The beginner, before undertaking this operation, will do well to consult, and become conversant with, the second part of this work which treats of the *galvanoplastic art proper*.

When the galvanoplastic dead-lustre has been successfully obtained, the deposit is perfectly regular, and of a pink shade. When, on the contrary, it is irregular, marbled, crystalline, of a vinous color, and dull or earthy in appearance, these defects are due to the following causes: either the bath is in a bad state of conductivity, or of

saturation; or the surface of the zinc is too considerable in proportion to that of the objects; or, lastly, the previous electro-deposits of copper or brass were insufficient or inferior in quality. The remedy for either of these inconveniences is easily applied, and simply requires a little care and attention.

The galvanoplastic dead-lustre being once obtained in a satisfactory manner, two preliminary operations are needed to insure the success of the gilding.

They consist in rapidly passing the object (with dead lustre), after rinsing, through a solution composed of:—

Water . . . . .	1000 parts.
Nitrate of mercury . . . . .	1 part.
Sulphuric acid . . . . .	2 parts.

Then, after rinsing, plunging it into another solution composed of:—

Water . . . . .	1000 parts.
Cyanide of potassium . . . . .	40 “
Nitrate of silver . . . . .	10 “

After coming out of this bath, the object has acquired a whitish tinge, and is again rinsed in fresh water, before being placed in the following gilding bath:—

Phosphate of sodium . . . . .	60 parts.
Bisulphite of sodium . . . . .	10 “
Cyanide of potassium (pure) . . . . .	1 to 1 $\frac{1}{4}$ “
Chloride of gold, neutral . . . . .	2 “
Distilled water . . . . .	1000 “

The mode of preparation of this bath is given at the beginning of Chapter XXI.

This bath should be nearly boiling, and worked with a strong galvanic current. The anode is a platinum wire, which, being more or less immersed in the liquid, allows of the regulation of the current according to the volume, weight, and surface of the object to be gilded.



This kind of gilding requires at the outset an energetic electric action, obtained by dipping the platinum wire deeply in the liquid, in order that the entire surface of the piece shall be covered instantaneously; then, as the thickness of the deposit increases, the anode should be progressively withdrawn from the bath until it dips very little. The gilding obtained by this method has a remarkable freshness of tone.

A few gilders, before introducing the articles into the electro-bath, pass them through a bath for gilding by dipping, which they call a *preparing bath*, and which is the same as that described on page 166, Chapter XIII.

Others gild in two operations; that is to say, after having deposited about half of the gold which it is intended that the object shall receive, it is removed from the bath, washed, passed again through quicking solution, and replaced in the gold bath for finishing the gilding.

After gilding, the articles are rinsed in clear boiling water for a few seconds, and dried in the stove, or in warm sawdust of fir wood. All friction should be carefully avoided, otherwise the dead lustre will be injured. These washings are necessary, because, if saline matters are not completely removed, they will react upon the zinc and the copper, and the gilding will be covered with verdigris.

When certain parts of this gilding are burnished, their color is green, if the frosted surface has been obtained in the silvering bath; or red, if the electro-coppering bath has been employed. These inconveniences are remedied by dipping the burnished article again, for a short time, into the gilding bath. It is evident that this last deposit of gold must be so thin that it will not sensibly impair the brightness of the burnished parts.

Dead-lustre electro-gilding upon zinc, like that obtained by the old processes, is adapted for those objects only

which have no friction to bear, and which are not often handled. This kind of gilding is especially applied to clocks and similar articles, which remain under glass.

The dead lustre obtained by a thick deposit of gold is always dull, earthy, and of an unattractive appearance.

The process of dead-lustre gilding, described in this chapter, may be applied to all metals and alloys, provided that those attacked by the solution of sulphate of copper be previously coated with copper or brass in the alkaline bath. Indeed, these previous coatings of copper or brass are always desirable, because they prevent crystalline and irregular deposits often formed upon metals which are not corroded by the bath of sulphate of copper. As the result of his experience, Roseleur affirms that the galvanoplastic dead-gilding upon cast or laminated copper, is much finer when the pieces have been previously covered with copper or brass in the alkaline baths.

We sum up, as follows, the operations necessary for dead-gilding zinc :—

1. Mending the pieces, that is, closing up all holes and fissures with the soldering iron, etc. ;
2. Cleansing in a solution of caustic soda or potassa ;
3. Rinsing in water acidulated with sulphuric acid ;
4. Effecting an electro-deposit of copper or brass, for a few minutes in hot alkaline baths ;
5. Scratch-brushing ;
6. Finishing the electro-deposit of copper or brass in the alkaline bath, hot or cold ;
7. Washing and imparting a dead lustre either in the silver bath, or in that of sulphate of copper ;
8. Rinsing, and passing through the quickening solution ;
9. Washing, and steeping in a silvering bath by dipping (many gilders omit this operation) ;

10. Rinsing, and gilding in the nearly boiling gold bath, in one or two operations ;
11. Washing in pure boiling water ;
12. Drying in sawdust, or in an oven, or in both ;
13. Burnishing certain parts, then slightly regilding, washing, and drying.

Faded gildings may be restored by dipping them, for a greater or less length of time, in a weak and tepid solution of cyanide of potassium, and afterwards in very dilute nitric or sulphuric acid. We may add that imperfect gildings may be removed by inverting the poles in a solution of cyanide ; that is, by connecting the gilded articles with the positive pole (carbon or copper), and making the anode serve as the negative pole (zinc). In this reversed order it is the anode which becomes gilded. This process is especially employed for removing the gold from articles of iron, steel, and even silver, which cannot be submitted to the *ungilding (stripping) bath* which we are about to describe. Silver, copper, and brass may also be removed by similar processes.

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## CHAPTER XXVII.

### USEFUL NOTES AND MEMORANDA CONCERNING ELECTRO-GILDING.

HINTS ON PREPARATION OF ARTICLES FOR GILDING—COLOR OF ELECTRO-DEPOSITED GOLD—RECOLORING ELECTRO-GILDED WORK—“GILDER’S WAX”—FREE CYANIDE—MANAGEMENT OF GILDING SOLUTIONS—REMOVING GOLD FROM GILDED ARTICLES (STRIPPING).

*Preparing Articles for Gilding.*—Watt (*Electro-Metallurgy*, 63 *et seq.*) prepares silver goods, such as cream-ewers,



sugar-bowls, mugs, etc., by scouring well with hot soap-water and silver-sand; if they are at all greasy, he applies a little caustic soda to them first. Small articles, such as silver brooches, pins, rings, thimbles, egg, salt and mustard spoons, etc., merely require to be scratch-brushed before gilding. When they have received the required deposit, they should be removed, and again brushed, when, if the color be too pale or too deep, he immerses them again *for an instant* in the gilding bath, and then plunges them into boiling water, when they will exhibit a fine gold color.

Silver filagree brooches, etc., he directs to be well scratch-brushed, dipped for a moment in the gilding bath, then removed, rinsed, and scratch-brushed again. When immersed the second time in the bath, the gilding is affirmed to be more uniform than it would otherwise be. For copper and its alloys, and for iron, steel, etc., his methods of preparation are substantially the same as those of Roseleur. Gore, Urquhart, Napier, and other authorities use substantially the same cleansing processes as recommended in this work.

Watt refers at length (*Electro-Metallurgy*, 66) to the difficulty of obtaining uniform gilding upon goods which have mountings pewter-soldered upon them—as is often the case with common jewelry—on account of the tardiness with which the solder accepts the gilding, and which may often require the operator to deposit much more gold than is necessary, or desired, on the other parts of the object before the obstinate soldered spots become covered.

Watt's remedy for this difficulty, which we have elsewhere briefly alluded to, consists in wetting the soldered spot with an acid solution of sulphate of copper (or concentrated silver solution) and touching it with a piece of steel, when the part in question at once receives a film of

copper (or silver) which may be strengthened by several repetitions of the operation. When the article is again immersed in the bath, the soldered part thus coppered takes the gilding by preference. This hint may be found useful to the operator.

It should, however, be borne in mind, that the above-named difficulty is due sometimes to a too feeble current, or to the want of cyanide in the bath.

In the gilding of cheap jewelry, French and Birmingham fancy goods, and articles that only require to be given a colored surface, Watt (*Electro-Metallurgy*, 67) proposes to gild with a copper anode, and as the gold becomes exhausted to add more from time to time, thus working from the solution, instead of from the copper anode. By this means, the operator is insured against depositing more gold than it would pay to put on this cheap class of work. It is impossible, however, by this procedure, to avoid contaminating the bath with copper, and we consider the plan of using a platinum anode, as recommended by Roseleur, as decidedly preferable, since it accomplishes the same object without affecting the quality of the bath.

*The color of electro-deposited gold*, as has been pointed out (leaving out of consideration the colorations produced by additions of copper or silver salts to the bath, and those produced artificially by subsequent treatment of the articles after their removal from the gilding solution) will vary according to the condition of the bath (*i. e.*, according as it is more or less exhausted of gold, or has a deficiency or an excess of cyanide), according to the strength of the current, and the surface of the anode exposed in the bath. In addition to the above causes, it may be useful to note the fact that the temperature at which the solution is worked likewise influences the depth of color of the gilding, the color being lightest when the



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 bath is worked cold, and becoming gradually darker the temperature of the bath is raised. It is generally admitted by electro-gilders, that the best results as to richness of color, with a given bath, are obtained when it is worked at, or slightly above, 130° Fah. Moving the articles in the bath likewise influences the coloring of the deposit, while, by preventing an uneven or streaked deposit, it adds materially to the beauty and uniformity of the gilding.

*Recoloring Gilded Work.*—For restoring the color of badly gilt work, especially of watch-chains, ear-rings, and other jewelry of small bulk, Urquhart (*Electro-Plating*, 188 *et seq.*) objects to any methods which involve the violent heating of the articles. He prefers the following procedure, which he recommends “for bad coloring, when it is too pale . . . and for ordinary gold chains—not gilded work—although it may be used for both.” His compositions are:—

For red gold: A mixture of equal parts of copper sulphate, sal-ammoniac, borax, and common alum, powdered together and moistened with water.

For yellow gold: An intimate mixture of powdered saltpetre, 6 parts; copperas, 2 parts; white vitriol, 1 part; alum, 1 part.

For green gold: A well-mixed composition of saltpetre, 5 parts; sal-ammoniac, 5 parts; Roman aloes, 6 parts; and verdigris, 5 parts.

The articles before being treated in the above compositions are to be dipped first in dilute nitric acid, then in strong nitric acid for an instant only, then in water. The mixture to be used is placed in a plumbago crucible, a little water added, and the composition made to boil by a gentle heat. The work, suspended from a horsehair, is then dipped into the mixture immediately after cleaning, as above described, and left in it for several minutes. It is



then taken out, and rinsed in a pan of boiling water. At this stage of the operation the work should look black, or nearly so. It is dipped again into the mixture until it has acquired the desired color. It is then finished by rubbing in the hands with whiting—if a chain—or by scratch-brushing.

Urquhart (see *ante*) and Gore (*Electro-Metallurgy*, 139) describe a composition employed to remedy a defective color in gilding, prepared by making into a wet paste, with a little water, a mixture in powder, of two parts of nitrate of potassium (saltpetre), one of sulphate of zinc, one of alum, and one of common salt. A layer of this paste is smeared over the article, which is then heated to blackness on an iron plate, over a clear fire, then plunged into water. By varying the mixture different tints of color are obtained. It need scarcely be said, that this treatment is only applicable to a good gold deposit.

A "gilder's wax," for improving the color of poorly gilded articles after Watt's formula (*Electro-Metallurgy*, 209), is made by adding red ochre, alum, and verdigris to beeswax in a melted state. By heating the article and passing the wax over it, a sufficient quantity will attach itself for the purpose. The subsequent treatment is the same as that described in our reference to waxing (Chapter XVII., page 184).

Mathey (Winckler, *Handb. d. Metallüberzügen*, 167) proposes the following composition for a "gilder's wax," viz:—

Yellow wax	.	.	.	.	.	120 parts.
Acetate of copper	.	.	.	.	.	30 "
Sulphate of copper	.	.	.	.	.	30 "
Alum	.	.	.	.	.	30 "
Armenian bole	.	.	.	.	.	30 "

These ingredients are fused together and cast into

sticks. The article to be treated is first heated, then coated with a layer of the wax, then again heated until the latter begins to burn, when it is plunged in oil of turpentine which dissolves off the wax and the article is finally scratch-brushed. This composition gives a light red color. To obtain a green, the above receipt should be modified by substituting in place of the acetate and sulphate of copper, the sulphate of zinc or the nitrate of silver.

*Necessity of Free Cyanide ; Management of Gilding Baths.*—Concerning the necessity of having a certain quantity of free cyanide of potassium in the double cyanide baths for gilding, silvering, etc., that is, a quantity in excess of that required to dissolve the metallic salt, a few words by way of explanation may not come amiss.

The addition of free cyanide is designed not merely for the purpose of improving the conducting quality of the bath, as some operators suppose, but for an important reason intimately related to the chemical action taking place in the bath under the action of the current. While gold or silver is being deposited at the cathode, the cyanogen liberated at the anode attacks the latter, and forms cyanide of gold (or silver). This salt, however, is insoluble, and until the cyanide of potassium freed with the gold at the cathode could find its way across to the anode, the latter would be covered with an accumulation of cyanide of gold, which it would be difficult to dissolve off, and the function of the anode to keep up the supply of gold or silver in the bath, would be seriously impaired, or completely suppressed. If some *free* cyanide be present in the bath, however, it will dissolve away the cyanide of gold or silver as rapidly as it forms, thus keeping the metallic surface of the anode bright, and maintaining the metallic strength of the bath.

As we have previously pointed out, however, the quan-

tity of "free cyanide" present should not exceed certain limits; if these be overstepped, unfavorable effects at once appear. No fixed rule can be laid down to define the best proportions that should exist between the several ingredients of the bath, since the chemical action of the bath is influenced by so many conditions: *i. e.*, the strength of the current, the proportion of gold in solution, etc. etc. In a general way, it may be said, however, that a good proportion of "free cyanide" is from one-fourth to one-half the quantity that was required to dissolve the salt of gold.

If the quantity of free cyanide is not properly adjusted to the requirements of the bath, the fact will be speedily brought to the notice of the operator by the appearance of his work, or by the bad working of his bath. Too little free cyanide will be indicated by the deposit of gold being weak and pale, or the anodes will become encrusted, or both; too much cyanide, on the other hand, is likely to cause what is known as "foxy" gilding, and the bath works slowly, as the excessive cyanide may dissolve the gold away almost as fast as it is deposited. ✓

The remedy in each of these cases is obvious.

Too little cyanide is corrected by adding more; and too much either by working the solution with a very large anode, which will soon supply enough gold to neutralize the excess, or by an addition of some salt of gold, until the proper working condition of the bath is restored.

Watt (*Electro-Metallurgy*, 166 *et seq.*) very forcibly calls attention to the importance of avoiding an excess of cyanide, in the following terms, viz: "Cyanide should seldom be added to a bath, whether of gold or silver, when the anode, being at work, is clean and uniform in appearance. It is always objectionable to have too great an excess of this salt in the bath; therefore, it should



never be added until the batteries and their connections have been well examined. Sometimes, when the battery is somewhat exhausted, the anodes become slightly discolored, especially if a larger surface of goods is exposed than is proportionate to the size of the anode; in such case it will be necessary to increase the activity of the battery rather than to add cyanide to the bath. Cyanide is a good friend but a bad foe. All that a good bath requires is a slight excess of cyanide, if the battery is in good order, and but little organic matter has accumulated in the bath."

Another cause of the variable behavior of the cyanide gilding baths may be ascribed to the fact, previously pointed out, that the quantity of gold deposited on the article is not exactly equivalent to the amount dissolved at the anode, being sometimes greater and sometimes less.

As the result of a series of experiments on this subject Napier (*Electro-Metallurgy*, 169) affirms that in five instances only was the deposit exactly equal to the quantity dissolved from the positive plate. In many instances the difference did not exceed 3 per cent., though occasionally it arose to 50 per cent. The average difference was 25 per cent. In some cases double the quantity dissolved was deposited, in others the reverse occurred, both resulting from alterations made in the state of the solution, and the relative sizes of the negative and positive electrodes.

From this cause, therefore, the proportions of a gilding bath in frequent use will necessarily suffer some disturbance. When the solution is depositing a greater quantity of gold upon the cathode than is dissolved in the same time from the anode, the bath soon becomes charged with an excess of free cyanide. This condition of things

appears to take place in baths very rich in gold, and may be corrected by a judicious dilution of the solution.

On the other hand, when the solution is depositing less gold than is dissolved in the same time from the anode, less cyanide is liberated at the cathode. In this case a deficiency of gold in the bath may be suspected and remedied by a judicious addition of gold salt, or by the artifice of using for a time a very large gold anode and a comparatively small receiving surface. Where this unfavorable condition of the bath (*i. e.*, a deficiency of gold) is pronounced, it is apt to manifest itself also by the anode becoming blackened and slimy, and evolving gas. This condition of things generally manifests itself when the bath is nearly exhausted of gold, as where a gold anode has been used which is very small in comparison with the surface of the article at the cathode. This slimy appearance of the anode should not be confounded with the yellowish, or greenish, or even dark-colored, incrustation on the anode, above referred to, as an indication of a deficiency of free cyanide in the bath, since in this case the addition of cyanide would be worse than useless. It should be remembered, therefore, that the surface of anode exposed should be regulated by that of the articles in the bath.

The experienced operator, familiar with the varying behavior of his cyanide gilding solutions, is enabled to correctly interpret the signs which they indicate, and to so manage them as to keep them in good working condition for years.

#### REMOVING GOLD FROM GILDED ARTICLES—"STRIPPING."

Artists and manufacturers are often required to remove the gold from gilded objects, either for repeating anew an imperfect gilding, or for extracting the gold from worn-out



articles to be consigned to the melting pot. The method varies considerably, according to the metal upon which gold has been deposited.

Iron and steel are "stripped" without any injury to themselves, by dipping them into a bath of 10 parts of cyanide of potassium and 100 parts of water, and connecting them with the positive pole of a battery. A wire or foil of platinum is attached to the negative pole. This is simply inverting the ordinary position of the poles; and the gold upon the iron or steel is partly dissolved in the solution of cyanide, and partly deposited upon the platinum anode, from which it is removed in a regular gilding bath. When there is only a mere film of gold upon iron or steel, it may be removed by the cyanide alone, without the aid of electricity, but this method is slow.

Silver, copper, and their alloys may also be stripped of gold by this process; but, as the cyanide at the same time dissolves not only the gold but also the other metals, it is preferable to operate as follows:—

For ungilding silver, it is heated to cherry-redness, and immediately thrown into a pickle of more or less diluted sulphuric acid. The gold scales off, and falls to the bottom. The operation is repeated until gold no longer appears upon the surface of the silver, which is then white and frosty.

This process is imperfect, and is not adapted to light and hollow articles, for which the first described process is preferable.

For copper and its alloys, such as bronze, German-silver, brass, etc., two different methods may be followed, according to the nature and volume of the objects.

Small trinkets, thinly gilded, either by current or by immersion, are dipped into the following bath:—



Sulphuric acid (oil of vitriol) . . . .	10 volumes.
Nitric acid (aqua fortis) . . . .	1 volume.
Hydrochloric acid (muriatic acid) . . . .	2 volumes.

The above mixture is simply aqua regia in a large quantity of sulphuric acid, which excess of sulphuric acid allows of the solution of gold, without sensibly attacking copper or its alloys.

Ordinarily, the sulphuric acid is placed by itself in a stoneware jar, and the mixture of hydrochloric and nitric acids (aqua regia), kept in a stoppered bottle, is gradually added to it as the operation of "stripping" proceeds. The same sulphuric acid may last a long time, provided it is kept well covered, and the action of the acid mixture is promoted by additions, from time to time, of nitric and hydrochloric acids.

The articles should be withdrawn often, in order to watch the operation, which is terminated when no traces of gold are seen, and when the copper has acquired a uniform blackish-gray coating.

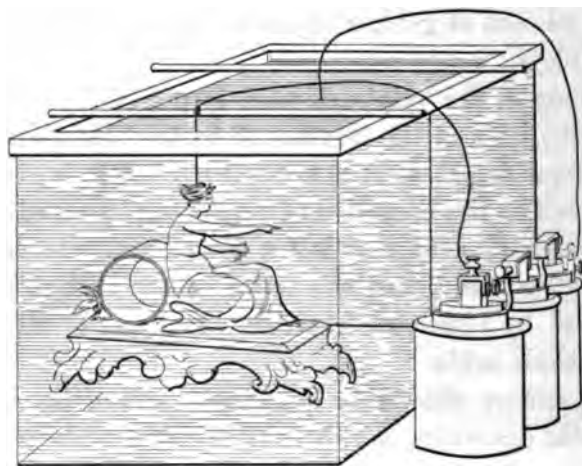
We may also ascertain that all the gold has been dissolved, by plunging the objects into the mixed acids for cleansing (see *ante*), in which they are perfectly cleansed when the gold has disappeared.

Nitrate of potassium (saltpetre) and chloride of sodium (common salt) may be substituted for the nitric acid and hydrochloric acid respectively. The result is identical; but in this case the salts must be introduced into the acid in a finely powdered state, and stirred with a glass rod, in order that they shall dissolve, and form aqua regia by their decomposition.

A few operators ungild small trinkets by a more or less protracted immersion in the acid mixtures for bright or dead dipping; but they spoil their acids and lose the gold.

For large objects, such as clocks, mantel ornaments, chandeliers, etc. (and also for smaller articles), a good mode of procedure is the following (Fig. 108):—

Fig. 108.



A glass or stoneware vessel, supporting two brass rods, is filled with concentrated sulphuric acid (66° Baumé). One of these rods is connected by a conducting wire with the last carbon of a battery of two or three Bunsen elements, in inverted order, and supports, by means of hooks, the objects to be ungilded, and which are entirely covered by the sulphuric acid. The other rod supports also by means of a hook, a copper plate facing the object, and is connected with the last zinc of the battery. The current traverses the sulphuric acid, and carries the gold from the positive to the negative pole; and, as the copper plate is not prepared for retaining the gold, it falls to the bottom of the bath in the state of a black powder, which is afterwards easily recovered.

As long as the sulphuric acid is concentrated (even under the action of the galvanic current), it does not sen-

ably dissolve the copper. But this is not the case when it becomes diluted with water; and as it rapidly absorbs atmospheric moisture, the vessel in which it is contained should be kept hermetically closed when the "stripping" process is not in active operation. The pieces to be "stripped" should be dry when introduced into the acid.

For removing gold from old or imperfectly gilded articles, Napier, and also Watt, directs the articles to be placed in (pure) strong nitric acid, to which some common salt in crystals is then added. By this method, it is affirmed, gold may be removed from any metal, even from iron, without injuring it in the least. This method is no doubt an effective one, but will require close watchfulness on the operator's part to prevent the solution of the underlying metal. We give the several related methods of Roseleur, in which sulphuric acid is used, the preference.

When we intend to sacrifice the gilded articles of copper or silver, it is sufficient to let them remain in pure nitric acid, which dissolves all the metals except the gold, which either floats on the surface of the acid as a metallic film, or falls to the bottom as a blackish powder. If then the liquid be diluted with distilled water and filtered, all the gold will remain on the filter, and the solution will contain the other metals.

We shall give, at the close of this work, the simplest and most practical processes for recovering, for future use, the gold saved by these different methods of "stripping."



## CHAPTER XXVIII.

## SILVERING.

BEFORE the discovery of the hydroplastic methods, there were in the arts two processes for silvering metals, and these two processes formed two separate industries. Artistic and useful objects of all kinds were manufactured from *plated silver*, i. e., copper plates coated with silver. On the other hand, articles entirely finished, as regards dimensions and shape, were *plated with silver foil*. There was, it is true, a method of silvering by the wet way; but the products were, and still are, so deficient in durability, that the process was known under the modest title of *Whitening with Silver*. We shall, nevertheless, examine this operation, which is still employed for whitening certain small wares, for which durability is of secondary importance, and which simply borrow the lustre and whiteness of silver; such are hooks and eyes, buttons, buckles for suspenders, articles for umbrella-makers, etc., which, sooner or later, return to the primitive color of their material—copper or brass.

## CHAPTER XXIX.

## PLATED SILVER.

PLATED silver is obtained by placing together a plate of copper of the first quality, and one of silver, after introducing some powdered borax between them, then bringing them to a welding heat, and rolling out. The two metals are reduced and drawn out about equally by the pressure of the rolls, and long sheets or bands of silvered metal are thus obtained, from which a great variety of articles may be manufactured.

The inconveniences of this mode of operation are manifold; and we shall point out four principal ones: In the first place, a great quantity of material is lost, since we must cut out the objects from a sheet entirely silvered, and the waste retains a large proportion of the precious metal; in the second place, the cut sections are denuded of silver, and these must be hidden either by silvering by some other method, or by some other artifice.

The third inconvenience is the absolute necessity of employing pure copper, which is more costly, less sonorous, and not so tough as the alloys of this metal.

The fourth defect, which is a capital one, arises from the fact that the coating varies in thickness according to the shape of the object manufactured from the plate. It is evident that, in the stamped, beaten-out, or embossed parts, the bottom of a vase for instance, the silver has increased in surface, and therefore that its thickness is less than that of the flat surfaces. Moreover, these raised

surfaces are the more exposed to friction, and it is just there that the coating of silver is the thinnest. We shall see further on that the conditions are reversed with electro-silvering, and that the parts in relief receive a more abundant deposit of silver, which is a great desideratum.

The best plated silver has one-tenth of silver, and is manufactured by uniting to an ingot of pure copper weighing 9 pounds, another ingot of pure silver weighing 1 pound. The two are rolled together until the desired thickness is obtained. It is even possible to produce a bad plated silver, with one-tenth of the precious metal; for, should we roll the two metals until the foil of silvered copper becomes, say  $\frac{1}{100}$  of an inch thick, the thickness of the silver will be only  $\frac{1}{1000}$  of an inch. Articles manufactured with such foil will possess only the strength imparted to them by the lead, mastic, or cement with which they are filled.

The silver of the plated metal will appear bright if the rolls are well polished, and dull if the rolls are unpolished.

If the rolls are engraved on their circumferences, it is obvious that the design will be reproduced in relief on the rolled plate.

A sheet of copper, rolled between two sheets of silver, will, of course, be plated on both sides.

To unite the several parts that compose an object of plated silver, the only practicable solder, which does not injure the silvering, is tin solder; and when the manufactured objects are required to resist a certain temperature, chafing dishes for example, screws or rivets are employed to unite the parts.

When the silver of the plated article became worn off in certain places, there was no satisfactory method of remedying it until the invention of the hydroplastic processes.



## CHAPTER XXX.

## LEAF-SILVERING.

THIS method, as distinguished from the use of plated silver, is only practised upon objects already manufactured, and with their finished shape; furthermore, it is adapted to all kinds of copper, bronze, German-silver, or brass. It is therefore, in certain respects, superior to plated silver; but it is very difficult of execution, and the silver is less adherent to the metal beneath.

The operation is conducted as follows:—

After annealing the articles, they are thrown, still hot, into a bath of sulphuric acid, containing a small proportion of hydrochloric and nitric acids. They present then a dull and dead surface, owing to a multitude of small depressions, which serve as so many points of attachment for the silver-leaf which is subsequently applied.

The objects, thus prepared, are firmly attached to an iron rod, which is held in a vise. Their temperature is raised to about 300° Fah., by pieces of incandescent charcoal laid on the part operated upon, and removed so as to open the pores of the metal, which, on subsequently cooling and contracting, so to speak, imprisons the molecules of the silver applied. The silver-leaves are taken from the book with small tweezers, and are cut to the proper dimensions upon a cushion, with an ivory or steel knife. After each fragment is deposited upon the object, it is made to adhere by gentle pressure with a soft pad, and the operation is finished by friction with a burnisher

of polished steel. The parts of silver foil which do not adhere are removed with a soft brush. It is possible in this manner to superpose a large number of leaves upon each other on the same object, but their adherence will be in an inverse ratio to their number.

Gold-beaters prepare silver leaf either bright, or dead. The latter is made to adhere only by the pressure of the pad, and not by the burnisher. This dead lustre does not, however, equal in fineness that obtained by the battery; it is true, however, that it resists handling, and the action of deleterious gases in the atmosphere, better than the latter.

Articles thus silvered are burnished only after the article is completely covered; round or cylindrical objects are burnished upon the lathe, and other forms by hand.

A practised eye will readily ascertain whether an object has been silvered with leaf, as the burnisher nearly always leaves upon the surface a series of zones or striæ.

This method of leaf-silvering, at the present time, is employed only for very large objects; or for ecclesiastical ornaments, such as high chandeliers, crosses, holy-water basins, etc.

Roseleur states that at one time the use of leaf silver for silvering spoons and forks was tried in France, but that the attempt was soon abandoned. The method of operation, he describes as follows: The articles were first covered with a film of matt silver by immersion, heated, and then covered with leaf silver. The adherence of the latter was obtained by the pressure of an iron scratch-brush striking vertically, and forcing the silver leaf, as it were, into the pores of the subjacent metal. Burnishing by the usual method finished the operation. It was therefore impossible by this method to obtain a dead surface.

## CHAPTER XXXI.

## SILVERING BY SIMPLE IMMERSION.

*Whitening.*

As previously remarked, it is not possible, by this process, to coat copper articles with more than a mere blush of silver.

The process is as follows:—

A certain quantity of pure granulated silver is dissolved in double its weight of pure nitric acid. The solution is largely diluted with water, and the metal separated as a heavy, white, curdy precipitate of the chloride, by the addition of common salt, or hydrochloric acid. The nitrate of silver has been entirely decomposed when the further addition of a drop of hydrochloric acid, or of a solution of common salt, to the clear, supernatant liquid, does not produce any turbidity. The clear liquid is then poured off, and the chloride of silver obtained is washed several times, in order to deprive it of the least trace of acid. If this precipitate is to be kept some time before use, it should be protected from the action of sunlight, which rapidly blackens it.

The chloride of silver, with a little water, is thoroughly mixed with at least eighty times its weight of finely powdered bitartrate of potassium (cream of tartar), and kept in a covered stoneware pot.

The composition of the paste used in this process is exceedingly variable. Each operator modifies it according to his fancy, by adding to the cream of tartar some

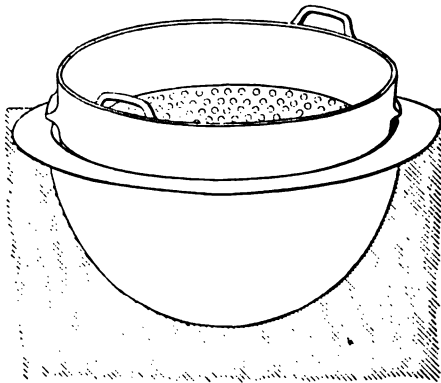


other substance, such as common salt (chloride of sodium), sulphate of sodium (Glauber's salt), bichloride of mercury (corrosive sublimate), caustic lime, calcined magnesia, etc., the greater part of which, if not hurtful, are useless. Roseleur proposes the following formula, which succeeds very well, and which is often preferred to the simple mixture of chloride of silver and bitartrate of potassium.

Pure silver	. . . . .	3 parts.
Powdered cream of tartar	. . . . .	250 "
Common salt	. . . . .	250 "

A few spoonfuls of the paste, prepared as above, are thrown into boiling water contained in a copper kettle. The paste soon dissolves either completely or in part, and forms the bath into which the articles are dipped, either with the aid of a hook, or with a basket of wire gauze, such as we have indicated in the chapter on immersion-gilding. It is customary, however, to have another

Fig. 109.



basin of copper, shallow and perforated with holes, and with lugs which rest on the flange of the outer kettle. These lugs permit the shallow basin to be placed inside of the other, as seen in Fig. 109, so that the articles to be

whitened are immersed somewhat in the bath. By means of the handles of this basin, it can be removed at once with its contents, without disturbing the bath.

The articles are stirred with a wooden spatula ; and at each operation a quantity of paste, proportioned to the surfaces to be whitened, is added.

These baths do not work well when freshly made, and they improve with use. They acquire finally a dark-green tint, due to the copper which is dissolved, and which takes the place of the deposited silver.

The articles are brightened by friction with sawdust, and scarcely ever by scratch-brushing.

The smallest particle of iron, zinc, or tin, introduced into the whitening bath, is sufficient to impart a red coloration to articles of brass or copper which may be in the bath.

Iron should be removed with the aid of the magnet ; and zinc may be eliminated by immersion in a pickle of hydrochloric or sulphuric acid, neither of which, when cold, sensibly attacks the copper articles. As for tin and lead, they must be removed by hand.

If, from some cause, the operation has not succeeded, the articles are plunged for a few seconds into a boiling solution of—

Water . . . . .	1000 parts.
Nitrate of silver . . . . .	10 “
Ordinary cyanide of potassium . . . . .	60 “

This bath, which retains its strength for a long time, considerably increases the whiteness of the deposit.

We shall shortly describe, *in extenso*, certain new processes of whitening, or immersion-silvering, which have almost completely, and with advantage, replaced the older process just examined.

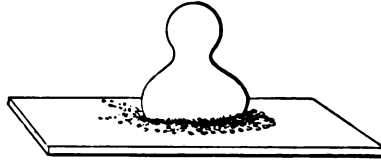
CHAPTER XXXII.

COLD SILVERING WITH PASTE.

RELATED to the above, is the old process of *cold silvering* with paste, with the thumb, cork, or brush, which holds an intermediate position between the dry and the wet methods of deposition. The results obtained, although not very durable, are better than those by the whitening process, and we are enabled to repair slight defects upon more durable silverings, and to produce mixtures of gold and silver, or gold and oxidized silver, upon *thinly* gilded objects. We thus avoid, for operations of small importance, the use of "stopping-off" varnishes.

The paste employed in this process is prepared by thoroughly grinding in a porcelain mortar, or with a

Fig. 110.



muller (Fig. 110), and, as far as practicable, sheltered from the light, the following substances:—

Water . . . . .	10 to 15 parts.
Fused nitrate of silver (or, preferably, the chloride) . . . . .	20 "
Binoxalate of potassium (salt of sorrel)	30 "
Bitartrate of potassium (cream of tartar)	30 "
Chloride of sodium (common salt) .	42 "
Chloride of ammonium (sal ammoniac)	8 "



Or, a simpler mixture of—

Chloride of silver . . . . .	10 parts.
Bitartrate of potassium . . . . .	20 “
Common salt . . . . .	30 “

When the mixture has been finely pulverized in a porcelain mortar, it is trituated with the muller upon a plate of ground glass until a particle rubbed between the fingers gives not the slightest granular feeling. The paste thus prepared is kept in a pot of opaque porcelain or in a vessel of black glass, so as to protect it from the solar rays, which decompose it rapidly.

When it is needed for use, sufficient water is added to it to form a thin paste, which is applied with a brush or pencil upon the cleansed articles of copper, or upon those gilded by dipping, or by the battery, provided that the coating be thin enough to allow the copper, through the coating of gold, to decompose the silver paste. The paste is allowed to dry naturally, or with the aid of a gentle heat.

According to the thickness of the gold deposit, the chemical reaction will be more or less decided, and the dry paste will assume a pink or green shade. The last named coloration indicates that a large quantity of the copper has been dissolved, and that consequently an equivalent quantity of silver has been reduced to the metallic state.

The piece is cleansed from the adhering salts by a prolonged rinsing in cold water, and the silver appears with quite a fine dead surface, the brightness of which may be increased by an immersion for a few seconds in a very diluted solution of sulphuric acid, or, preferably, of cyanide of potassium.

This silvering bears the action of the wire brush and of the burnisher very well; it may also be “oxidized,”

a proof of its superiority over the previously described whitening process.

Should a first silvering not be found sufficiently durable, it is possible, after scratch-brushing, to apply a second or a third coating.

The deposit, as we have said, takes also upon copper, but the silvering is not so white, and is less adherent than upon a gilded surface.

This process is advantageous for keeping in good order the reflectors of lanterns for vehicles, etc.: in which case the paste is rubbed with a fine linen pad upon the reflector, which acquires a dull and leaden appearance; then, with another rag, a thin magma of Spanish-white, or other similar substance, is spread over the reflector and allowed to dry. Lastly, a rubbing with a fine and clean linen rag will restore the brilliancy and whiteness of the plated piece.

For keeping in order silver-plated reflectors in general, and in particular those used on railways, Roseleur prefers the following method:—

Prepare a silvering bath of—

Water	. . . . .	100 parts.
Nitrate (or chloride) of silver	. . . . .	5 “
Cyanide of potassium	. . . . .	30 “

Add to this sufficient Spanish-white (levigated chalk), in fine powder, to produce a thin magma, which should be kept in a well-closed pot. This paste, by means of a brush, or a pad of old linen, is spread all over the surface of the reflector, and allowed to dry almost entirely, when it is briskly rubbed over by means of another clean and dry rag of old linen. The silvering produced is the brighter as the operation is more frequently repeated. It is evident that this process is equally suited to all silver-

plated articles, such as carriage decorations, harness mountings, etc.

The various powders or liquids sold under the names of *silvering liquid*, *conservator of plated silver*, *California liquor*, etc., and which are much used in coffee-houses for hiding for a few days the worn-off plating of their spoons and forks, are nothing else than the above paste, dissolved in a greater or less proportion of ordinary or salted water.

Other liquors sold under the names of *aurophile* and *argentophile*, for cleaning old gildings and silverings, are simply solutions of cyanide of potassium, and are applied according to the methods which have been indicated for reviving old gildings.

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## CHAPTER XXXIII.

SEQUEL TO SILVERING WITHOUT THE BATTERY: SILVERING BY  
SIMPLE IMMERSION—HOT—COLD.

### *Silvering by Immersion—Hot.*

THERE are two processes of silvering by the wet way and without the battery, which are as different in their operation as in their results. One of them is especially intended for silvering hooks-and-eyes, buttons, buckles, etc., and is practised, at the temperature of ebullition, in a bath of the double cyanide of potassium and silver.

This bath is made by dissolving in a kettle of enamelled cast iron, and in 900 parts of water, 50 parts of ordinary cyanide of potassium.

In a separate vessel of glass, or porcelain, dissolve 15 parts of fused nitrate of silver in 100 parts of water.



This second solution is gradually poured into the first, and the whole is stirred with a glass rod. The white or grayish-white precipitate produced at first is soon re-dissolved, and the resulting solution is filtered if a perfectly clear bath be desired. The bath thus prepared requires only to be raised to the boiling-point to effect the immediate silvering of the cleansed copper articles plunged in it.

The objects should be simply immersed and at once withdrawn; a more protracted immersion will result in a less satisfactory silvering.

The silvering should immediately follow the cleansing, although the rinsings after each operation should be thorough and complete.

This bath, which produces a light but brilliant silvering, is well adapted for set jewelry, which cannot be scratch-brushed without injury, and to which a bright lustre is absolutely necessary as a substitute for the foil of burnished silver placed under the precious stones of real jewelry to heighten their refractive power and fire. The employment of quicking solution is useless, and even injurious for this bath.

It has been demonstrated by experience that it is useless to attempt to keep up the strength of this solution, by new additions of cyanide and of silver salt; a bath thus reinvigorated gives results far inferior to those of the first solution. The bath should, therefore, be worked out as long as the silvering is satisfactory, and when exhausted added to the waste. Many manufacturers who follow this process use a battery and a soluble anode in order to obtain a more durable deposit; but this mode of operation is no longer a simple immersion, and is properly an electro-silvering process, which will be examined further on.

A few immersion silver-platers formerly used a solution

which, when boiling, produced a very fine dead or partly dead silver coating, upon copper cleansed according to the methods indicated at the beginning of this work.

They prepared their bath by dissolving with the aid of heat, in a well-scoured copper kettle—

Distilled, or rain water . . . . .	500 parts.
Ferrocyanide of potassium (yellow prussiate of potassa) . . . . .	60 “
Carbonate of potassium (pearl ash) . . . . .	40 “

And, when the liquid was boiling, they added the well-washed chloride obtained from 30 parts of pure silver. The bath thus prepared should be boiled for about half an hour, and filtered before using. By this method, part of the silver becomes deposited upon the copper kettle, and should be removed when a new bath is prepared. This inconvenience is probably the cause of the abandonment of this process, for Roseleur affirms that he knows of no method of silvering in vogue to-day that yields more beautiful results.

All the baths for silvering, which contain a great excess of cyanide of potassium relatively to the proportion of the silver salt, will silver well, by immersion, even in the cold, copper articles properly cleansed; whereas this property diminishes in proportion to the increase of the amount of silver in the bath.

The manufacturers of small articles, partly copper and partly iron, such as those used for harness-mountings and carriage ornaments, employ a particular process of silvering, and their bath is composed of—

Water (pure) . . . . .	500 parts.
Caustic potassa . . . . .	16 “
Bicarbonate of potassium . . . . .	10 “
Cyanide of potassium . . . . .	6 “
Nitrate of silver (fused) . . . . .	2 “

The cyanide, caustic potassa, and bicarbonate are dissolved, in an enamelled cast-iron kettle, in 400 parts of water, and then the nitrate of silver, separately dissolved in the remaining quantity of water, is added to the first.

For the silvering operation proper, a lot of articles are cleansed, thoroughly rinsed, and put into a small enamelled kettle. Enough of the silver bath is poured in, to cover the articles entirely, and the whole is brought to a boil for a few seconds, and stirred with a wooden spatula. When the silvering appears satisfactory the liquid employed is added to the spent liquors, so that the same liquid is never used for two batches of articles. This process furnishes a somewhat durable dead silvering, and of a more or less grayish-white, which is increased in whiteness and brightness by soap and burnishing. In this manner small buckles, buttons, materials for window shades, and carriage nails are silvered.

*Silvering by Simple Immersion (Cold).*

This process, although more convenient, and furnishing a better and more durable silvering than the other processes by simple immersion, is very little used. Nevertheless, Roseleur recommends it highly, on which account we reproduce it in full.

This process is the more convenient, because the bath is used cold and is therefore always ready for use, and also because it does not require weighing in preparing and maintaining it.

The deposit is the finer and more unalterable, because only chemically pure silver is deposited, without any mixture of subsalts, as is the case with the other baths, the products of which sooner or later become yellowish. It is also the more durable, because the deposit, although without the aid of electricity, may be made nearly as thick



as desired, and in the direct ratio to the duration of the immersion.\*

\* This last assertion is in direct contradiction to the general theory of deposition by simple immersion, which holds that the metal deposited is replaced in the solution by an *equivalent* of the immersed metal, which continues to dissolve as long as it is not entirely covered by the deposited metal.

To account for this apparent conflict of theory and practice, Roseleur offers the following ingenious and rational explanation of this phenomenon. We have seen that when an article of iron is plunged into a solution of sulphate of copper, part of the iron is dissolved as sulphate of iron, while an equivalent proportion of copper is separated from the solution and coats the iron. In the same manner when we plunge an object of copper into a bath of double cyanide of silver and potassium, part of the copper is dissolved and forms a double cyanide of copper and potassium, while an equivalent proportion of silver is deposited upon the remaining copper. In either case, the exchange is arrested as soon as the copper is coated with a continuous layer of silver, which prevents the solution of the underlying metal.

The same phenomenon takes place at first, during the operation of cold silvering by the double sulphite of sodium and silver, and an equivalent proportion of double sulphite of sodium and copper is formed. But, afterwards, another and a different reaction sets in, by which the silver deposit continues to increase in thickness, without any further solution of copper, and this is due to certain chemical changes of the component parts of the bath.

To understand these changes it will be necessary to explain that silver has very little affinity for either sulphurous acid or oxygen, and, on the other hand, that sulphurous acid possesses a great tendency to become sulphuric acid by taking up more oxygen. In such a bath, therefore, silver will continue to be deposited, being separated in the metallic state *by the reducing action of the sulphurous acid*, without the solution of any more copper to take its place in the bath. This is proved by the fact that if a bath of this kind be allowed to remain in a glass vessel, it will be slowly and spontaneously decomposed, and will silver the glass itself. The sulphuric acid formed reacts upon a portion of the undecomposed sulphite of sodium, sets free an equivalent of sulphurous acid, which maintains the bath in the state of bisulphite, while, at the same time, an equivalent of sulphate of sodium is formed, which does not interfere with the silvering process.

This bath is formed of bisulphite of sodium, to which is added a salt of silver, preferably the nitrate, until it begins to be dissolved with difficulty. It is therefore with a *double sulphite of sodium and silver* that the cold silvering by immersion is effected. It is evident that the bisulphites of potassium, ammonium, and other alkalies, may be substituted for the bisulphite of sodium, but the latter is to be preferred, because its preparation is cheaper, easier, and better known.

Roseleur recommends the following method for the

#### PREPARATION OF BISULPHITE OF SODIUM FOR COLD SILVERING.

Into a tall vessel of glass or porcelain (Fig. 111) introduce—

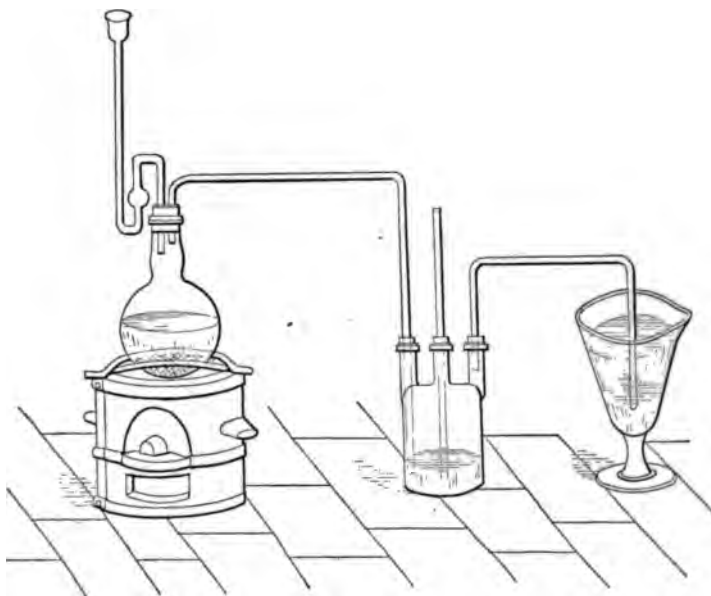
Water . . . . .	500 parts,
Crystallized carbonate of sodium . . . . .	400 "

and pour mercury, about an inch or so deep, into the bottom of the vessel, so that the glass tube conveying the sulphurous acid gas dips into it. The object of this artifice is to prevent the clogging of the delivery tube by the crystals formed during the operation. Then rig up an apparatus for the production of sulphurous acid, as indicated in the chapter on CHEMICAL PRODUCTS, and pass the washed gas through the vessel containing the carbonate of sodium. A part of this salt becomes transformed into sulphite of sodium, which dissolves, and a part is precipitated as bicarbonate. The latter, however, is transformed into sulphite of sodium, by the continued action of sulphurous acid, and carbonic acid gas escapes with effervescence.

When all has become dissolved, the passage of sulphurous acid should be continued until the liquid slightly reddens blue litmus paper, and then allowed to stand aside

for twenty-four hours. At the end of that time, a certain quantity of crystals will be found upon the mercury, and the liquid above, more or less colored, constitutes the bisulphite of sodium of the silvering bath. The crystals

Fig. 111.



are separated from the mercury, drained, and kept for gilding baths. They are not suitable for silvering.

The liquid bisulphite of sodium thus prepared, should be stirred with a glass rod, in order to eliminate the carbonic acid which may still remain in it.

The liquid should then be again tested with litmus paper; and if the blue color is strongly reddened, carbonate of sodium is cautiously added little by little in order to neutralize the excess of sulphurous acid. On the other hand, if red litmus paper becomes blue, too much alkali is present, and more sulphurous acid gas must be passed



through the liquid, which is in the best condition for our work, when it turns litmus paper violet or slightly red. This solution should mark from 22° to 26° Baumé, and should not come in contact with iron, zinc, tin, or lead.

PREPARATION OF THE (COLD) SIMPLE-IMMERSION  
SILVERING BATH.

A vessel of stoneware, glass, or porcelain is about three-fourths filled with the liquid bisulphite of sodium, and a moderately concentrated solution of nitrate of silver in distilled water is gradually added, while the bath is continually stirred with a glass rod.

By the contact of the two liquids, a white, flocculent precipitate of sulphite of silver is produced, which, with the aid of stirring, is dissolved by the bisulphite of sodium, with the formation of the double sulphite of sodium and silver. The silver solution is added as long as the precipitate readily disappears, and is stopped when it begins to dissolve with difficulty.

Roseleur is authority for the declaration that in this state the bath is always ready to work, and produces, almost instantaneously, a magnificent silvering upon copper, bronze, or brass articles which have been thoroughly cleansed and "quicked," although this last operation is not absolutely necessary.

He affirms that we may obtain with this bath, and according to the length of time of the immersion—

1. A very fine whitening by silver, which is as cheap as any of the previously described processes;

2. A bright silvering sufficiently durable, and especially adapted for jewellers' uses;

3. A dead silvering still more durable, for a multitude of objects, without the aid of electricity, and in the cold.

In the measure that the silver of the bath becomes

impoverished, it is made good by additions of nitrate of silver; but when, as will happen in the course of time, the proportion of bisulphite present is no longer sufficient to dissolve the silver salt, it becomes necessary to add some bisulphite of sodium to restore the bath to its primitive state. Roseleur has used the same bath, now and then reinvigorated by additions of bisulphite of sodium, or of nitrate of silver, for five consecutive years, for silvering trinkets, etc.; and in this same bath as many articles were daily silvered as a man could conveniently carry, and at prices varying from five cents to one dollar per pound.

The silver, which is slowly deposited upon the sides of the vessel, may be easily dissolved in nitric acid for future use.

Roseleur lays special stress upon the process, and recommends it to his confrères with the conviction that it will probably eventually replace all the other known methods.

#### ADDITIONAL FORMULA FOR DIRECT- OR IMMERSION-SILVERING.

The foregoing formulæ for silvering without the aid of the battery, may be varied considerably without noticeably affecting the quality of the work. Thus, for a thin silvering adapted for such small articles as pins, buttons, buckles, hooks-and-eyes, clock faces, barometer and thermometer plates, and many other articles of copper, brass, etc., Gore (*Electro-Metallurgy*, 152 *et seq.*) gives the following formulæ:—

1. Chloride of silver and bitartrate of potassium, equal parts.
2. Chloride of silver, 1 part; alum, 2 parts; common salt, 8 parts; and cream of tartar, 8 parts.

3. Chloride of silver, 1 part; prepared chalk, 1 part; common salt,  $1\frac{1}{4}$  parts; and pearl ash, 3 parts.

These solutions are used by adding a small quantity of water, sufficient to form the ingredients into a paste of the consistency of cream, and the articles are either thoroughly stirred about in it, or rubbed over with it until they have become sufficiently whitened.

A "novargent" solution, described by the same author, and which is proposed for the replating of old plated wares, consists of hyposulphite of sodium, 100 parts, and the chloride (or any other salt) of silver, 15 parts.

Watt (*Electro-Metallurgy*, 152 *et seq.*) refers to the last-named hyposulphite solution as a very useful one for plating with either silver or gold without the battery. He employs it for coating small articles of steel, brass, or German-silver, by simply dipping a sponge in the solution, and rubbing it over the surface of the article to be coated. He affirms that this procedure yields a very satisfactory and firmly adherent coating on steel. He recommends a solution of gold prepared and used in the same manner for direct gilding. For coating parts of articles that have stripped or blistered, he applies a *concentrated* solution of either gold or silver, made in the same way, to the part with a camel's-hair brush, touching it at the same time with a clean strip of zinc.

Urquhart (*Electro-Plating*, 116 *et seq.*) for the thin sil-  
vering of small articles, mixes, to a thin cream in water, the chloride of silver with the addition of some common salt. He applies the mixture to the previously wetted articles with a piece of cork, or a rubber made of a rag upon a wooden handle. When sufficiently whitened, the article should be washed, dried in sawdust, and, if possible, varnished.

Another solution, recommended as yielding a better



coating and more readily, is made of chloride of silver, 1 part; washing soda, 3 parts; common salt,  $1\frac{1}{4}$  parts; mixed together with a little warm water to the consistency of thin cream. This mixture improves with use, and may be replenished as it is found necessary by adding a little chloride of silver thereto. In carrying out these operations, the strictest cleanliness must be observed, and the fingers are in no case to be used to apply these mixtures, for which purpose, in addition to the suggestions above named, soft tooth brushes, pads of cotton, or sponge are well suited.

For direct silvering, Adrielle (Winckler, *Handb. d. Metallüberzügen*, 98 *et seq.*) dissolves—

Metallic silver . . . . .	20 parts,
in Nitric acid . . . . .	40 “

At the same time he prepares a solution of—

Cyanide of potassium . . . . .	200 parts,
in Water . . . . .	2500 “

He then mixes the two solutions, and stirs into the same, 40 parts of precipitated chalk. This mixture, which serves as his silvering liquid, is directed to be kept in flasks of blue glass, because of its disposition to decompose under the influence of sunlight. It is called by the patentee “argentine water.”

In using this liquid for silvering, it should first be thoroughly shaken up to properly distribute the chalk, and one part of the liquid used should be mixed with two parts of water. The articles are rubbed with this mixture, with the aid of linen pads saturated with it. When they appear sufficiently whitened, they are brightened with dry chalk, then washed in water and dried. More durable silvering will be obtained if this liquid is used with less water.

Elsner proposes (*Id.* 99) the following procedure for immersion silvering: He dissolves—

Chloride of silver . . . . .	7½ parts,
in Aqua ammonia . . . . .	60 “

and prepares another solution composed of—

Cyanide of potassium . . . . .	37½ parts.
Carbonate of sodium (cryst.) . . . . .	37½ “
Chloride of sodium (common salt) . . . . .	15 “
Hot distilled water . . . . .	1000 “

These two solutions are mixed, preferably in a large porcelain dish, boiled for a quarter of an hour, and the resulting liquid, after filtration, constitutes his silvering bath. The articles to be silvered, after proper preparation, are dipped for a few minutes into this liquid at the *boiling point*, thoroughly washed and dried.

Kuhn's (*Id.* 99) immersion-silvering liquid is composed as follows:—

Nitrate of silver . . . . .	2 parts.
Sal ammoniac . . . . .	1 part.
Hyposulphite of sodium . . . . .	4 parts.
Precipitated chalk . . . . .	4 “
Water . . . . .	50 “

This mixture is freshly prepared as rapidly as it is used, and is rubbed upon the articles, cold, in the manner above indicated.

Stein (*Id.* 114) triturates to an impalpable powder in a porcelain mortar, a mixture of—

Nitrate of silver . . . . .	1 part,
Cyanide of potassium . . . . .	3 parts,

then adds sufficient distilled water to the dry powder to form a thin paste, and brings this upon the articles with the aid of a woolen pad. As soon as the articles appear to be sufficiently silvered, they are washed and dried with

a soft linen rag. The above proportion of cyanide should not be varied, since if more is used the deposited silver will be redissolved, or if less is used it will have a grayish color. The addition of common salt does not appear to act well; nor does the chloride of silver appear as well adapted, according to Stein, as the nitrate. He recommends this procedure particularly for the direct silvering of polished articles of copper or brass.

Landois (*Id.* 115) prefers, for direct cold silvering, a solution prepared by dissolving cyanide of silver in a concentrated solution of common salt, and filtering. Clear surfaces of copper or brass are quickly coated with metallic silver on being immersed in this liquid, and the deposited silver is said to be very adherent. The subsequent operations are the same as above described.

The formulæ for direct silvering might be almost indefinitely multiplied, but those above described comprise all that are sufficiently important to warrant their insertion in this work. The numerous miscellaneous receipts that we have not deemed it worth while to admit, are simply modifications of those above described.

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## CHAPTER XXXIV.

### ELECTRO-SILVERING.

**WE** have now arrived at the most important part of our subject—that which has created as great a revolution in our domestic customs, as in the artistic working of the metals.

Without tarrying among the various formulæ given by sundry inventors, for electro-silvering baths, we shall de-



scribe one which, for a long time, has held the place of acknowledged superiority. It is composed of—

Water . . . . .	1000 parts.
Cyanide of potassium, pure*	50 "
Pure silver . . . . .	25 "

This bath is prepared as follows:—

1. A porcelain dish or capsule, of the capacity of a quart, receives—

Pure granulated silver . . . . .	25 parts.
Pure nitric acid of 40° Baumé . . . . .	50 "

The whole is heated over a charcoal furnace, or gas lamp, the dish being supported upon an iron triangle, and protected by a strip of wire-gauze from direct contact with the flame.

The acid rapidly attacks and dissolves the silver with the production of abundant nitrous vapors, which one should be careful not to inhale. When the reddish vapors have disappeared, there remains in the dish a liquid more or less greenish, bluish, or colorless, according to the proportion of copper contained in the commercial silver employed, which is seldom entirely pure.

The heat is then increased in order to evaporate the excess of acid, which escapes in the form of white fumes. The material in the dish dries, swells up, and, with a further increase of heat, fuses like wax.

The dish is then removed from the fire, and, protecting the hands with a cloth, the fused mass is made to flow upon the sides, where it soon solidifies.

\* As we have previously remarked, the chemical composition of commercial cyanide of potassium is exceedingly variable. The facility with which many foreign substances may be incorporated with it during its preparation, explains why many commercial cyanides do not contain more than 25 or 30 per cent. of the real article.

We have thus obtained the fused nitrate of silver (lunar caustic), which is more or less white, or gray, according to the purity of the silver employed.

When the whole is quite cool, the dish is turned upside down upon a clear sheet of paper, and by a gentle tap on the sides, the mass is detached.

2. The nitrate of silver is dissolved in ten or fifteen times its weight of distilled water, and treated with a ten per cent. solution of pure cyanide of potassium (Roseleur suggests the use of hydrocyanic (prussic) acid), which immediately produces an abundant white precipitate of *cyanide of silver*. A sufficiency of the reagent has been employed, when, after allowing the precipitate to subside, the addition of another drop to the clear supernatant liquid produces neither turbidity nor precipitate.

The whole is then thrown upon a linen filter stretched upon a wooden frame, and the cyanide of silver remains on the cloth, while the nitric acid and the excess of cyanide pass through. The precipitate left upon the filter is washed two or three times with pure water.

3. The cyanide of silver thus prepared is placed in the vessel intended for the bath, and stirred into the 1000 parts of water prescribed in the formula. The cyanide of potassium is then added, which, after solution, also dissolves the cyanide of silver. The silvering bath is therefore a solution of *the double cyanide of potassium and silver*.

Referring to the proper mode of preparing the electro-silvering bath, Roseleur remarks that operators on a small scale, in order to render the operation more rapid, frequently substitute the nitrate, or the chloride of silver, for the cyanide. This mode of operation is not economical in the long run, since, after having maintained the strength of their baths with such materials, these baths

will become loaded with chloride of potassium, or nitrate of potassium, and, becoming too dense, will not be readily traversed by the electric current. Moreover, in cold weather, these salts will crystallize upon the immersed articles, and, as silver will not be deposited upon these crystals, the silver coating will be marred by spots which cannot be removed by burnishing it, and the operation will have to be begun anew.

In this connection, we will recall the fact that Roseleur, in the preparation of his double cyanide electro-gilding solution, uses the same method, to which he very properly here objects, in the preparation of the electro-gilding solution (see pages 204-205 of this work, and our remarks on page 209).

We should say, nevertheless, that amateurs or operators who employ small baths, often revived, may substitute for the cyanide of silver the chloride, or, better still, the nitrate of this metal. But, in the latter case, the quantity of cyanide of potassium should be increased. Such baths will be prepared as follows:—

1. The nitrate of silver is prepared in the manner indicated above, and 15 parts of it (nearly equal to 10 parts of pure silver) are dissolved in 1000 parts of water.

2. The cyanide of potassium (pure), about 25 parts, is then added to the above solution.

After stirring to facilitate complete solution, the liquid is filtered, in order to separate the iron contained in the cyanide. This operation, however, is not absolutely necessary, as the iron rapidly falls to the bottom of the bath, and the solution becomes lumpy.

In this case, it will be noticed, we have only 10 parts of silver per 1000 of water; but this is enough for ordinary purposes. On the other hand, some silver electroplaters employ much richer baths, holding up to 1



parts of metal per 1000 of water, but an average of from 20 to 25 parts furnishes very good and uniform results.

The proportion of cyanide of potassium employed is much more than is required for dissolving the indicated quantity of silver, since  $1\frac{1}{2}$  parts of good cyanide is rather more than sufficient for 1 part of silver; but experience demonstrates that, unless there be an excess of cyanide of potassium, the baths do not conduct electricity well, and the deposit of silver is granulated, striated, and irregular. The necessity of the presence of *free* cyanide in electroplating and silvering baths has been fully explained in Chapter XXVII., page 256 *et seq.*, to which the reader is referred.

The operation is effected with the current, and with baths, either warm or cold. The latter method is generally adopted for articles which require great solidity. The hot process is employed for small articles, although it is preferable also for steel, iron, zinc, lead, and tin, which have been previously electro-coppered.

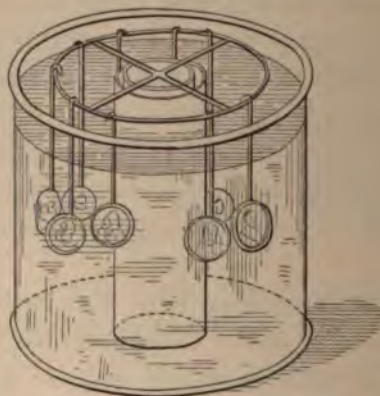
The hot electro-silvering baths are generally kept in enamelled cast-iron kettles, and the articles are either suspended, or moved constantly about in them. The preliminary operations of cleansing in acids and passing through "quicking" solution are necessary. A somewhat energetic current is needed, especially when the articles are moved about, in order to operate rapidly. The current is too strong, when the articles connected with the negative electrode become gray or black, or produce an abundant disengagement of gas bubbles.

In the hot silvering baths, the separate battery is often replaced by the use of a zinc wire wrapped around the articles. The points of contact of the two metals are often black or gray, but the strain rapidly disappears by

plunging the object into the bath for a few moments, after it has been separated from the zinc, and carefully scratch-brushed.

A few gold and silver electroplaters employ, instead of separate batteries, the simple apparatus (Fig. 112), which

Fig. 112.



consists of a glass, porcelain, or stoneware vessel for containing the bath, in the centre of which is a porous cell filled with a solution containing 10 per cent. of cyanide of potassium, or of common salt. The cylinder of zinc, immersed in this exciting liquid, carries a circle of brass wire, the cross wires of which intersecting at the centre are soldered to the zinc. It is then sufficient to suspend the well-cleansed articles to the brass circle by means of wires. At the beginning, the operation goes on rapidly, and the deposit is good; but, after a certain length of time, the solution of zinc traverses the porous cell by exosmose, and the purity of the bath is impaired.

When the bath becomes impoverished it is revived by additions of equal parts of cyanide of potassium and of silver salt. It is also necessary to replace the water in proportion as it evaporates.

Roseleur, whose usually eminently practical instructions we have largely followed in this work, affirms that the previous coating with copper, of articles of steel, as well as those of Britannia-metal, iron, lead, tin, and zinc, is indispensable as a preparatory step to securing an adherent coating of silver. So far as this statement relates to steel and Britannia-metal, this usually correct authority is altogether wrong.

In the United States, which has some of the largest silver-plating establishments in the world, notably the Meriden Britannia Company at Meriden, Conn., the Wm. Rogers Manufacturing Co., of Hartford, Conn., and others, the practice of previous coppering is not adopted either with Britannia-metal (white-metal, as it is sometimes called) or steel. Indeed, we may affirm on the best authority that this practice has not been in vogue in any establishment of importance for many years—steel table-knives being plated directly on the steel, and table-ware, such as cake-baskets, ice-water pitchers, coolers, etc., receiving their silver deposits directly on the Britannia. It is doubtful in fact if coppered wares, such as Roseleur describes, would be marketable. It would appear, therefore, that this practice, which appears to be obsolete in England also, is confined to the French platers.

The practice of different establishments, of cleansing their work, differs somewhat, but all aim at the same result, viz., to secure a smooth, adherent coating of metal upon an inferior base.

The practice in the Meriden Britannia Co.'s works, at Meriden, Conn., as observed by the author, is substantially as follows: With "white-metal:" The article is first cleansed of all grease by immersion in boiling alkali; then into dilute muriatic acid; then into a "striking" solution, viz., a weak cyanide of silver solution with a large propor-



tion of free cyanide of potassium, and a large silver anode operated with a very strong electric current. The purpose of immersion in this solution is to effect an instantaneous deposit of silver on the metal, to better insure a perfect coating in the silvering bath proper. The articles remain in the "striking" solution for a few seconds only, as its action, owing to the large proportion of free cyanide it contains, is very prompt, and as soon as they have received a thin coating, which takes place almost immediately, they are removed to the electro-plating bath, where they remain until they have received the proper coating of silver. In many cases, especially with articles of considerable size, cleansing in boiling alkali must be supplemented by "scratch-brushing," in which case the acid dip may be dispensed with, and the article, after thorough rinsing and again dipping in alkali to remove finger marks, is immersed at once in the "striking" solution.

German-silver, or nickel, articles are first cleansed in boiling alkali, washed, then dipped in a mixture of two-thirds sulphuric and nitric acids, then into quicking solution, then into the "striking" solution, and from this into the plating bath.

Steel articles are cleansed in boiling alkali, rinsed, dipped in muriatic acid, then in the "striking" solution, and from this into the plating bath. In case the articles require scouring the acid dip is dispensed with. For steel two "striking" solutions are used, one somewhat richer in silver than the other, the weaker solution being used first.

In the Wm. Rogers Manufacturing Co., Hartford, Conn., one of the oldest and best establishments in the United States, the following is the general outline of the methods in use for preparing work for plating:—

**FOR CLEANSING STEEL (cutlery).**—Immersion in boiling alkali for the removal of grease; scouring; rinsing; dipping in strong muriatic acid; then for a few seconds in a silver “striking” solution; then in the plating bath until the required amount of silver is deposited.

[The formulæ for the “striking” solution, which will be given further on, is low in silver, rich in cyanide, and worked with a strong current and a silver anode.]

**NICKEL-SILVER (German-silver) (for spoons).**—Immersion in boiling alkali; scouring, if necessary; rinsing in water; immersion in acid mixture, composed of two-thirds sulphuric acid and one-third nitric acid; dipping in weak “quicking” solution (either very dilute potassium-mercury cyanide, or acidulated nitrate of mercury); immersion for a few seconds in the silver “striking” solution; and from this into the plating bath.

**BRITANNIA-METAL (hollow-ware).**—Cleansing in alkali as above; brushing; rinsing in water; again immersing in alkali to remove finger marks, if necessary; immersion in the “striking” solution, and from this into the plating solution. A “quicking” solution for Britannia, sometimes employed, is composed of a strong solution of sal-ammoniac and corrosive sublimate, into which the articles are dipped after cleansing in strong potash. The metal will plate without being scoured. The Hartford Britannia Company employs substantially the same method of procedure. Whether articles require to be scoured or not will depend, of course, upon their freedom from grease or dirt of any kind, and the operator must use his judgment as to whether he may safely dispense with it in preparing his work for plating.

The above described preparatory operations correspond in a general way with the most approved English methods, as witness the following brief statement from Gore (*Elec-*

*tro-Metallurgy*, 162 *et seq.*): "Copper, brass, and German-silver are the best substances to deposit silver upon; lead is a very bad metal for the purpose, because it is so soft. Articles of iron or zinc are usually coated with a film of copper, in a cyanide solution, before putting them into the plating liquid. Those formed of Britannia-metal, tin, or pewter, are not dipped into acid before plating, but into a strong and boiling-hot solution of pure caustic potash, and are then either "scratch-brushed," or taken direct from the alkali, without rinsing in water, and immersed in a cyanide of silver solution (at about 190° F.), containing a considerable proportion of free cyanide, with a large anode, and an electric current of considerable intensity is passed through the vat for several minutes, until the articles receive a thin coating; they are then transferred to the ordinary plating solution to receive the full amount of deposit.

"Steel articles, after being cleansed in the hot potash, are dipped (without brushing) into a solution of one pound of cyanide of potassium to a gallon of water; and then coated thinly with silver in a similar manner before plating. Those of lead are first scraped or otherwise made quite clean and bright, by mechanical means, and then treated in the same manner as those of Britannia-metal. Articles of copper, brass, or German-silver, after being properly cleansed, are dipped into the solution of nitrate of mercury, or a very dilute one of cyanide of mercury and potassium, then rinsed in a vessel of water, and immediately suspended in the depositing vat."

The silver "striking" solution, as used by the William Rogers Manufacturing Company, of Hartford, Conn., has the following composition, viz:—



*Rogers's "Striking" Solution.*

Cyanide of potassium . . . . .	6 ounces.
Silver . . . . .	$\frac{1}{2}$ ounce.
Water . . . . .	1 gallon.

Use strong current.

The following is the composition of the

*Meriden Company's "Striking" Solution.*

Cyanide of potassium . . . . .	12 to 16 ounces.
Silver . . . . .	8 to 10 dwts.
Water . . . . .	1 gallon.

The plating solution commonly employed by the **William Rogers Manufacturing Company**, of Hartford, Conn., is the following composition:—

*Rogers's Formula.*

Cyanide of potassium . . . . .	6 ounces.
Silver (in chloride) . . . . .	4 "
Water . . . . .	1 gallon.

The usual plating bath of the **Meriden Britannia Company** has the following proportions:—

*Meriden Company's Formula.*

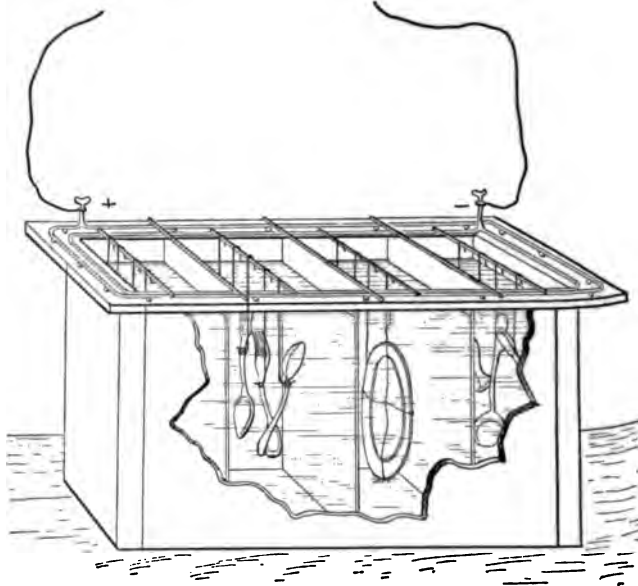
Cyanide of potassium . . . . .	12 ounces.
Silver . . . . .	3 "
Water . . . . .	1 gallon.

When these baths deposit their metal rapidly without the aid of electricity, it is a proof that they are too rich in cyanide, or, what amounts to the same thing, too poor in silver. A deposit effected under such conditions is rarely adherent, especially when it is made upon articles previously coppered, because then the excess of cyanide dissolves the film of deposited copper, and the silver which takes its place is easily rubbed off with the finger. This phenomenon will be particularly observed with

articles of steel, tin, lead, etc., which have been coated with copper before plating. The remedy consists in adding to the bath just so much of silver salt, that a piece of copper will not become sensibly silvered in it, without the aid of electricity.

The cold electro-silvering baths are disposed differently according to the articles to be operated upon. Those generally employed for electro-plating tablespoons and forks, etc., are contained in large, rectangular wooden troughs (Fig. 113), lined with gutta percha, or made of

Fig. 113.



wrought iron with riveted joints. They are sufficiently high to allow of about 4 inches of liquid being above the immersed objects, which should be supported equidistant from top, bottom, and sides, in which case the deposition of metal is likely to be of uniform thickness at both extremities of the objects. Each vat has a wooden

rim or flange attached to, and passing all around its upper edge. Upon this rim is fixed a rectangle of brass tubing, to which is soldered a binding screw connecting it with the positive pole of the battery. Inside of this rectangle is attached another smaller rectangle of brass tubing, passing all around the flange like the first, the two being completely insulated from each other. This second rectangle also has a binding-screw, which serves to connect it with the negative pole of the battery. Rods or tubes of brass placed transversely rest with their extremities in clean metallic contact with the outer or larger rectangle, and these are destined to support, and are in good metallic contact with, a number of sheet silver anodes by means of iron, which extend down into the bath. Other rods of brass, also lying crosswise like those just mentioned, rest with their extremities in the inner and smaller rectangle, and from these are supported by means of wires the objects to be silvered. By using a flange slightly inclined upwards, or provided with a step, the outer rectangle will be placed somewhat higher than the inner one, so that cross-rods carrying the anode will cross without touching the lower-lying inner rectangle. The same object will also be accomplished by using a larger tube—say one inch in diameter—for the outer rectangle, and a smaller one, one-half inch, for the inner one. It is scarcely necessary to add that all the points of contact of the cross tubes with the rectangles, the supporting frames, and the suspension wires with the cross tubes, and the binding-screw and other connections, must be kept scrupulously clean, and for this purpose must be frequently examined.

Having provided a vat of this description, a certain number of spoons, forks, etc., fixed to one of the cross tubes (Fig. 114), by means of copper wires, are cleansed at the



same time, and the tube is placed in position with its extremities resting on the inner or negative rectangle of the bath. Then with its ends resting upon the positive conductor of the trough and adjacent to the first a second cross tube is placed in position, to which is attached a silver anode (Fig. 115).

Fig. 114.



Fig. 115.

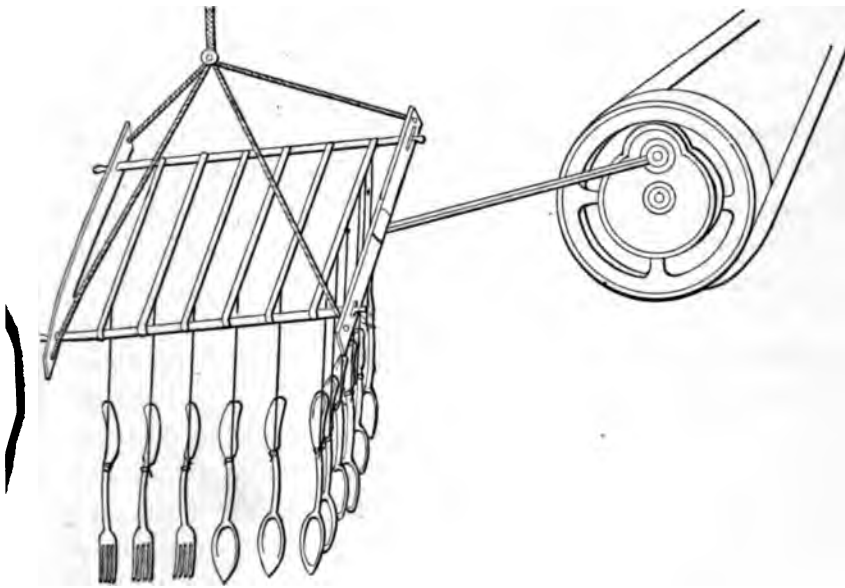


Next comes another series of spoons and forks, faced by another anode, and so on, in such a manner that each series of articles is disposed between two anodes. The cross tubes carrying the articles to be silvered all rest, of course, upon the negative conductor, and the anodes upon the positive.

This disposition is evidently the best for obtaining a sensibly equal deposit upon all the pieces; nevertheless, unless the articles are kept in constant motion, it will be found necessary to reverse the objects during the operation (*i. e.*, turn them upside down) in order that the lower portions shall not receive the heaviest deposit. This will otherwise be the case as the richest part of the solution is the densest, and therefore lies near the bottom of the vat. Moreover, the change of position of the articles prevents the formation of longitudinal striæ, which are often seen upon smooth articles left undisturbed in the solution for a long time.

These striæ are generally due to the existence of a multitude of small, convection currents, ascending and descending side by side, and formed by the successive displacement of denser and lighter liquid layers. They do not occur in liquids kept in a state of constant agitation. The denser layers, being richer in metal, deposit it more abundantly in the direction which they follow, and form grooves which cannot be filled by the lighter and poorer currents. It is, therefore, advantageous either to keep the bath, or the objects, in constant motion; and in large plating works, where motive power is available, a small portion of it may be used for imparting a swinging motion

Fig. 116.



to the objects to be silvered. In this case, the frame supporting the articles does not rest upon the vat, but is suspended above the bath, and receives a slow swinging motion from a small eccentric or its equivalent (Fig. 116).

Any other mechanical movement, producing the same results, may be employed.

The amount of silver deposited on plated goods varies according to circumstances. Different establishments have several grades of goods which they designate by special trademarks. A coating of the thickness of common writing-paper, which is considered to be an excellent one, corresponds to about an ounce and a quarter, or an ounce and a half of silver to the square foot of surface. The silver will adhere strongly, if the articles have been properly prepared before plating.

Where the voltaic battery is used as the generator of the current, the time required for laying a satisfactory coat of silver will vary, according to the grade of the plating required, from three or four hours to twelve hours. With the dynamo-electric machine, however, which has come into almost universal use in the larger plating establishments, a fair coating can be laid in three-quarters of an hour, and a heavy coat (triple-plate) in from two to three hours, according to the intensity of the current, the condition of the bath, and the relative proportions between the surfaces of anode and cathode.

The practice obtains among a few platers of removing their articles from the bath after they have received a thin coating of silver, thoroughly scratch-brushing, and returning them. It is questionable, however, if the advantages supposed to be gained by this practice are sufficient to warrant the extra labor, and to offset the risk of spotting the articles with finger marks. As one very experienced plater expressed himself to us on the subject, it is "love's labor lost."

In order to secure an extra heavy coating of silver on the convex surfaces of spoons and forks, which, being subject to greater wear than the other parts, require extra



protection, the Meriden Britannia Company uses a frame in which the articles, supported therein by their tips, are placed horizontally in a shallow silver bath, and immersed just deep enough to allow the projecting convexities to dip into the bath. By this artifice, these portions are given a second coating of silver of any desired thickness. This mode of procedure, which is termed "sectional plating," accomplishes the intended purpose, simply and satisfactorily. The common plan, elsewhere named, of allowing the backs of these articles to face the anode for a longer time than the front, has the obvious objection that it necessitates the deposition of an unnecessarily heavy coating upon the other portions of the same surface exposed to the anode. Similar devices are in use in other establishments.

The following tabulation exhibits the amount of silver deposited upon the several grades of plated tableware manufactured by the William Rogers Manufacturing Company, of Hartford, Conn.

Per gross.	Extra plate.	Double plate.	Triple plate.
Teaspoons . . . . .	48 dwts.	4 oz.	6 oz.
Dessertspoons and forks . . . . .	72 "	6 "	9 "
Tablespoons and med. forks . . . . .	96 "	8 "	12 "

Electro-silvering baths do not generally work so well when freshly prepared as after they have been used for a certain time, and have become *electrolyzed*; the deposit is not always uniform, and is often granulated, bluish, or yellowish. When this is the case, it will be found useful to mix a portion of old baths with those recently prepared. New baths may be artificially aged by boiling them for a few hours, or by adding to them one or two thousandths of aqua ammonia.

The greatest reproach to electro-silver-plating is that the deposit does not retain its color, but becomes yellow-

ish on exposure to the air. This phenomenon is due to the simultaneous deposit, by galvanic action, of pure silver and of a subsalt, the *subcyanide of silver*, which is rapidly decomposed and darkened by light. It is therefore expedient to eliminate the latter compound, in order that this inconvenience shall disappear. This may be accomplished by the following methods:—

1. The articles are left immersed in the bath for some time after the electric current has been interrupted, when the subcyanide of silver is dissolved by the cyanide of potassium.

2. After having smeared the objects with a paste of borax, they are heated in a muffle until the salt fuses and dissolves the subcyanide. This process anneals and softens the metal.

3. The electrodes are inverted for a few seconds, after plating, thus transforming the articles into anodes, and the electric current carries away the subcyanide of silver in preference to the metal. It is evident that this operation should not be prolonged, otherwise the silver will be entirely removed from the objects, and will be deposited on the silver plates.

#### *Bright Silvering.*

As deposited from the cyanide bath just described, the surface of the precipitated silver has a mat or dead appearance, which is well described as “*chalky*.” To brighten this deposit it is necessary to resort to burnishing, which, especially in the case of objects of very ornate design, or with those of hollow shape, which require to be bright inside, is a tedious and troublesome operation.

It is found, however, that the addition of a small quantity of bisulphide of carbon to the cyanide plating solution will cause the silver to be deposited bright. This

observation was made by accident, and became the subject of a British patent, issued in 1847, to Lyons and Milward. Since that time the process devised by these inventors has been, with unimportant modifications, extensively used by platers.

Lyons and Milward describe their process as being intended for producing bright deposited silver by adding to the cyanide of silver solution "compounds of sulphur or carbon," of which they name bisulphuret of carbon, trichloride or other chloride of carbon, sesquichloride of sulphur, or hyposulphite of sodium or potassium. The bisulphide of carbon, which they consider preferable, may be used either alone or dissolved in sulphuric ether, or in conjunction with any of the substances above named. The following procedure they find best adapted for their purposes: "We take the bisulphuret of carbon and combine it with the metal to be deposited, previously dissolved in a solution of the cyanide of potassium or sodium in the manner well known, and proceed as follows: We place six ounces of bisulphuret of carbon in a stoppered bottle and pour over it a gallon of the cyanide solution, from which we are about to deposit. We allow this to remain twenty-four hours. We then decant carefully a portion of the solution, which will have combined with a part of the bisulphuret of carbon, and for every twenty gallons of solution to be acted upon we add about two ounces of the solution containing the bisulphuret of carbon and stir it well with the twenty gallons, when it is ready for use; but we find it necessary to add fresh portions of the solution containing the bisulphuret of carbon every day when in use in about the same proportion; but in case the solution has remained many days upon the bisulphuret of carbon a smaller portion than two ounces will suffice to produce the effect. We have found the other



named ingredients when used in larger proportions to produce similar results, but not so advantageously as the bisulphuret of carbon; and we have found that a much larger proportion of bisulphuret of carbon produces an improved dead deposit in place of the bright effect previously described; and we would state that the bisulphuret of carbon may be combined with solutions of metals by other means than those we have described. We have succeeded by first dissolving it in sulphuric ether (or hydrocyanic acid with the aid of heat), and find the effect upon the solution to be the same."

The proportion either of silver or of free cyanide in the silver bath to which the brightening solution is added does not appear to noticeably affect the result. The brightening solution acts more slowly than the usual plating solution and requires a stronger current. The brightening exhibits itself first at the lowest portions of the articles and spreads from these gradually over the whole surface, requiring usually about a quarter of an hour to completely brighten.

The brightening solution is intended to be used simply to impart a superficial finish upon plated articles, and is unfit for ordinary use in plating. A "bright" vat should, therefore, be kept for finishing only, and is found especially serviceable in plating surfaces that are difficult to scratch-brush. In adding brightening solution to the plating bath, the caution should be carefully observed to use as little of it as possible; the addition of too much is apt to cause the articles to become spotted and streaked with a bad, brownish discoloration.

Urquhart (*Electro-Plating*, 1880, page 136) conveys the following hints on the "bright" plating process: "This is a process employed in the plating factory by which a brilliant appearance or finish is given to the

goods after they have been plated in the ordinary way. It saves a great deal of trouble, because the surface is finished as if it had been burnished. It is questionable whether the solution is of use to the amateur, as it does not appear to work well in very small volumes.

“To make this solution, place a quart of ordinary plating solution in a special bottle, add to it four ounces of liquor ammonia, two of ether, and four of bisulphide of carbon. Shake well, and stir in an ounce or two of this mixture to every twenty gallons of plating liquid it is required to brighten about twice a day. This is done as the bath is working. All the bisulphide of carbon mixture must not be added at once, this would spoil the whole solution. As the plating goes on, a little should be stirred in after the day's work, as mentioned. It is of the greatest importance to use as little as possible of this destructive bisulphide of carbon, as it is very apt to ruin the solution altogether; and no solution should be thus ‘brightened’ that is required to plate ordinarily with again, as it will be unfit for the purpose.” Should the spotting or discoloration of the articles indicate that too much “brightening” liquid has been used, the same author recommends as the best remedial plan, to work upon a silver cathode until the excess is worked off.

Plante's method of bright silvering consists in the addition of sulphide of silver to the plating bath. Of other methods suggested for the same object, Gore (*Electro-Metallurgy*, 168) makes mention of sulphur and colloidion; a solution of iodine and gutta percha in chloroform, which is affirmed to be more permanent in its effects than the bisulphide of carbon; also one and a half ounces each of the carbonate and the acid carbonate of potassium, added once in nine or ten days to a plating liquid containing twelve ounces of cyanide of potassium, and



three and a half of silver per gallon. This authority remarks concerning these suggested substitutes, that they do not equal the bisulphide. Respecting this operation, it may be said that it is the generally expressed opinion of experienced platers that it is difficult to secure uniform results. The experience of the William Rogers Manufacturing Co., of Hartford, as expressed to the author, is to the effect that if the articles are disturbed or moved in the "bright" vat, they will plate a dirty-white color. If kept perfectly still, and all conditions are favorable, they will plate bright, but to obtain uniformly good results is difficult and uncertain, and if too much brightening solution has been added, the bath is sure to work unevenly, and to plate roughly and badly. On the other hand, the Meriden Britannia Company, in response to inquiries, state that they employ the "bright" bath regularly, and find no serious objection to its use.

Gore affirms, in explanation of the peculiar behavior of the brightening solution, that the silver deposited is not the pure metal, and that he has found sulphur in it "by dissolving it in pure dilute nitric acid, determining the amount of silver, and testing for sulphuric acid in two separate portions."

Finally, it may be added that it is important to rinse the "bright" plated articles in boiling water *immediately* after their removal from the bright vat, and that the rinsing should be so thorough as to completely remove all traces of the brightening liquid, as otherwise the articles will quickly blacken.

From all that has preceded, our readers will be able to draw the conclusion that while the use of brightening solution is attended with some difficulties and uncertainties, they may be overcome by the exercise of proper care and good judgment.



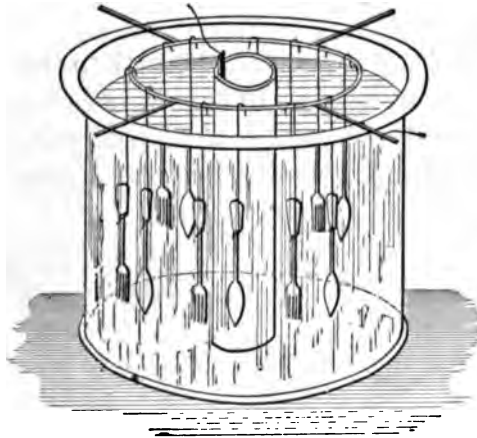
## CHAPTER XXXV.

## SILVERING BATH FOR AMATEURS.

AMATEURS, or those who simply wish to make a few experiments in electro-silvering, will find the following disposition very satisfactory, since the expenses are small, and the results certain.

The bath is kept in a cylindrical vessel (Fig. 117) of stoneware, glass, or porcelain, and of appropriate size. The spoons, forks, etc., after the proper preparatory treatment, are attached by clean copper wires to the

Fig. 117.



circumference of a brass ring, supported upon the rim of the apparatus by three or four soldered wires. The ring is connected with the negative pole of the battery, and the positive pole with a platinum anode, which is im-

mersed in the centre of the bath. (A silver sheet rolled into the form of a cylinder is preferable to the platinum wire.) It results from this disposition that all the objects suspended from the brass ring are equally distant from the anode, and receive the same amount of deposited silver. Nevertheless, the articles to be silvered should be now and then turned upside down, and also laterally, so that each face of the object will be, in turn, presented to the silver anode. These changes, moreover, present the advantage that the points of contact with the suspending wires receive their quota of metallic deposit. When this precaution is not followed, the place where the wire was attached appears as a furrow without silver, and defaces the appearance of the piece.

Points, edges, corners, and all parts in relief, offer a more easy passage to the electric current, and therefore receive a thicker coating of metal. As those are the parts most exposed to wear, this circumstance is a most fortunate one.

As the convex parts of electro-plated spoons, forks, etc., are subject to much more friction in usage than the concave parts, the former should be allowed to face the anode longer than the latter in order to receive a somewhat heavier deposit.

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## CHAPTER XXXVI.

### GENERAL OBSERVATIONS ON THE MANAGEMENT OF CYANIDE PLATING SOLUTIONS.

As is the case with the cyanide gilding solutions, the composition, strength, and working quality of the cyanide plating solution are liable, in operation, to constant changes,

and from causes analogous to those set forth in our observations on the former. Fortunately, however, the cyanide silvering solutions do not present as much difficulty in their proper management as the corresponding gilding solutions.

We shall give in what follows a number of practical hints respecting the proper management of plating solutions which will be found serviceable.

Newly prepared silver solutions, as we have previously mentioned, do not work as satisfactorily as those that have been in use for some time, and to meet this objection, many operators adopt the plan of adding to a freshly prepared silver solution some old silvering liquid, which improves its working.

In the course of time, and according to the constancy with which they have been kept in service, the baths become charged with impurities. They become contaminated from the floating particles of dust in the plating room, and other mechanical impurities; they become charged with the salts of foreign metals, from the solution of the metallic articles introduced for plating, and from the impurities of the silver used as anodes; they become too heavily charged, also, with cyanide and silver salt, and with carbonate of potassium from the decomposition of the cyanide, or from impure cyanide, so that the density of the baths becomes so great as to offer considerable resistance to the passage of the current, etc. etc. From either of these causes, or from all combined, the quality of the plating will be more or less seriously impaired.

When the solution has become dirty from mechanical impurities, which is readily seen on any slight disturbance of the bath, which causes them to rise, the plating will be damaged by the settlement of particles upon the articles, producing objectionable streaks or spots. When-



ever the bath appears to require it, therefore, it should be filtered.

If the solution is too dense, even though the relative proportions of silver and cyanide are right, the bath will be troublesome to manage, especially in hot weather. The increased density of the solution hinders the freedom of movement of its particles, the constituents are more disposed to stratify in layers of different specific gravities, the heavier silver salt accumulating below, and the lighter cyanide in excess above; in consequence of which the lower parts of the articles will receive a disproportionately heavy deposit, while their upper portions will receive comparatively little, and the upper parts of the anode will be strongly attacked. When this behavior is observed, the remedy to be applied is the proper dilution of the solution. It is a good plan, and one which the experienced plater does not omit, to stir the solution well after each day's work. In addition to this, the operator should by no means neglect the precaution to keep the articles in the bath in constant motion, by some such mechanical device as that shown in a preceding chapter (page 301). By careful attention to these simple details, the annoyances above described may be largely diminished or entirely obviated.

By observing attentively the behavior of the anodes under the galvanic action, the operator will acquire valuable indications respecting the composition of the bath, the proper proportion of its component parts, and the results which he may expect from it.

Thus, should the anodes become *blackened* during the passage of the electric current, it is a sure proof that the solution contains too little cyanide of potassium and too much silver. In this case, the deposit, though adherent, takes place entirely too slowly, and the bath loses more

ever than it gains from the anodes. He should then add, with precaution, some cyanide of potassium.

If, on the other hand, the anodes remain *white* during the passage of the current, the proportion of cyanide of potassium is too great, the deposited silver is often without adherence, and the anodes lose more metal than is deposited. The remedy consists in adding the silver salt until it dissolves with difficulty.

To sum up, when the bath is in good working order, the anodes become *gray* during the passage of the electric current, and *white* when the circuit is broken.

The specific gravity of the bath may vary considerably without sensibly impairing the quality of the work.

Besides the examination of the anodes, there is another simple and rapid process for ascertaining the state of the bath, and establishing the proper ratio between the silver and the cyanide. About half a pint of the liquid is removed and introduced into a tall glass, and to this a solution of 10 parts of nitrate of silver in 100 parts of distilled water is added, drop by drop. If the white precipitate produced is rapidly dissolved by stirring, the liquid is too rich in cyanide, or, what is the same thing, too poor in silver; should the precipitate remain undissolved, notwithstanding prolonged stirring, the liquid is too rich in silver and too poor in cyanide of potassium. Lastly, when the precipitate is dissolved but slowly, the liquid is in the best condition. The remedy for each of these deficiencies is obvious.

Generally the same causes that are operative in causing the continual alterations that have been pointed out in our comments on the management of the cyanide gilding-solution, are those which cause the analogously constituted electro-plating bath to suffer continual changes.

If the anode surface exposed is disproportionately large



in relation to the receiving surface, the bath becomes too rich in silver, and the proportion of free cyanide is relatively diminished; an excess of free cyanide will have a similar effect. If, on the other hand, the anode is relatively small as compared with the receiving surface, the bath will become impoverished in silver; and if the bath is deficient in free cyanide, the result will be the same; or the two causes combined will aggravate the evil.

When, after long usage, the density of the cyanide bath becomes too great and its electric conductivity diminishes, the silver is deposited, but the cyanide remains behind and is partly decomposed into carbonate of potassium, which retards the silvering process by preventing the free passage of the electric current. When this condition of things exists, it will be well to add to the bath, instead of the cyanide of potassium, hydrocyanic acid, which combines with the potassium of the carbonate to form fresh cyanide, while the carbonic acid escapes in gaseous form. We have thus rehabilitated the cyanide with its dissolving properties, and, after proper dilution, the bath will be restored to its normal working condition.

The bath may also be regenerated by the addition of the cyanides of calcium or barium, the bases of which form insoluble carbonates, while the cyanogen combines with the potassium of the carbonate.

As has been elsewhere remarked, the cyanide plating baths may vary considerably from the standard before the fact becomes patent by the obvious inferiority of their work; a fact of some importance for the inexperienced plater to know. On this account it may be well to add to the foregoing hints on the management of such solutions, the statement that the rate at which the anode is being dissolved, will (in addition to its appearance) afford him an approximate knowledge of the condition of the bath.



The loss of weight of the anode should agree very closely with the gain in weight of the plated articles, if the bath is working properly. If the anode is losing more than the goods are receiving, the indication points to an excess of free cyanide in the bath; if the reverse be the case, a deficiency of free cyanide may safely be suspected.

In either case the remedies are obvious. It is a good rule to observe, not to correct the irregularities that show themselves in the working of the bath, by fresh additions of cyanide or silver salt, until the operator has assured himself by careful examination that the fault does not lie with an insufficient or excessive current, or a disproportion between the surface of the anode and of the recipient. Every fresh addition increases the quantity of the substances in the bath, and to maintain its density within proper limits its volume will soon become greatly increased by the necessary dilution with water.

When a bath is in good working order, the operator should, by careful attention to the hints and precautions herein given, strive to keep it so. Such attention will go very far towards accomplishing this desirable result, but no amount of advice will take the place of experience.

A durable electro-silvering, that is to say, a thick, continuous, and adherent metallic deposit, is of such importance at the present day, that we repeat again in a synoptical form the several operations recommended by Roseleur for obtaining good results.

#### ROSELEUR'S METHOD FOR COPPER, BRASS, AND GERMAN-SILVER.

##### FIRST OPERATION.

Boil the articles a few minutes in a solution of—

Water . . . . .	10 parts,
Caustic potassa . . . . .	1 part,

and wash in fresh water.

SECOND OPERATION.

Dip into a cleansing pickle composed of—

Water . . . . .	10 parts,
Sulphuric acid . . . . .	1 part,

and rinse.

THIRD OPERATION.

Plunge for a few seconds into the following mixture:—

Nitric acid of 36° Baumé, yellow . . . . .	100 parts,
Common salt . . . . .	2 “
Calcined soot . . . . .	2 “

and wash rapidly in abundance of water.

FOURTH OPERATION.

Dip rapidly into the following mixture, prepared the day before:—

Yellow nitric acid of 36° Baumé . . . . .	100 parts,
Sulphuric acid of 66° Baumé . . . . .	100 “
Common salt . . . . .	4 “

and wash very rapidly in fresh water.\*

FIFTH OPERATION.

Immerse the articles for a few seconds, or until they are entirely whitened, in a solution of—

Water . . . . .	100 parts,
Nitrate of mercury . . . . .	1 part,

with the addition of sufficient sulphuric acid to render the solution clear on stirring with a glass rod.

Rinse in fresh water.

SIXTH OPERATION.

Immerse the articles in the bath, under the influence of a weak current, and at the expiration of a quarter of an hour examine carefully each supporting rod. If the

\* Some operators substitute for the third and fourth operations scouring with pumice-stone powder. For the preparation of Britannia-metal, steel, etc., see our description, Chapter XXXIV., page 293.

re being coated uniformly and without spots the current is allowed to proceed; on the contrary, should the deposit be crystalline, the pieces are withdrawn, scratch-brushed, passed through a hot solution of potassium, rinsed in fresh water, plunged into the "quicking" solution, rinsed again, and then returned to the silver bath, where they are permitted to remain until they have received the quantity of deposit desired.

SEVENTH OPERATION.

The current is arrested for a few minutes before the pieces are withdrawn from the bath, in order that the silver may redissolve the subsalts of silver deposited on the surface of the pure metal.

EIGHTH OPERATION.

The pieces are removed from the bath, wash in fresh water, and then pass through a weak pickle of sulphuric acid.

NINTH OPERATION.

Final scratch-brush.

TENTH OPERATION.

Final polish, if desired.

Directions for electro-silvering very large pieces, or pieces of diverse forms, must obviously be contained in separate chapters. In general, the vats of appropriate shapes, the soluble or insoluble anodes being placed, sometimes in the middle, sometimes near about the sides.

Articles when removed from the bath have a dead surface which is crystalline and micaceous when the bath is fresh, and dull and earthy looking with old solutions. The surface lustre is easily scratched, and becomes yellowed with the air. In order to preserve its freshness, the article should be covered with a thin coat of colorless alcohol.

We have already seen that an article, rendered



yellow by the alteration of the subcyanide silver, may be restored to its primitive whiteness by the combined action of heat, borax, and a feeble solution of either nitric or sulphuric acid; or, more simply, by an immersion for a few minutes in a tepid solution of cyanide of potassium, without the battery.

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## CHAPTER XXXVII.

### METHODS BY WHICH THE WEIGHT OF DEPOSITED SILVER IS ASCERTAINED.

To ascertain with exactness the quantity of silver deposited upon a given surface and in a given time, is an important problem for the silver electroplater to solve. With the different dispositions previously described, we cannot arrive at very correct results, and, although a long practice may facilitate the operation, there is always more or less guesswork and uncertainty.

We give herewith some of the methods employed by electro-platers, following the directions given by Roseleur: Let us suppose that twelve tablespoons are to be coated with two ounces of silver. The articles are cleansed by the processes already described, then dried in sawdust or otherwise, and weighed in a scale. However rapid this manipulation may be, the surface of the metal will be slightly oxidized and tarnished by contact with the fingers or by the sawdust; and, in order to restore their former brilliancy, the articles must be plunged into a strong pickle of sulphuric acid, and then into the "quicking" solution. After rinsing, and a more or less protracted immersion in the bath, the operator will judge, by his practical expe-

it is nearly time to withdraw the spoons from the bath. He thereupon removes, dries, and weighs them, and returns them again to the bath with the above-cautions; and this operation must usually be repeated several times until the proper weight of silver is deposited.

In adopting this plan: they cleanse the spoons or forks immediately into the bath, except one, treated as above and is used to control the operation. This piece is now and then removed from the bath to ascertain its increase of weight, and when it has reached the correct proportion of silver as determined by calculation, it is assumed that the balance of the articles also received their proper quantity and that the operation is complete.

These methods are obviously defective and erroneous. In any place, the operation is tedious, and it will be out of a thousand if the correct result is arrived at. To determine the quantity of silver deposited on the piece to control the operation will be materially to alter the condition of the wire from which it is hung, the pressure of its contacts and its distance from the bath in which it will be apparent that the most errors may be reached, if the quantity of silver to be deposited upon the other articles be calculated from the increase of weight of the test piece.\*

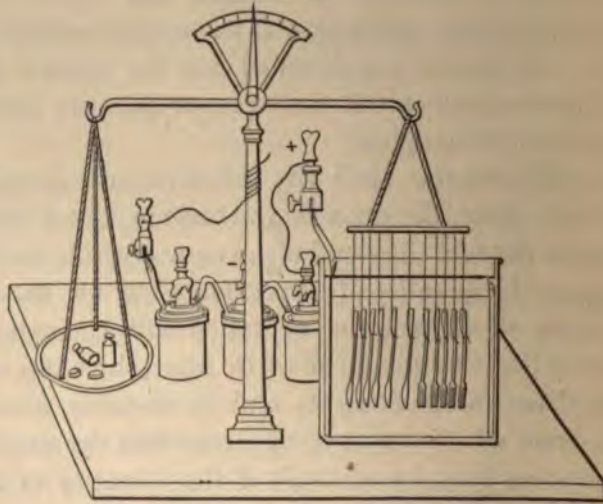
Amalgamated articles will become sensibly oxidized during the operation which precedes their weighing.

Before the operation, the objects have been dried in order to determine the proportion of deposited silver, they should not be returned to the bath without having been cleaned in a hot solution of potassium cyanide, which dissolves the grease from the handling, through the "quicking" solution, and rinsed. Alcohol substituted for the hot solution of cyanide, but the results are not so accurate and the expense is greater.

This inconvenience is obviated, and the precise moment when the given proportion of silver has been deposited may be recognized, by the following very simple procedure.

After having removed one of the pans of an ordinary balance, substitute for it a metallic frame which supports the articles to be silvered, and which communicates through the beam and column of the balance, with the negative electrode of the battery. The anode is connected with the positive pole (Fig. 118).

Fig. 118.



When the articles, spoons and forks for instance, suspended from this frame, are placed in the silvering bath, the equilibrium of the balance is established by placing weights in the other pan. The quantity of silver that it is intended the articles shall receive being determined, the corresponding weight is placed in the scale-pan. It is scarcely necessary to add that the operation will be finished when the equilibrium of the balance is re-established.

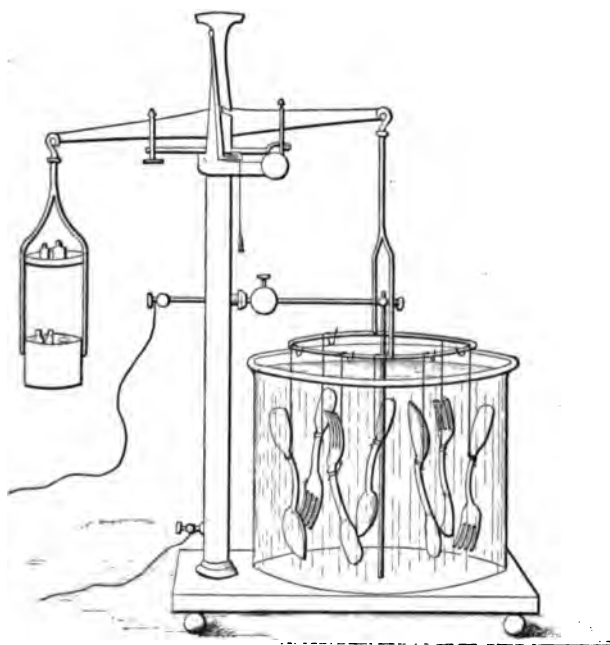
This method is not mathematically accurate, since the



cles are more bulky after than before the silvering process; nevertheless it is sufficiently exact for all practical purposes.

A careful operator will employ a balance for each bath, especially when silvering spoons and forks. The supporting frames may be circular, in order to have the anode in the centre of the bath so that the articles shall be at equal distances from it in order that they shall all receive same amount of deposit. The central anode may be forced by another circular anode laid on the sides of

Fig. 119.



vessel, so that the articles are exposed to the action of the current on both sides. Lastly, there is no difficulty in disposing a signal bell in connection with the pointer of the balance that it will indicate the precise moment

when equilibrium is established and the operation completed (Fig. 119).

We see that, in this arrangement, the articles to be silvered are connected with the negative pole through the column, the knife-edges, and the beam of the balance. The anodes communicate with the positive pole by means of a conducting wire passing through the column of the balance, but insulated from it by a glass tube which surrounds it. This apparatus may be modified in many ways.

An apparatus of the character of that just described, will obviously enable the operator to determine with great precision the weight of silver deposited; it will save much labor, it will economize battery power; and finally, where several of the above-described baths are employed, there will be no danger of a complete stoppage of work by reason of a faulty bath, which is frequently the case where a single depositing vat is used.

Mechanical devices for automatically breaking circuit, when the predetermined amount of silver has been laid on articles in the plating-bath, and for indicating the fact by signal, or otherwise, are numerous. Some of these have been made the subject of patents, and in various modifications such devices are in use in all the large establishments.

## CHAPTER XXXVIII.

## ROSELEUR'S PLATING-BALANCE.

A PLATING-BALANCE WHICH DEPOSITS WITHOUT SUPERVISION, AND WITH CONSTANT ACCURACY, A PREDETERMINED QUANTITY OF SILVER, AND WHICH AUTOMATICALLY BREAKS CIRCUIT WHEN THE OPERATION IS TERMINATED.

WE describe in this chapter an automatic plating-balance, designed by Roseleur, a very elaborate but perfect apparatus for its intended purpose. We give the description in the words of the inventor.

The several forms of plating-balance in general use, though very convenient, are still imperfect, for the reason that the operator must be present when the operation is finished, in order to withdraw the objects from the bath, or to arrest the action of the battery. The personal attention thus demanded is not always possible, and is frequently irksome and inconvenient, especially where baths are kept in operation day and night which will deposit a great excess of silver, if they are not arrested in time.

We have succeeded in avoiding all the inconveniences pointed out by means of the plating-balance about to be described.

Of the four sizes of this apparatus manufactured, the smallest is sufficient for a half-dozen of forks or spoons, and is intended for the use of amateurs, chemical laboratories, etc.

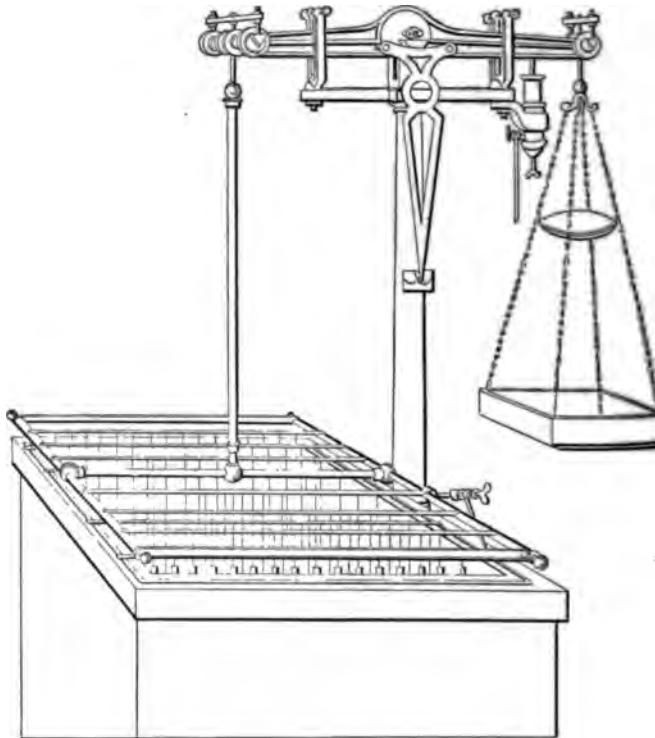
The other three sizes are designed for manufacturers,



and will carry four, six, or twelve dozens of forks and spoons, or a proportionate quantity of other articles.

The balance designed for the use of manufacturers has the following parts (Fig. 120):—

Fig. 120.



1. A depositing vat of wood lined with gutta-percha which renders it impervious, and which is not acted upon by the bath.

Around the upper ledge of this trough is carried a brass rod attached by small nails penetrating the wood through the gutta percha. This rectangle (Fig. 121) has a screw connection at one extremity for attaching the

ducting wire from the positive pole of the battery, and supports the several anodes suspended in the liquid, from cross-rods of brass, by means of hooks of platinum wire.

Fig. 121.

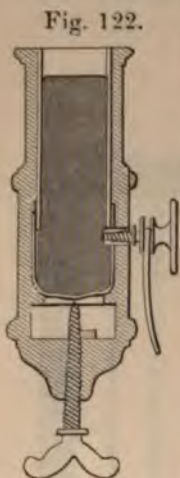


These cross-rods have their extremities filed flat, so as not to roll, and to increase their surface of contact with the brass rectangle.

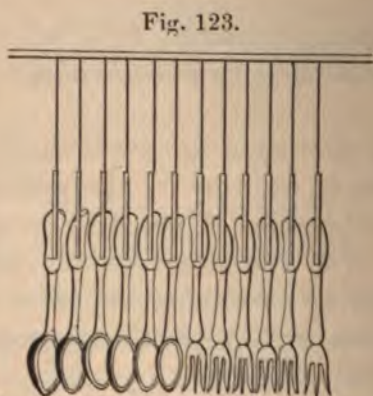
2. A cast-iron column screwed at its base to the side of the trough, and which carries near the top two projecting arms of cast iron, the extremities of which are vertical and forked, and may be opened or closed by iron clamps. These forks are intended for sustaining the beam, and preventing the knives from leaving their bearings under the influence of too violent oscillations.

At the centre of the two arms are two wedge-shaped recesses of polished steel to receive the knife-edges of the beam.

One of the arms of the column carries at its end a horizontal ring of iron, in which is fixed a heavy glass tube supporting a cup of polished iron, which is insulated from the column (Fig. 122). This cup has at its lower part a small pocket of lamb-skin or of India-rubber, which, by means of a screw beneath, may be raised or lowered. This flexible bottom allows us to lower or raise at will the level of the mercury introduced afterwards into the iron cup. Another (lateral) screw permits connection to be made with the negative electrode.



3. A cast-iron beam, carrying in the middle two sharp knife-edges of the best steel, hardened and polished. At each extremity there are two parallel bearings of steel separated by a notch, and intended for the knife-edges of the scale-pan that receives the weights, and those



of the frame supporting the articles to be silvered. One of the arms of the beam is provided with a stout platinum wire, placed immediately above and in the centre of the

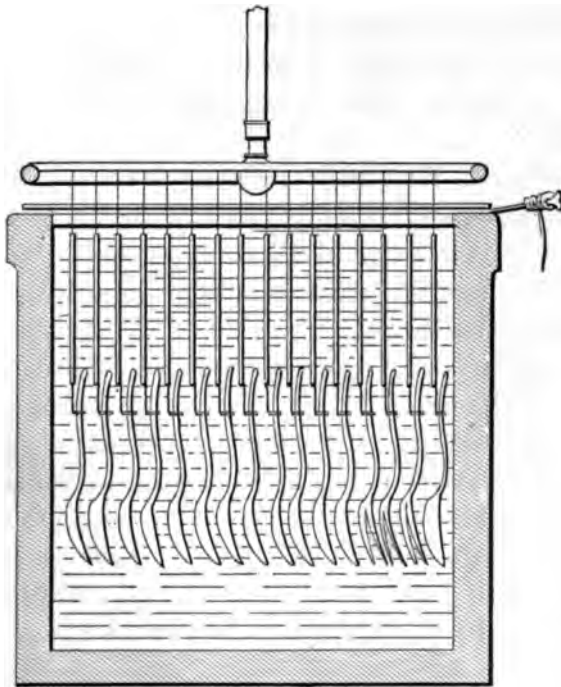


p of mercury. According as the beam inclines one way or the other, this wire plays in or out of the cup.

4. A scale-pan for weights, with two knife-edges of cast steel, which is attached to four chains supporting a wooden beam for the reception of weights. A smaller pan above intended for the weights corresponding to that of the lower to be deposited.

5. The frame for supporting the articles to be silvered, which is also suspended from two steel knife-edges, and the rod of which is formed of a stout brass tube attached below to the brass frame proper, which last is equal in

Fig. 125.



mensions to the opening of the vat, and supports the various cross-rods bearing the articles.

6. Lastly, a certain number of suspension cross-rods (Fig. 123), made of brass, and flattened at their extremities so as not to roll and to have a larger surface of contact. The slinging wires are of copper, and are soldered with tin into holes drilled for their accommodation. These wires are bent at their extremities in such a manner that the fork or spoon may easily be inserted or removed. Fig. 124 represents this terminal hook in full size.

The straight portion of these wires which dips into the liquid is covered with a small tube of India-rubber, which prevents the useless deposit of silver upon them. The looped portions, however, become coated with silver, which may be removed by the use of acids, after having raised the India-rubber tube.

Fig. 125 represents a vertical and transverse section of the depositing vat, when in operation.

#### DISPOSITION OF THE APPARATUS.

The vat is set upon four blocks, one at each corner, so that, having a free circulation of air under it, the bottom will not rot, and the whole is, by the aid of a spirit-level, set perfectly horizontal.

The column is then screwed on, and made vertical by the aid of the plumb-bob. After having withdrawn the iron clamps from the forks, the beam is put in place with great precaution, so as not to injure the knife-edges which rest in the bearings at the centre of the column. The clamps are then put in place, and the beam should now oscillate freely upon the knife-edges without friction.

Then the frame supporting the articles to be silvered, with its two knife-edges, is put in place; and finally the scale-pan with its knife-edges.

A small quantity of mercury is then poured into the

six bearings where the knife-edges rest, until all the polished parts of the latter are covered. This mercury presents the following advantages:—

1. It prevents the corrosive action of the acid vapors of the work-room upon the polished parts of the knife-edges and their bearings.

2. The friction is lessened, and the weighings are more correct.

3. It considerably increases the surfaces of contact for the passage of the electric current.

4. It prevents the loss of temper which the knife-edges would otherwise suffer by the excessive heat to which they would be exposed.

Lastly, the insulated steel cup is filled with mercury, until the point of the platinum wire attached to the beam just touches it when the equilibrium is established, that is to say, when the index marks zero. The surface of the mercury should be, now and then, cleaned of any dust which may prevent the passage of the current. The small flexible pocket is used for raising or lowering the level of the mercury, and thus permitting of the exact adjustment of the balance.

#### USE OF THE BALANCE.

1. The depositing vat is filled up with the silver bath to within a few inches of the upper edge.

2. The anodes are hooked upon their respective rods, each of which rests upon the brass rectangle nailed upon the vat, forming a connected system, communicating by means of the binding screw with the positive electrode.

The silver anodes should dip entirely into the liquid, otherwise they will be rapidly cut at the water line, while, with complete immersion, the platinum supporting wires



are unacted upon.\* The anodes are placed parallel to each other, one at each end of the trough, and the intermediate ones are about 8 to 10 inches apart in order to leave a sufficient space for two cross-rods, supporting the spoons and forks.

3. Two transverse wooden bars are placed under the suspending frame, thus insulating it from contact with the anodes, and the cross-rods supporting the objects are placed upon the frame in such a manner that there are two rods for each space between two silver anodes. We must be careful to preserve the same distance between the anodes and the spoons or forks, and, in order to avoid all uncertainty, the positions of the rods for the anodes and for those supporting the articles, are marked with a file. It is evident that if these equal distances be not preserved, the articles nearer the anodes will be charged more rapidly, and that the total amount of silver will not be equally divided. Furthermore, since two rows of objects are situated between two anodes, the surfaces facing the anodes will be coated more rapidly. It is necessary therefore, during the operation, to change the position of the supporting rods end for end. This manipulation is necessary if only a single row of articles is placed between, and at equal distances from, two silver anodes.

Before being introduced into the bath, the articles should be thoroughly cleansed and "quicked." For the rapid and easy handling of forks and spoons during these operations, a convenient holder (Fig. 126) is shown herewith,

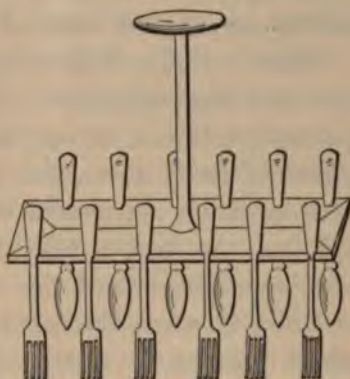
\* These anodes are plates of pure laminated silver, and should be at least as high as the articles to be silvered. Their width is from 1 to  $1\frac{1}{2}$  inches less than that of the vat. As it often happens that the rolls have left upon the silver traces of grease and of oxide of iron, the plates should be heated to a dull red and cleansed before using, or a simple cleansing in boiling lye is sufficient.

made of gutta-percha, and composed of a handle attached to a plate having twelve notches sufficiently narrow at their entrance to allow of the introduction of the forks and spoons by their thin edges only. From the entrance

Fig. 126.



Fig. 127.



the notches gradually widen, so that the forks and spoons when introduced will stand upright by their own weight. The edges of the notches are likewise bevelled, in order to diminish their surface of contact with the metal to be cleansed.

When twelve spoons or forks have been cleansed in boiling lye, and passed through the acid pickle, they are suspended to this support, and successively dipped into aqua fortis, the mixed acids, and the "quicking" solution. The holder and its contents are then plunged into a large tub filled with water, when, by giving it a sudden down-and-up motion, the articles are released and fall from the notches.

This gutta-percha holder is scarcely attacked by the cleansing acids, and presents the advantage of giving more rapidity in the operation, great cleanliness, and a sensible economy. Two of these supports are necessary;



one of which is being filled while the other is being passed through the cleansing acids.

When all the articles for the same bath are thus prepared they are suspended from the rods. This labor is made easy by supporting each rod at its extremities upon two long hooks fixed to the wall, and then introducing each piece into the hook of the slinging wire.

When a rod is thus charged, it is taken by its extremities, and the suspended articles are plunged first into quicking solution, or very dilute sulphuric acid, then into a bath of fresh water, and lastly into the silvering bath. The operation is repeated with the other rods.

When the bath is filled with the articles, the wooden box is weighted until the equilibrium of the balance is established, when the index marks 0. The wooden bars which prevent the supporting frame from resting directly upon the trough, and thus making contact with the anodes, are raised up.

The equilibrium of the balance is now destroyed by placing upon the intermediate scale-pan a weight equal to that of the silver which we desire to deposit on all the articles. Following the inclination of the beam, the platinum wire attached to it penetrates the mercury contained in the iron cup; and it is then sufficient to connect the battery with the apparatus by the two conducting wires communicating respectively with the cup and the anodes, in order to commence plating.

It will be readily understood from the foregoing description that when the articles have been coated with a proportion of silver equal to the weight in the pan on the other side of the beam, the equilibrium of the balance will be re-established, and the platinum wire will be raised out of the mercury, thus breaking the electric cir-



cuit, and stopping the deposition of silver, precisely as if one of the conducting wires had been cut.

The operation will, therefore, run its course without personal surveillance or attention; and, what is more, the results will not be modified, whatever be the length of time the articles remain in the solution. An excess of silver cannot be deposited, since there is no electric current; on the other hand, should the bath dissolve a certain proportion of the deposited silver, the articles become lighter, and the equilibrium of the balance is again broken, resulting in the platinum wire re-entering the mercury, and closing the circuit anew. We have therefore a series of oscillations, due, on the one hand, to a slight excess of the electro-deposit, and on the other to its partial solution in the cyanide, and the result is that the amount of the deposited silver remains within the proportions determined upon in advance.

GENERAL DIRECTIONS FOR KEEPING THE PLATING-BALANCE  
IN ORDER.

When a silvering operation is complete, the weights should be carefully removed from the scale pan, in order that the supporting frame carrying the silvered objects shall come to rest gently and squarely upon the vat. Any violence in this operation may endanger the knife-edges. The rods with the articles may then be easily removed.

The parts of the apparatus which demand the greatest cleanliness are the two binding screws through which the current is transmitted; the points of contact of the rods carrying the articles, with the supporting frame; and lastly those of the anode rods with the rectangular brass rod fixed to the vat.

Acids should never be used for cleansing any part of

the apparatus. The best substances for the purpose are sand and emery paper, or, preferably, a rag with finely powdered pumice-stone or ashes.

The apparatus should, in all cases, be handled gently, as any rough usage will be apt to endanger the sharpness of the knife-edges; and, lastly, the apparatus should not be called on to carry a greater weight than that for which it is intended.

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## CHAPTER XXXIX.

### BURNISHING.

BURNISHING is the operation by which the asperities or surface irregularities of an object are flattened down by friction, with an instrument called the burnisher, so that all the molecules of the surface are, as far as practicable, levelled to the same plane which then reflects the light as does a well-polished mirror.

Burnishing is therefore an important operation for improving the appearance of electro-deposits, which are constituted by the juxtaposition of a multitude of small crystals with vacant spaces between them, and with facets reflecting the light in every direction. There is, moreover, a great advantage in flattening down these crystals, as by so doing we close the meshes of the network presented by all deposits obtained by the humid way. The deposited metal is at the same time hardened, and, so to speak, forced to penetrate into the pores of the underlying metal. The durability of the coating is thus increased to such an extent, that there is no exaggeration in affirming that, with the same amount of silver, a burnished article will last twice as long as one which has not been so treated.

The instruments employed for burnishing are made of various materials, but all of them must fulfil the requisite conditions of great hardness and a perfect polish.

Hardened cast-steel and several varieties of quartz such as agate, flint, and blood-stone, answer the purpose. For burnishing metallic electro-deposits, steel and blood-stones are especially used. There are several qualities of blood-stone. It should be hard, and must have a close texture without seams or veins; it should leave no white lines on the burnished parts, nor take off any metal, and its color should be of an intense black-red. Burnishers of steel must have a fine, close grain, and be susceptible of taking perfect polish. Should the polish of any of the burnishing tools become impaired by use, it is restored by friction upon a pad of skin or leather attached to a wooden block, which is fixed to the bench by four protruding points of iron (Fig. 128). The pad is charged with polishing rouge

Fig. 128.



(colcothar, sesquioxide of iron), in impalpable powder, or, preferably, with pure alumina obtained by the calcination of ammonia alum. Venetian tripoli; rotten-stone, putty-powder, emery, and many other hard substances in a state of fine division, may also be employed.

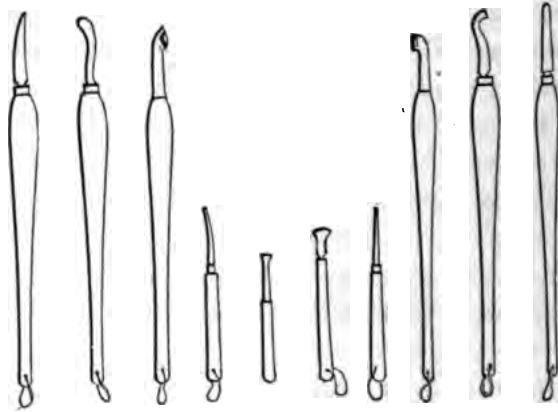
The shapes given to burnishing tools are various (Fig. 129). Some are lance-shaped, others resemble a tooth, or a knife; others imitate a hind's foot, the olive, a half sphere, a dog's tongue, etc. etc. A considerable stock of these instruments is necessary.

The burnishing operation is divided into two distinct parts: the first consists in roughing, and the second in



finishing. The tools are also of two kinds: the first presents quite a sharp edge, whereas the latter has a rounded

Fig. 129.



surface. An experienced worker cannot be induced to part with a good burnishing tool, since he is so fully cognizant of its value for rapid and successful work.

The operation is conducted in three different modes: by hand, on the lathe, and by the arm. The tools for the hand or the lathe are fixed, by means of copper ferrules, to wooden handles, cylindrical and short, in order that the hand be not influenced by their weight. On the contrary, the tools for the arm or the vise are fastened to wooden handles sufficiently long to rest their slender part upon the arm or the shoulder, whereas the stouter portion is grasped by the hand.

The burnisher's tool and the objects are frequently moistened with certain solutions, some of which simply facilitate the sliding of the instrument, while the others have a chemical action which affects the shade of the burnished articles. The first category comprises pure water, solutions of soap, decoctions of linseed, and infu-

sions of the roots of marshmallow or liquorice; the second includes wine-lees, cream of tartar, vinegar, alum-water, etc.

To burnish the gold applied upon electro-deposits of copper (as is the case in dead gilding by that method), it should simply be wet with saliva, for fear of producing a disagreeable red shade. A solution of dark soap is generally preferred by operators, although when old it imparts an unpleasant tinge, due to the decomposition of sulphur compounds, that it often contains.

In some establishments, in which plated table-ware in large quantity is turned out, ingeniously devised burnishing machines driven by power are in use, by which much of the manual labor is spared. Without an illustration it would be useless to attempt a description of these machines. The knife, spoon, etc., each supported by its tip in a suitable holder, are slowly rotated, while the burnishing tool moves quickly over the surface, performing the work rapidly and satisfactorily.

When the burnishing is completed, the surface is wiped off longitudinally with an old, soft, calico rag; sawdust, and cloth, and tissue paper produce streaks.

The finish obtained by burnishing is satisfactory when it reflects the luminous rays like a mirror. Should the presence of mercury, or a bad deposit, or any other cause prevent the tool from producing a bright surface, the object is said to be greasy.

Articles which have been previously polished, such as steel mountings of lady's hand bags, and the like, and which generally receive a mere film of electro-deposit, are not burnished, but simply rubbed with a chamois skin and rouge of the finest quality.

On the other hand, electro-deposits that are too thick, or that have been laid too rapidly, cannot be burnished,

but are polished on the buffing-wheel—a wheel made of a large number of circular disks of cloth, held firmly together by flanges of wood, and mounted on a spindle—or by rubbing with a skin impregnated with a mixture of oil and some hard powder, like pumice-stone, tripoli, putty-powder, rouge, etc. Coarse powders are used at the beginning, and finer ones at the end of the operation.

There is, therefore, a great difference between polishing and burnishing, since the former levels the surface by removing the asperities, whereas the latter crushes and flattens them.

Polished silver deposits are more agreeable to the eye than burnished ones; but the hardening of the latter renders them more durable.

## CHAPTER XL.

### “STOPPING-OFF” VARNISHES.

“STOPPING-OFF” is the manipulation by which certain parts of a metallic article (which may be already covered with an electro-deposit on its whole surface) are coated with another metal. For instance, if it be desired to gild the parts in relief of an object, the body of which is silvered the other portions are “stopped-off,” and *vice versa*. This operation is easily performed, and simply requires a little practice and care, and especially a firm hand to make thin lines with the hair pencil.

The method of procedure is as follows:—

After having thoroughly scratch-brushed and wiped the object, the parts which are intended to remain with the primitive color are covered by means of a brush with



a "stopping-off" varnish, which is dried in the air, or in a stove, or over a gentle fire until it no longer sticks to the fingers. The object is then ready to be put into the bath.

"Stopping-off" varnishes are generally solutions, in boiled linseed oil, or essence of turpentine, of certain resins, like copal, elemi, gallipot, etc.; and, as these varnishes are not sufficiently colored to distinguish the places where they have been laid on, they are mixed with a certain proportion of red-lead, or, preferably, chrome-yellow (chromate of lead), which at the same time enhances their drying properties. The coloration of the varnish may also be produced with artificial ultramarine, or Prussian blue.

For a varnish that will resist the solvent power of the hot alkaline gilding liquid, Gore (*Electro-Metallurgy*, 182) recommends the following composition, viz:—

Translucent resin . . . . .	10 parts.
Yellow beeswax . . . . .	6 "
Extra-fine red sealing-wax . . . . .	4 "
Finest polishing rouge . . . . .	3 "

A general receipt for a varnish by the same author is "best quick-drying copal varnish, with some peroxide of iron, or ultramarine mixed with it, for 'stopping-off' in hot cyanide solutions; or mixed with chromate of lead, if for use in cold liquids. It dries in about three or four hours." It is manifest that compositions for this purpose may be varied almost indefinitely, according to the convenience or personal preference of individual operators.

It is evident that the galvanic deposit will coat only those parts unprotected by the varnish. As far as practicable, the temperature of the bath should be low, and the current weak, for fear of having frayed lines along the

edges where the deposit touches the varnish, in consequence of the latter becoming softened, or from gas bubbles which are disengaged at the negative pole under the action of a strong electric current. When the deposit is completed, the varnish is removed with warm essence of turpentine, and afterwards with tepid alcohol; but it is preferable to use gasoline or benzole, which dissolve rapidly, and in the cold, nearly all resinous and fatty bodies, and which volatilize readily. The varnish may also be destroyed by a brief immersion in concentrated sulphuric acid when cold.

It often happens that several colors and metals are associated upon the same object, such as silvering, both bright and dead; gilding, yellow, green, red, white, or pink; and platinum, etc. The choice of the combinations which will appear the most pleasing is for the artist to determine. We have already stated in the chapter on "stopping-off" varnishes, which follows the gilding processes, that such varnishes were employed for avoiding the deposit of the precious metals where their presence would be useless.

## CHAPTER XLI.

### ORNAMENTING PLATED SURFACES.

OLD (ANTIQUÉ) SILVERING—"OXIDIZED" SILVER—NIELLED  
SILVERING—DEAD SILVER—SATIN-FINISH.

*Old (Antique) Silvering.*—Articles silvered by the wet way may be given a *patina*, or antique appearance, by various methods, of which several are described in what follows.

This operation consists in imparting to silvered articles

certain tints resembling those of old artistic productions made of solid silver. With this object, the groundwork and hollow portions, which are not subject to friction, are covered with a blackish-red and earthy coating, while the parts in relief are left with a leaden, but brilliant lustre.

This operation is very simple. A thin magma of finely powdered plumbago (black lead) with spirits of turpentine (to which a small proportion of red ochre is sometimes added, for imitating the coppery tinge of certain old silverware) is smeared all over the articles. After drying, a gentle rubbing with a soft brush removes the parts without adherence; and the reliefs are set off (discharged) by means of a rag dipped into alcohol. *Old silver* is of a pleasing appearance upon objects imitating antique cups, chandeliers, vases, statues, etc.

Old silver is easily removed, and the primitive brightness of the metal restored, by the use of a hot solution of caustic potassa, or cyanide of potassium. Benzole may also be employed.

In order to impart the old silver tinge to small articles, such as buttons, rings, etc., they are agitated in the above magma, and then "tumbled" with a large quantity of dry sand until the desired shade is obtained.

A great many operators, at the present day, produce the antique silvering by beginning with the oxidizing process about to be described, and setting off the reliefs by means of a hard brush and pumice-stone, or Spanish-white. This last process is almost exclusively used for metallic mountings of books and albums.

*Oxidized Silver.*—This term is a misnomer, since the operation involves not an oxidation, but a combination with sulphur or chlorine. We have retained the word, simply because it has been consecrated by custom.

It is well known that sulphur, soluble sulphides, and



hydrosulphuric acid (sulphuretted-hydrogen) blacken silver. This phenomenon may be noticed every day in the action upon this metal of the yolks of eggs (especially such as have lost their freshness), noxious gases, etc. It is also known (and the art of photography is based upon this phenomenon) that insoluble silver salts, and particularly the chloride of this metal, rapidly blacken under the influence of solar light.

It is thus easy to blacken silver, and consequently to "oxidize" it (using the word in its conventional sense), by treating it with one of the reagents above named. We may use vapors of sulphur, hydrosulphuric acid (free or combined), liver of sulphur or other polysulphides, hypochlorite of lime (bleaching-powder), or Javelle water. In the majority of cases, heat will be required to render the action of these substances more rapid.

The operation is generally conducted as follows:—

Four or five one thousandths (that is to say, 4 or 5 parts to the thousand) of sulphide of ammonium, or, preferably, of pentasulphide of potassium (liver of sulphur) are added to ordinary water brought up to a temperature of about 150° to 175° F. As soon as the articles are dipped into this solution they become covered with an iridescent film of silver sulphide, which, after a few seconds more in the liquid, becomes blue-black. The article is then removed from the water, rinsed, scratch-brushed, and, if necessary, burnished.

As far as practicable, liquid should be used at once after its preparation, otherwise the prolonged heat will precipitate too much sulphur, and the deposit will be wanting in adherence to such an extent that it may be removed with the finger, leaving after it a red tinge resembling copper, although the material may be brass or German-silver. Moreover, the "oxidation" obtained in

the freshly prepared liquid is always brighter and blacker than that produced in old solutions, which is invariably dull and gray.

If the coating of silver be too thin, and the liquid too strong, the alkaline sulphide dissolves the silver, and the underlying metal (copper, etc.) is laid bare. In this case, we are obliged to cleanse and silver again, and to use a weaker blackening solution.

The silvering obtained with the paste previously described, exhibits the "oxidized" effect very well.

The same object is often oxidized and gilded by the following method: After the whole surface has been gilded certain portions are "stopped-off" by covering with varnish in order to silver the remainder. Should the process of silvering by paste be employed, the gilding should be very pale, because it is not preserved, and is deeply reddened by the sulphurous liquid. When this inconvenience occurs from a too concentrated liquid, it is partly remedied by rapidly washing the article in a tepid solution of cyanide of potassium.

The "oxidation" by sulphur, we have said, is blue-black. For a number of years another coloring, called *deep black*, has been substituted for it, which may be obtained directly upon cleansed copper. The manipulation is very simple, and is as follows: from 100 to 150 parts of hydrous carbonate of copper are dissolved in a sufficient quantity of aqua ammonia, and the cleansed articles of copper are rapidly plunged into this solution, cold or tepid, where they become instantaneously covered with a fine black deposit. This coat is so thin that burnished articles look as though varnished black.

Similar effects may also be obtained by depositing on the surface of the article, or on certain portions thereof, a film of metallic platinum. The platinum solution is pre-



pared by dissolving a certain quantity of the metal in aqua regia, evaporating the resulting chloride to dryness, and, when cold, dissolving the mass in a small quantity of sulphuric ether or alcohol. This solution is applied with a brush to the parts of the surface to be oxidized. The spirit or ether almost instantly evaporates, leaving a film of platinum behind which, according to its thickness, imparts either a steel-gray or nearly black lustre to the surface. Instead of the ethereal or alcoholic solution, a hot aqueous solution of the platinic chloride may be used with equally satisfactory results. (Consult Platinizing by Simple Immersion, Chap. XLIV., p. 357.)

Dr. Elsner (*Chem. tech. Mittheilungen*) produces a brownish tint on plated goods, by applying to the surface a solution of sal-ammoniac, and a finer tint by means of a solution of equal parts of sulphate of copper and sal-ammoniac in vinegar. For a fine black effect, the same author uses a warm solution of sulphide of potassium or sodium.

Watt (*Electro-Metallurgy*, 134) gives the following formula, which is a modification of that of Elsner above given, viz:—

Sulphate of copper . . . . .	2 parts.
Sal-ammoniac . . . . .	2 "
Nitrate of potassium (saltpetre) . . . . .	1 part.

Dissolve in a little acetic acid, and apply with a camel's-hair brush to the surfaces to be "oxidized." The articles should be slightly warmed before applying the mixture. Fearn's procedure for imparting a pink coloration on silver surfaces, consists in immersing the article for a few seconds in a hot, concentrated solution of chloride of copper (cupric chloride). The article must then be well washed in water and dried, or may be dipped in alcohol, and the spirit allowed to burn off.

"Oxidized" silvering is intended, in many cases, as a substitute for the nielled silver, of which a description follow



*“Dead” Silver.*—A very pleasing “dead” appearance, which resembles frosted silver, may be obtained on plated articles, by depositing a blush of copper on the surface in a sulphate of copper solution, and laying a very thin coat of silver over the copper.

*Satin-Finish.*—The sand-blast is in use in certain establishments to produce the peculiar dead, lustrous finish, known technically as satin-finish, on plated goods; a template of some tough resistant material, like vulcanized-rubber, is made of the proper design, and when placed over the article protects the parts which it is desired to leave bright, from the depolishing action of the sand; while only the open portions of the template are exposed to the blast.

The apparatus employed for this purpose consists of a wooden hopper with a longitudinal slit below, through which a stream of fine sand is allowed to fall by opening a sliding cover. Closely surrounding the base of the hopper is a rectangular trunk of wood, extending some distance below the base of the hopper and tapering towards the bottom, to concentrate the sand jet. This trunk is closed about the sides of the hopper and open below, and is designed to direct the stream of sand upon the surface of the article presented beneath its orifice. To increase the rapidity of the depolishing action of the sand, a current of air under regulated pressure is admitted into the upper part of the trunk, which, when the sand valve is opened, propels it with more or less accelerated velocity upon the metallic surface below. For this purpose, either a “blower,” or an air-compressor with accumulator may be used; and the pressure may be regulated at will. The sand is thus driven with more or less velocity down the trunk by the air-blast admitted above, and, falling upon the surface of the article presented at

the bottom, rapidly depolishes the exposed parts, while those protected by the template are not affected. The articles are presented at the orifice of the trunk by the hands of the operator, which are suitably protected by gloves, and as rapidly as the depolishing proceeds he turns the article about until the work is done. The progress of the work is viewed through a glass window set in a horizontal table which surrounds the apparatus and which forms the top of a large box, into which the sand falls, and which is made tight to prevent the sand from flying about. A portion of this box in front, where the workman stands, is cut away, and over the opening is hung a canvas apron which the operator pushes aside to introduce the work. The sand that accumulates in the box below is transferred again to the hopper as required, and is used over and over again.

The satin-finish produced by the sand-blast is exceedingly fine and perfectly uniform, and the work is done more rapidly than with the use of brushes in the usual way.

*Niel, or Nielled Silvering.*—This product, which still bears the name of the inventor, is obtained by the sulphuration of certain parts of a silver object. But this sulphuration instead of being made directly upon the surface, as in the method just described, is made by inlaying the silver surface with a sulphide of the same metal prepared beforehand. Nielling may therefore be called a species of enamelling.

After having prepared the nielling composition, an operation which consists in forming a triple sulphide of silver, lead, and copper,\* and reducing it to a fine powder.

\* For preparing the nielling composition a certain proportion of sulphur is introduced into a stoneware retort, or a deep crucible. A mixture of silver, copper, and lead is heated in another crucible, and

which is mixed with a small proportion of a solution of sal ammoniac, the artist executes the engraving upon the surface, and covers the whole, hollows and reliefs, with the nielling composition. The article is then heated in a muffle until the composition melts, when it will be found to adhere firmly to the metal. The design is brought out in very effective contrast by denuding the surface in relief, without touching the hollows, which receive a fine black.

This method is costly, since each article must be engraved. The arts have called to their aid another and a simpler process, which consists in engraving in relief a design on a plate, which, applied to a sheet of silver, subjected to great pressure in a die, reproduces a faithful copy of the engraving. The silver sheet thus stamped is ready for use without the nielling. A large number of copies may be made from the same matrix.

This is the method by which a quantity of nielled

metal is melted and poured into the fused sulphur, which transforms these into sulphides. A small portion of sal ammoniac is then added, the excess being removed from the crucible, or retort, the product is cooled and is then ready for use.

Give herewith the proportions indicated by Mr. Mackenzie, who has paid much attention to the subject.

Ingredients of the first crucible:—

Flowers of sulphur . . . . .	750 parts.
Sal ammoniac . . . . .	75 “

Ingredients of the second crucible, which, after fusion, is poured into the plate:—

Silver . . . . .	15 parts.
Copper . . . . .	40 “
Lead . . . . .	80 “

Mr. Mackenzie is of the opinion that it is preferable to diminish the proportion of lead, the sulphide of which impairs the blue shade of the metal and corrodes too deeply.



articles are manufactured, such as so-called Russian snuff-boxes, cases for spectacles, bon-bon boxes, etc.

Roseleur suggests the following plan for obtaining effects similar to nielled silvering, which he recommends to the attention of artists and manufacturers: a pattern of the design cut out of thin paper, like lace paper is dipped into a thin paste of nielling composition, or into a concentrated solution of some sulphides, and then applied upon the plate of silver which is afterwards heated in the muffle. The heat will destroy the organic substance, and a pattern will remain formed by the composition absorbed by the paper.

## CHAPTER XLII.

### DISSOLVING SILVER FROM SILVERED ARTICLES ("STRIPPING").

WHEN a silvering operation has failed from want of adherence of the deposit, or by reason of a granular surface, or when we desire to replate old and worn articles, it is absolutely necessary to remove the silver in order to restore the surface of the metal to its primitive state, and to permit of the proper repetition of the series of cleansing operations.

The operation is conducted either in the cold, or with the aid of heat.

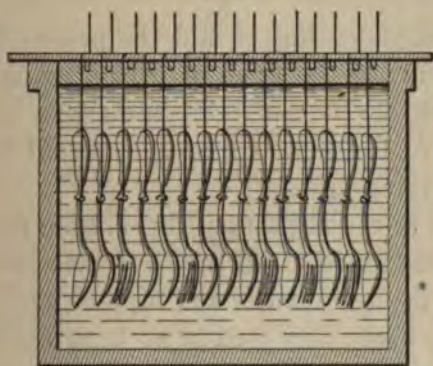
The following is the procedure recommended by Roseleur and other experienced electro-platers for dissolving silver in the cold, viz: The objects are suspended in a large vessel (Fig. 130) filled with the following mixture: Sulphuric acid of 66° Baumé (concentrated oil vitriol), 100 parts; nitric acid of 40° Baumé (concentrated

ed aqua fortis), 10 parts, in which they should remain for a greater or less length of time, according to the thickness of the coating of silver to be dissolved.

This liquid possesses the remarkable property, when diluted with water, of dissolving the silver without sensibly affecting copper and its alloys, such as bronze, brass, German-silver, packfong, similor, etc. The articles introduced into it should therefore be dry and when not in use the liquid should be kept in a hermetically closed vessel, as it eagerly absorbs moisture from the air.

As far as practicable, the articles, a number of which are usually "stripped" together, should be placed in the liquid without touching each other, and in a vertical position, as shown in Fig. 130.

Fig. 130.



In proportion as the action of the liquid diminishes, small and successive additions of nitric acid are given to it. While the process of dissolving silver in the cold is therefore regular and certain, its action is considered too slow by some operators, especially when the proportion of silver is great. Another, and more rapid, process is then resorted to, viz:—



A shallow pan of enamelled cast-iron (Fig. 131) is nearly filled with concentrated sulphuric acid and the whole brought up to a temperature of from 300° to 400° F. Then, at the moment of using it, pinches of

Fig. 131.



dry and pulverized nitrate of potassium (saltpetre) are thrown into it, and the article, held with copper tongs, is plunged into the liquid. The silver is rapidly dissolved, while the copper, or its alloys, is but slightly corroded.

It is scarcely necessary to add the precaution that the articles should not be allowed to remain in the "stripping" liquids any longer than is actually necessary for the removal of the silver, in order to avoid the corrosion of the underlying metal.

According to the rapidity of the solution fresh additions of saltpetre are made. All the silver has been dissolved, when, after rinsing in water and dipping the articles into the cleansing acids, they present no brown or black spots, that is to say, when they behave like new.

These two methods are not suitable for removing the silver from wrought and cast-iron, zinc, or lead, for which purpose it is preferable to employ a cyanide bath with the electric connections arranged in the inverted order; in other words, to make the articles the anodes; or, to use mechanical processes.

These desilvering (stripping) liquids become green after a certain amount of use, and, in order to recover the



ver, they are first diluted with four or five times their volume of water, and then treated with hydrochloric acid, or common salt. The precipitation is complete when the supernatant liquid does not become turbid by a fresh addition of common salt, or of hydrochloric acid.

The resulting chloride of silver is separated from the liquid either by decantation or filtration, and is afterwards reduced to the metallic state by one of the methods to be hereafter indicated.

Where gold is to be removed from silver, which will sometimes be necessary, the methods described in Chapter XXVII. (page 260) should be followed. Occasionally so it becomes necessary to remove copper from silver—where, for example, a thin copper mould must be dissolved from a solid electro-deposit of silver. In such case it is recommended to immerse the article in boiling diluted hydrochloric acid, or in a hot solution of perchloride of iron (ferric chloride), made by dissolving, with the aid of gentle heat, the peroxide of iron (jeweller's rouge) in hydrochloric acid, to complete saturation. Some authorities suggest the removal of copper from silver, by making the article the anode in a sulphate of copper solution, and passing the current until the copper has disappeared; but there is a risk of losing some of the silver by solution, especially if the current employed is strong.

As above remarked, worn and defectively coated articles that are to be replated should under no circumstances be replated without having first been "stripped." Some operators replate without this precaution, but the work thus performed is usually inferior, because of the difficulty of securing the perfect adhesion of the second coating of silver, on the portions of the original coating that remain, from which portions the newly-laid silver will often show tendency to separate or "strip." A few unpleasant

experiences of this kind will soon impress on the mind of the operator more forcibly than precept, that in the long run it is safer to thoroughly remove an old coating before attempting to replate.

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## CHAPTER XLIII.

### ELECTRO-SILVERING—CONCLUDING REMARKS.

IN preparing the cyanide plating solution by the chemical method described in this work (Chapter XXXIV, p. 288 *et seq.*), care should be taken by the operator, in dissolving his silver in nitric acid as directed, to use the *pure* acid, free from chlorine, with which the common commercial nitric acid is always more or less contaminated. Otherwise, a variable quantity of chloride of silver will be formed, which will render it impossible to obtain a clear solution of the nitrate in water, and which will interfere with the nicety of the subsequent operations. To test the quality of the acid, it will be sufficient to pour a little of it into a test-tube with some distilled water, and to add to it a drop of nitrate of silver solution, when the liquid should remain clear. If a milky turbidity or precipitate occurs, the acid should not be used. The same precaution should be observed with respect to the water in which the nitrate is dissolved previous to its precipitation with cyanide of potassium (or with hydrocyanic acid). For this purpose it is preferable to use distilled water, as ordinary water supplied to cities and towns invariably contains more or less of chlorides in solution. If, however, impure acid or water is used for the purpose, the insoluble matter should be allowed to subside, and, after the



liquid has been drawn off, should be reserved to recover the silver it contains.

In precipitating the nitrate of silver solution with cyanide of potassium special care must be taken not to add too much of this reagent, which would redissolve some of the precipitated cyanide of silver. To avoid this it is a good plan to conduct the operation in a glass vessel where it can be well observed, and towards the end of the operation, which can be told by the formation of a less voluminous precipitate upon addition of cyanide, to allow the precipitate to subside, and to add at intervals small quantities of cyanide at a time, stirring after each addition. By conducting this operation with the proper care, the point of perfect neutralization may be very closely arrived at. If by accident or carelessness too much cyanide has been added, the excess must be neutralized by the addition of a fresh supply of nitrate of silver, with due precaution, until the further addition of a drop causes no turbidity.

The cyanide plating solution may also be prepared with the aid of the electrical current, that is, by passing a strong current through a solution of cyanide of potassium ( $1\frac{1}{2}$  to 3 ounces of cyanide to the gallon according to purity) with a large sheet of silver as the anode, and a small strip of silver or of platinum as the cathode, and passing the current until enough silver has gone into solution to give the bath the standard strength. The amount of silver dissolved can readily be told by weighing the anode, and comparing the weight with that before the operation; and the proper saturation of the solution may be told by suspending an article at the cathode, and observing how readily it takes a silver deposit.

Napier's plan (*Electro-Plating*, 135 *et seq.*) for making "silver solution with the battery" is to employ a solution



of cyanide of potassium ( $1\frac{1}{4}$  ounces to the gallon), and to place in the vat one or more porous cells, which he fills up with the cyanide solution to the same height as the liquid in the outer vessel. In these porous cells he places small sheets of iron or copper, and connects them with the negative electrode; and in the outer vessel he suspends one or more sheets of silver, which he connects with the positive electrode. By using a strong current, and sufficiently large surfaces of silver, with this arrangement he is enabled over night to charge a bath with 60 or 80 ounces of silver.

This plan of preparing the plating solution is not generally in use, though it is handy for small operators. It saves considerable labor which the chemical method involves, and it effectually prevents any loss of silver. It has the disadvantage, however, of charging the bath with caustic potassa, an equivalent of which is decomposed for each equivalent of silver dissolved. The objections to the method, on this score, have already been stated in connection with the preparation of cyanide *gilding* solution by the same process (Chapter XXI., p. 210 *et seq.*).

Some operators modify the chemical method of preparing the electro-plating solution by using the oxide, the carbonate, or, as previously mentioned (Chapter XXXIV., p. 289), the nitrate or chloride of silver to the cyanide of potassium solution until no more will dissolve, and then adding what they consider to be a sufficient quantity of the latter to form free cyanide. Glassford and Napier (*Mem. Chemical Soc.*, London, vol. ii. 96) have shown very clearly that these procedures can accomplish *no saving of cyanide*, since precisely the same quantity of this reagent, namely, two equivalents of cyanide to each equivalent of silver, will be required to convert the silver oxide, carbonate, etc., into cyanide, and then into do

cyanide, as by the standard method we have described and recommended. Not only is there no saving, but the carbonate of potassium, caustic potassa, etc., used to precipitate the nitrate of silver, as carbonate, or oxide, is wasted; and more than this, the operator employing these methods is introducing into his bath large quantities of foreign substances (caustic potassa, carbonate of potassium, chloride of potassium, or nitrate of potassium), which are not only useless, but which directly or indirectly impair the efficiency of the plating solution.

As many electro-platers have the practice of converting their silver nitrate into chloride by the addition of common salt or hydrochloric acid, and dissolving the chloride thus formed in cyanide of potassium, this may partly explain the frequent difficulties they encounter in having these solutions to work in a uniformly satisfactory manner.

While all writers on electro-plating agree in the opinion that the introduction of foreign ingredients into the plating solution should be avoided as much as possible, none have so clearly and concisely stated the objections thereto as Gore, from whom we quote the following paragraph (*Electro-Metallurgy*, 159):—

“If, instead of cyanide of silver, we add oxide of silver to the cyanide of potassium liquid, it converts part of the cyanide into caustic potash; if we add carbonate of silver, it converts it into carbonate of potassium; and if chloride of silver, it converts it into chloride of potassium; and each of these substances, especially the last, diminishes the action of the liquid upon the dissolving plate; decreases its solvent power for cyanide of silver, makes its particles less mobile, and causes it to act in some degree upon base metals, and thus endangers the adhesion of the deposits upon them. Some electro-platers think the presence of these salts not injurious, but most consider

them highly detrimental. One hundred ounces of silver, converted into chloride, and dissolved in cyanide of potassium solution, produce sixty-nine ounces of chloride of potassium as an impurity in the liquid, or if converted into nitrate, and so dissolved, produce ninety-three and a half ounces of nitrate of potassium as impurity."

Finally, we may add that a large number of solutions for electro-plating have been made the subject of patents by various inventors, but in quality of results obtained and uniformity of operation, none can compare favorably with the standard double cyanide solution. The most promising of these numerous formulæ is a solution of chloride of silver dissolved in hyposulphite of sodium. This solution yields its metal readily with a very moderate current, but its tendency to decompose under the influence of sunlight, and to deposit its silver as sulphide, is a serious objection to it, which it has been impossible to overcome.

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## CHAPTER XLIV.

### PLATINIZING.

IN the year 1846 M. Roseleur had discovered and patented a procedure which was capable of furnishing deposits of any desired thickness. All previous efforts had resulted in obtaining only a mere film of platinum upon copper and its alloys. In 1847 he presented to King Louis Philippe a ewer and basin, upon which he had deposited about 400 grammes (nearly 13 ounces) of pure platinum, certain parts of which were dead, while others were burnished.

Notwithstanding the early date of this discovery, the



publicity given to the patent, which was offered without royalty to the public, and the complete description of the process in Roseleur's work, it is only within recent years that platinizing has found favor and secured an introduction into the arts.

*Platinizing by Simple Immersion.*

Platinum may be deposited either by simple immersion, or by galvanic action.

Copper and its alloys appear to be best adapted to receive a satisfactory platinum deposit; iron, zinc, lead, and tin coated with this metal, even after a previous coppering, yield only defective results.

Silver, on the other hand, accepts an adherent deposit of platinum, as we had occasion to notice in treating of the ornamentation of plated surfaces (Chapter XLI., p. 344), where a thin film of platinum is deposited on such surfaces, by bringing them in contact with a solution of the chloride either in water or in alcohol or ether. This operation is nothing else than a species of direct or simple immersion-platinizing. The platinum salt is reduced by the silver, with the formation of chloride of silver, which is disposed to make its appearance on drying as a whitish incrustation on the "oxidized" surface. A dipping in weak ammoniacal water will dissolve this coating. The color of the platinum thus deposited will vary from steel-gray to nearly black, according to the concentration of the platinum solution and its temperature.

For copper and its alloys, Roseleur proposes to immerse the articles in the following solution, kept boiling:—

Distilled water . . . . .	100 parts.
Caustic soda . . . . .	12 "
Platinum, or its equivalent of neutral chloride	1 part.

The deposit is bright, quite durable, but of a dark color resembling that of "oxidized" silver.

*Electro-deposits of Platinum.*

Solutions suitable for obtaining electro-deposits of this metal are numerous; the operation will succeed, in fact, with alkaline, neutral, or acid solutions, containing platinum chloride. The following formulæ will give, with the aid of heat and electricity, platinum deposits quite pleasing in appearance:—

*First Formula.*

Distilled water . . . . .	100 parts.
Carbonate of sodium . . . . .	40 "
Platinum . . . . .	1 part.

Temperature of the bath, from 150° to 175° Fahr.

*Second Formula.*

Distilled water . . . . .	100 parts.
Phosphate (or borate) of sodium . . . . .	60 "
Platinum . . . . .	1 part.

*Third Formula.*

Distilled water . . . . .	100 parts.
Pyrophosphate of sodium; or chloride, or iodide of sodium . . . . .	30 "
Platinum . . . . .	1 part.

These several formulæ are open to the objection furnishing only exceedingly thin deposits, since if the coating were permitted to go on increasing, most of it would be without adherence, and often in the form of scales. The deposit is black or steel-gray in color.

On the other hand, the procedure about to be described, which is that of MM. Roseleur and Lanoux, when properly carried out, will permit of the deposit of any desired thickness of platinum upon the same surface, and with a

color and lustre identical with those of platinum articles found in the arts.

One part of finely laminated platinum (platinum-sponge is preferable) is covered in a long-necked glass flask with a mixture of 15 parts of hydrochloric acid and 10 parts of nitric acid of 40° Baumé. It is then heated upon a plate of perforated sheet-iron, so that the bottom of the flask alone receives the heat. An abundant disengagement of orange-yellow fumes ensues, and the platinum disappears, leaving a reddish liquid, which should be heated until it becomes viscous enough to adhere to the sides of the flask. This latter part of the operation may be effected in a porcelain evaporating dish, the shallow form of which hastens the evaporation of the excess of acids. After cooling, the residuum is dissolved in 50 parts of distilled water, and, if necessary, filtered.

In a separate vessel, 10 parts of phosphate of ammonium are dissolved in 50 parts of distilled water, and the two solutions are mixed. A copious precipitate of phosphate of ammonium and platinum is formed in a liquid of orange color, which should not be separated, and into which should be poured, with constant stirring, another solution, composed of 50 parts phosphate of sodium in 100 parts of distilled water.

The mixture is made to boil, and the evaporated water is replaced, until no more ammonia is disengaged (which is ascertained by the smell), and until the liquid, which was previously alkaline, begins to redden blue litmus paper. By the reactions which take place, the previously yellow liquid becomes colorless, which indicates the formation of a double salt of sodium and platinum.

The solution is then ready to deposit platinum upon articles of copper, or its alloys; it is used hot, and with a strong electrical current. A platinum anode is used, but



as this is not dissolved by the solution the metallic strength of the bath must be maintained by occasional additions of the chloride of platinum.

Roseleur affirms that copper capsules thus coated with platinum resisted twenty successive evaporations of nitric and sulphuric acids alternately employed, though at last they were corroded.

According to the same authority, it is necessary to avoid with great care the contact of iron, zinc, lead, or tin with the bath, as these metals will decompose it, that is to say, platinize themselves by simple immersion, and the deposited metal will be black and pulverulent.

Dead-platinizing is pearl-gray; it is very hard, and cannot be brightened by scratch-brushes of brass, which render its surface yellow. Iron brushes, or, preferably, powdered pumice-stone, should be employed.

Platinum deposits may be burnished by energetic friction, and the lustre obtained is very durable.

As most platinized articles, such as chandeliers, fire grates, lamps, etc., are very lightly platinized, they are generally polished before coating. After the operation, they are rubbed with polishing rouge and chamois, whereby the difficulty of burnishing the platinum itself is avoided.

Platinum may be removed from copper by a very long immersion in the baths indicated for ungilding, but the operation is not always successful.

#### *Other Formulæ.*

Boettger (*Pharmaceutical Journal*, iii. 351) coats copper and brass with platinum as follows: he dissolves the double chloride of platinum and ammonium in water, adds thereto a few drops of ammonia, and uses the solution thus prepared, moderately heated, and with a con-

stant current. The deposited platinum is said to be adherent and lustrous.

Another solution of Boettger's for platinizing copper and brass either by simple immersion or by the current, consists of one part of double chloride of platinum and ammonium, and eight parts of sal ammoniac in water. The same author (*The Polytechnic Review*, vi. 255) recommends the following solution for obtaining electro-deposits of platinum. He treats freshly precipitated double chloride of platinum and ammonium, at boiling temperature, with a concentrated solution of the neutral citrate of sodium. The resulting liquid has a deep orange-red color, and a feeble acid reaction, and yields with a current of moderate intensity an adherent, lustrous coating of platinum.

Gore (*Electro-Metallurgy*, 120) refers to a solution made by dissolving the chloride of platinum in one of cyanide of potassium, the proportion of metal being kept at about one ounce to the gallon, and the bath used with a moderate current and warm. Jewreinoff prepares a solution for the electro-deposition of platinum on copper, brass, and iron as follows: Convert 10 parts of metallic platinum into chloride, and add thereto a solution of 10 parts caustic potassa in water. Dissolve the yellow precipitate by the addition of 20 parts of oxalic acid in aqueous solution, with the aid of heat, and add to the solution 30 parts of caustic potassa solution. The solution is strongly alkaline (soda may be substituted for potassa in this formula). A constant and moderate current is recommended, and Jewreinoff affirms that a platinum anode is dissolved in this liquid in the same proportion as platinum is deposited, so that the metallic strength of the bath is maintained without additions of platinum salt. This assertion we have had no opportunity to verify, but we



regard it as questionable. Gore, referring to similarly constituted solutions, says that it is difficult to obtain reguline white metal from them.

For platinizing sheets of silver Jewreinoff (Winckler, *Handb. d. Metallüberzügen*, 215) converts 3 parts of platinum into chloride, dissolves this in 300 parts of distilled water, and adds 20 to 25 parts of sulphuric acid. By using a platinum anode, the silver sheets soon accept a grayish coating of platinum, which simply requires to be washed.

A method of platinizing by contact with zinc, which is described as well suited for small articles is as follows (*Chemical News*, xix. 226): To a strong solution of platinic chloride, add powdered carbonate of sodium, until effervescence has ceased. Then add some glucose, and finally add enough common salt to cause a whitish precipitate. The small articles of copper or brass, to be coated, are placed in a colander of zinc, and immersed in the bath, kept at about 140° Fahr., for a few seconds. They are then removed, and dried in hot sawdust.

The deposition of platinum is attended with special difficulties, both on account of the non-solubility of the anode, which requires the operator to be adding fresh platinum salt from time to time where a solid deposit is desired; and also because of the disposition of the metal to give a black and pulverulent deposit. Roseleur's procedure is admitted to be the best that has thus far been devised for deposits of any thickness; and the citrate bath of Boettger is highly spoken of by those who have had occasion to use it.

*Palladium*, which belongs to the same group of metals as platinum, has also been experimented with as a coating for other metals. It appears to be more readily deposited from its solutions by the current.



For obtaining deposits of this metal, solutions have been made by dissolving the chloride in cyanide of potassium, or by saturating a solution of the cyanide of potassium with the metal, by the current, in the manner described with gold and silver. Cyanide of potassium appears to take up a considerable quantity of the metal, and the cyanide solution is said to yield the metal freely, so that heavy reguline deposits are not very difficult to obtain.

Bertrand (*Comptes Rendus*, tome. lxxxiii., 857) describes the double chloride of palladium and ammonium, perfectly neutral, as a good solution with which to obtain palladium deposits, either by immersion or by the current. An anode of palladium is dissolved, while the deposit is going on. Palladium, however, is one of the rarer metals; it does not protect other metals as well as platinum, and its behavior is therefore of no practical importance.

We had the opportunity, while this work was in course of preparation for the press, of seeing some remarkably fine electro-deposits of *iridium*, the hardest and most refractory and unalterable, of all the metals of the platinum group. These iridium deposits, upon various metals, exhibited a fine steel-gray lustre and color. The inventor, Dr. W. L. Dudley, of Cincinnati, stated to us that he had solved the problem of coating metals with iridium by the use of a suitable solution of the metal, and the proper regulation of the current, and that a company was engaged in practically working the process in Cincinnati.

To maintain uniformly the proper strength of the plating solution, a plate of iridium is employed as an anode. The metal, from samples which we had the opportunity of observing, is deposited in reguline form, and is susceptible of taking a good polish. A thin platinum sheet, electro-plated with iridium, retains its flexibility, and when

the coating is not too thick, its adherence is excellent. Engraved copper-plates covered with iridium in this way, are claimed to possess decided advantages over steel-plates.

On account of the pending of applications for patents on the process, in foreign countries, which might be vitiated by a premature publication, the inventor was unable, to our great regret, to give us details as to his methods.

From the specimens of the work that we have seen, however, we do not question the entire accuracy of his claims, and feel satisfied that his invention will be of considerable practical value.

## CHAPTER XLV.

### NICKEL-PLATING.

NICKEL-PLATING is strictly an American industry, in the sense that it was first successfully practised on the commercial scale in the United States, and here received that practical demonstration of its usefulness that has since made it the most successful and most widely practised branch of the art of electro-plating. Coming first into prominence and popularity about ten years ago, it has since that time rapidly grown, until to-day it has developed into an industry of great magnitude and importance. The almost silvery whiteness and admirable brilliancy of the electro-deposited nickel; its cheapness as compared with silver; the hardness of the electro-deposited metal, which gives the coating great power to resist wear and abrasion; the fact that it is not blackened by the action of sulphurous vapors, which rapidly tarnish silver; and the fact that it exhibits but little tend-

ency to oxidize even in the presence of moisture, are sufficient to explain the great popularity which nickel-plating enjoys.

The industrial development of the art, however, which has been surprising both in respect to its rapidity and extent, may be attributed in a large measure to certain favoring circumstances, quite independent of the excellent adaptability of the metal for electro-plating purposes. These circumstances are, first, the great advances that have been made within this period in the production of nickel on the commercial scale, by which the cost of the metal has been greatly reduced, and its purity greatly increased (for which we are indebted mainly to the American Nickel Works of Camden, N. J., under the scientific management of Mr. Joseph Wharton\*); and,

\* Mr. Wharton has produced at his works in Camden, N. J., since the year 1876 to the close of the year 1882, 1,466,765 pounds of metallic nickel. He began experimenting very early to determine whether nickel could not be produced in a pure and malleable condition, susceptible of being worked in nearly the same manner as iron, and of being applied in the manufacture of various objects demanding a strong, non-oxidizable metal. He succeeded so well that he was enabled to display at the International Exhibition in Vienna, in 1873, a sample of nickel in the form of axles and axle-bearings; and at the Philadelphia Exhibition, three years later, he exhibited a remarkable series of objects made of wrought nickel, such as bars, rods, etc. These objects from their unpretentious character did not attract the attention they deserved. As a matter of justice to this indefatigable and intelligent worker, the fact should be placed on permanent record that he had succeeded as early as the year 1873, and with the lean and sulphuretted ores of Lancaster Gap, Pennsylvania, which yield only from  $1\frac{1}{2}$  to 2 per cent. of nickel, in producing the metal in malleable condition.

The recent discovery of pure carbonated and oxidized ores of nickel in the French colony of New Caledonia, has greatly stimulated the production of this metal and lessened its price; and the highly ingenious refining process recently discovered by Dr. Fleitmann, which is



second, the introduction and perfection, within this period, of the now almost universally employed dynamo-

now altogether used in the production of the pure metal, has tended in the same direction.

The subject is of such interest that we deem it proper, though only incidentally bearing upon the objects of this work, to quote the following brief account of Fleitmann's process, from a paper read before the American Institute of Mining Engineers at their meeting in Boston, in 1882, by Prof. W. P. Blake, of New Haven, viz:—

Dr. Fleitmann, of Iserlohn, Westphalia, Prussia, has improved and cheapened the operation of refining nickel and toughening it, and has reduced the liability to the presence of blow-holes in castings by adding to the molten charge, in the pot, when ready to pour, a very small quantity of magnesium. This is immediately decomposed, magnesia is formed, and graphite is separated. It would seem that the magnesium decomposes the occluded carbonic oxide, or reduces it to a minimum. The magnesium must be added with great care, and in small portions, as it unites explosively with the charge. It is stirred in. About one ounce of magnesium is sufficient for 60 pounds of nickel. From three-quarters of an ounce to 54 pounds of metal have been used with success by Mr. Wharton. The nickel from the ore at Lancaster Gap seems not to require as much as the foreign metal. It is to be noted that complete malleability of nickel was obtained at Wharton's works in Camden, before Fleitmann's invention or process, but this last is more rapid and better than the old method. The metal so treated becomes remarkably tough and malleable, and may be rolled into sheets and drawn into wire. Cast plates can be successfully rolled. The cast plates, such as are made for anodes, after reheating, are rolled down to the desired thickness. It is found that it is a great improvement to the nickel anode plates to roll them down. They dissolve with greater uniformity in the bath. Nickel so treated with magnesium has been rolled into sheets as thin as paper. Expensive works for rolling the metal have been erected by Mr. Wharton at Camden. There is already a train of 40-inch rolls, 18 inches in diameter, with annealing-ovens and gas-furnaces and their adjuncts, and a 90 horse-power engine. The largest sheet of pure nickel yet rolled at Camden is 72 inches long and 24 inches wide.

Dr. Fleitmann has also succeeded in welding sheet-nickel upon iron and upon steel plates, so as to coat them equally on each face with

electric machines, which placed at the disposal of the electroplaters a constant, powerful, and cheap source of electricity, in the place of the uncertain, troublesome, and comparatively expensive voltaic battery, to the use of which they had of necessity been hitherto confined. Watt (*vide Electro-Metallurgy*, p. 86 *et seq.*) was among the first, we believe, to call attention to these facts. He states, for example, that "the difficulty in obtaining pure nickel anodes of large surface for many years checked the progress of this useful art, whilst the slow and uncertain action of the Daniell battery rendered it ill-suited to the deposition of this peculiar metal on the large scale;" again, "it is doubtful whether nickel-plating would ever have held a really high position in the arts, if the dynamo-electric machine had not been introduced;" and in another place: "Indeed, as we have said, it is doubtful if this branch of the art (i. e., nickel-plating) could even have been extensively pursued with advantage on a large scale, if battery power alone were available." In considering the subject of the present very extensive application of nickel-plating, therefore, the above facts and explanations should not be lost sight of. So general has the demand for nickel-plating become, and so universally is it employed, that, for the sake of economy, hundreds of establishments throughout the United States engaged in the manufacture of the most miscellaneous articles of brass, copper, iron, and steel

are of nickel. The quantity preferred by weight is  $\frac{1}{10}$  iron and  $\frac{2}{10}$  nickel, one-tenth of nickel being placed on each surface. To secure adhesion, the iron or steel must be perfectly flat and clean. A pile is made up with outer facings of sheet-iron, to protect the nickel from oxidation. When the whole is heated to the proper degree it is passed through the rolls. The two metals become so firmly united that they afterward be rolled down two or three together, or separately, to the thickness desired.

have introduced the nickel-plating plant, and do their own plating. Furthermore, innumerable small articles of metal of trifling value are nickel-plated after a fashion, by the manufacturers, not to protect them from the action of corrosive agents, but simply to catch the eye of the purchaser and to make them sell. As may readily be imagined, this state of things has produced a severe competition among those engaged in the business of nickel-plating which, while it has had the effect of bringing down prices to extremely low figures, has incidentally also had the effect of causing a very general deterioration of its quality.

An enumeration of the great variety of products that are nickel-plated would be impossible; among them may be named dental and surgical instruments of every description, harness- and saddlery-trimmings, carriage-fittings, spoons and forks, locksmith's work, brass cocks and faucets, and the decorative metal-work of plumbing and sanitary wares, scale- and balance-beams and weights, mountings of guns and pistols, the metal parts of lamps and lanterns, fire grates and fixtures, stove decorations, door-plates, cuspadores, watch- and clock-cases, hand rails in railway cars and car-seats, etc., stair rods, points of lightning rods, show-cases, the external parts of sewing machines, steam and water valves, gauges, and other machinery accessories. These are only a few of the many products for which nickel-plating is extensively used.

From the very brief account that Roseleur gives of this subject, it would appear that the art of nickel-plating had received little or no attention in France up to the time of the preparation of the fourth edition of his work (1880); furthermore, from the somewhat contemptuous reference with which he dismisses it, it is apparent that at that time he had no knowledge of the remarkable progress and development of the art in this country, and



no conception either of the perfection to which the processes had been brought, or of the beauty and utility of the results obtained.

Although, however, it would appear from the remarks of M. Roseleur, just referred to, that nickel-plating had received but little attention in France up to the year 1880, the art appears to have been transplanted to England with much success. The same author we have quoted above, says in reference to this subject: "The time has now arrived, however, when it may be fairly stated that the art of nickel-plating has become, in proper hands, one of the most successful, and at the same time one of the most extensive branches of electro-deposition. For several years nickel-plating in this country (*i. e.*, England) had been principally confined to some three or four houses. Now, however (1880), the process has been most extensively adopted in London and throughout the kingdom, as also in many foreign countries. There is no doubt that its extensive application in the United States acted as a stimulus to our own manufacturers, who have steadily, though tardily, recognized in nickel a most useful coating for certain kinds of metal work."

*Nickel Solutions.*—One of the earliest allusions to the electro-deposition of nickel is that of M. Ruoltz (*L'Institut*, No. 414, p. 410), referred to in the *Jahresbericht* for the year 1841 (*Berzelius, Jahresb.*, xxii. p. 96). The reference is as follows: "The same method, that is, the use of a solution of the double cyanide in water (prepared by dissolving the metallic oxides in cyanide of potassium), may be employed for coating other metals with copper, tin, cobalt, *nickel*, and zinc." In the year 1843, Smee (*Elements of Electro-Metallurgy*, 2d ed., London, 1843) states that "metals may be covered with nickel by proceeding as in former cases. The solution

to be used is the chloride of nickel with a nickel positive pole. The single battery process is to be preferred, but pure nickel, though *very brilliant*, is apt to be rather brittle." In the same year (1843), Dr. R. Boettger published an interesting account of his experiments in plating with nickel (*Jour. für praktische Chemie*, xxx. p. 267 *et seq.*, 1843), from which we make the following quotation: "No salt of nickel or of platinum has yet been found well adapted to plating baser metals with nickel or platinum. Experience has taught that a compound of cyanide of nickel with cyanide of potassium, according to the statement of Ruoltz, by no means attains the object, nor is the platinum salt recommended by him any better.

"From a long series of experiments expressly made on this point, I believe I have discovered, and can give the assurance, that among all the salts of nickel none is well adapted to plating, especially on copper or brass, the ammonio-sulphate of nickel; at least, the cyanide of nickel and potassium recommended by Ruoltz is far inferior to it, even in a very long-continued, constant current. Sheet copper comes out of the solution of ammonio-sulphate of nickel almost *silver-white* and *brilliant*. I have obtained in this manner, after the action of a moderately strong galvanic current for half an hour, a considerable deposit of nickel on copper, quite sufficient to deflect violently from the magnetic meridian a magnetic needle suspended by a fibre of silk. A drop of common nitric acid on the nickel coating exhibited in a given time no sensible action on the subjacent metal, while sheet copper, which had been allowed to remain in a gilding bath under the influence of the current for the same length of time, was almost instantly attacked by nitric acid. From this it may be inferred that the



galvanically deposited nickel coats the copper more rapidly, adherently, and uniformly than gold similarly deposited."

"To prepare the salt of nickel here referred to, the impure nickel of commerce suffices completely. To this end, it is dissolved in nitric acid, a stream of sulphuretted-hydrogen is passed through the solution for some time in order to precipitate all copper and arsenic, and the filtered solution is then precipitated by carbonate of soda. The well-washed carbonate of nickel is dissolved in dilute sulphuric acid, and the solution is placed beneath a bell-glass over concentrated sulphuric acid, in order to obtain it crystallized. These crystals are pulverized, transferred to a suitable flask, and ammonia gradually poured over them, until sufficient has been added to dissolve them. The resulting fine, dark-blue solution, may be directly used for the purposes above named."

It may be proper to add, in this connection, that one of the uses suggested by Boettger for his solution is for the preparation of pure sheet nickel.

In the fourth edition of his work (*Manipulations Hydroplastiques*, Paris, 1880), Roseleur affirms that as early as the year 1849 he had succeeded, in the establishment of M. Kraitz, at Grenelle, in obtaining on table-ware an excellent deposit of nickel of considerable thickness, with the use of the double sulphite of nickel and ammonium as the depositing solution.

The next important contribution to the art of depositing nickel by galvanic means, is made by Mr. G. Gore, who, in 1855, employed the double salts of nickel and ammonia, *i. e.*, the double chloride. In the edition, also, of his *Electro-Metallurgy*, published in 1860 (Griffin & Co., London, 1860), will be found a method for the electro-



deposition of nickel by means of a solution of the double chloride of nickel and ammonium.

In 1862, MM. Becquerel, *père et fils*, read before the French Academy a paper on the "Electro-Chemical Reduction of Nickel," etc., an abstract of which appears in the *Comptes Rendus* (tome lv. No. 1, July, 1862, p. 19), from which we make the following extract: "Nickel, we operate with a solution of sulphate of nickel to which has been added caustic potassa, soda, or ammonia, preferably the latter alkali, to saturate the excess of acid. Sulphuric acid becoming free is saturated by oxide of nickel placed on the bottom of the vessel, or by adding alkali to the solution, ammonia by preference. At the end of a certain time we obtain a brilliant, white deposit with a slightly yellow tint. According to the moulds employed it may be obtained in cylinders, bars, or medals. They possess, like cobalt, magnetic polarity when taken out of the solution. The ammoniacal solution of the double sulphate of nickel and ammonium, and even that which is not ammoniacal, likewise furnish metallic nickel."

In 1869, Isaac Adams, Jr., of Boston, obtained a patent in the United States for an "Improvement in the Electro-Deposition of Nickel," in which he describes a method of preparing the double salts of nickel—the double sulphate of nickel and ammonium, and the double chloride of nickel and ammonium—by which the same are obtained free from certain impurities, to the presence of which, he claimed, the difficulties in the way of obtaining a satisfactory deposit of this metal by galvanic means were ascribable. He describes in his patent specification a method of preparing these two compounds in such a manner as to be free from the presence of potash, soda, lime, alumina, and nitric acid, and directs that the electro-deposition of nickel by means of either of these double

salts must be done from a solution that is free from acid or alkaline reaction. He likewise claims as his invention a method of preparing the nickel-plates to be used as anodes in the depositing cells, which consists in melting the nickel and combining it with iron, for the purpose of avoiding the bad effects produced by copper and arsenic when these are present as impurities in commercial nickel. The effect of the addition of iron to the nickel (the amount being the chemical equivalent of the copper and arsenic present), Mr. Adams affirms, is to prevent the deposition of the above named impurities with the nickel. Quoting from the patent, "the iron itself is almost wholly precipitated as a peroxide, and is not deposited with the nickel to a sufficient extent to injure the character of the deposit. Neither does it injuriously affect the solution. The effect of the iron upon the copper is either to prevent it from being dissolved, or, if dissolved, to immediately reduce it upon the anode where it forms a coating which may be reduced from time to time by scraping. The arsenic forms an insoluble precipitate with the persalt of iron."

Mr. Adams continues:—

"Having prepared the solutions and anodes, as herein described, nickel may be readily deposited; but, in order to carry on the deposition continuously, it is necessary to observe certain precautions: First, the use of a battery of too high an intensity must be avoided. An intensity of two Smee cells is sufficient. A high intensity decomposes the solution and liberates free ammonia, thus rendering the solution alkaline, and impairing its value. Whenever the smell of free ammonia arises from the decomposing-cell the operator may be certain that the solution is being injured. It is important that the depositing shall not be forced by the use of too strong a current. Second, it is

important that great precaution should be used to prevent the introduction into the solution of even minute quantities of potash, soda, or nitric acid. When an article to be coated is cleaned in acid or alkaline water, or is introduced into it for any purpose, the greatest care must be taken to remove all traces of these substances before the article is introduced to the nickel solution, as the introduction of the most minute quantities of acids or alkalis will surely be injurious. It is important that the solution be kept free from all foreign substances, but its purity from those above named is especially important. Third, the anode of the depositing-cell should present a surface to the action of the solution somewhat larger than the surface upon which the deposit is being made, particularly in the double sulphate solution. The reason is that nickel dissolves so slowly, that if the exposed surface is not larger than the surface on which the deposit is made, the solution will not keep saturated. On the other hand, if the anode is very much larger than the positive pole it tends to give a deposit of black powder. Fourth, if zinc is to be coated it should first be coated with copper, as it is difficult to make nickel adhere to zinc, and there is danger that the zinc may be acted on and injure the solution.

“With solutions and anodes thus prepared and used, the deposition of nickel can be carried on continuously and almost as surely and certainly as the deposition of copper from the common sulphate solution, though the limits of the battery-power which may be used are narrower. The metal deposited is compact, cohesive, and tenacious. It may be deposited of nearly uniform thickness over any surface, however large. The deposited metal is capable of being annealed by a heat below a low-red heat. It then becomes flexible, malleable, and ductile. The deposit may be made of any required thick-



ness, either to furnish effectual protection to the metal on which it is deposited, or to be removed and used separately from the surface on which it may be deposited."

In the same year, but a few months earlier than the date of the patent above referred to, a patent had been granted to the same inventor for the use of a solution of the sulphite of nickel, in a solution of sulphite or bisulphite of ammonium. This solution is identical, apparently with that which M. Roseleur claims (see *ante*) to have used as early as 1849 with excellent results in the establishment of M. Kraitz, at Grenelle, but which, as we glean from a "*Notice supplémentaire sur le Nickelage*," which he has lately issued, he has discarded in favor of the double sulphate.

The Adams patents were the first on the subject of nickel-plating in the United States, and the rapid development of the art to the proportions of an important industry, which took place within a few years thereafter, gives color to the claim that Mr. Adams is entitled to the credit of being the originator of the art of nickel-plating. We have elsewhere pointed out that the true explanation of the remarkable growth of this art is to be found in the substantial improvements in the metallurgical treatment of nickel by which anodes of any desired size, and of great purity, were placed at the service of the nickel-plater; and more especially in the invention and improvement of the dynamo-electric machine, which has made the nickel-plater independent of the uncertain and troublesome chemical battery. Had it not been for the want of these two important elements of success in this branch of the galvanoplastic art, plating with nickel would unquestionably have been extensively practised years before it actually assumed a position as a successful and popular industry.

It cannot be denied, however, that Mr. Adams, by di-

recting the attention of technologists to the excellent qualities of the double salts of nickel and ammonium, at a time when everything was ripe for the new industry, materially assisted in calling it into existence, and in assuring its commercial success.

The years immediately succeeding 1869 were very prolific of inventions relating to the art of nickel-plating, most of which, however, were comparatively valueless. We select for notice a few that appear to have meritorious features.

In 1877, Mr. Unwin, of Sheffield, England, devised an ingenious process of preparing the double salts of nickel and ammonium. This consists in preparing a strong solution of sulphate of ammonium, by dissolving the salt in hot water in the proportion of about four pounds of the salt to each gallon of water, then filtering, if necessary, and allowing the liquid to become cool. The double sulphate of nickel and ammonium is obtained by adding this solution to one of the sulphate of nickel. The novelty of Mr. Unwin's process, however, resides in the fact that he does not stop the addition of the sulphate of ammonium when sufficient has been added to combine with all the sulphate of nickel present, but continues to add it in large excess. "I do this," says Mr. Unwin, "because I have discovered that the double sulphate of nickel and ammonia is far less soluble in the solution of sulphate of ammonia, than in pure water, so that it is precipitated from its solution in water on adding sulphate of ammonia. I therefore continue adding the solution of sulphate of ammonia, continuously stirring, until the liquid loses nearly all its color, by which time the double sulphate of nickel and ammonia will have been precipitated as a light-blue crystalline powder, which readily settles to the bottom of the vessel. I then pour off the liquid from the crystalline precipitate of dou



sulphate of nickel and ammonia and wash the latter quickly with a strong, cold solution of sulphate of ammonia as often as I consider necessary for its sufficient purification." By this procedure it will be perceived that the double salt of nickel and ammonium is thrown down in a pulverulent, granular condition, readily soluble in water, and therefore ready for use in the depositing vat, without waiting for the tedious process of crystallization.

In 1878, Edward Weston, of Newark, N. J., noticing its favorable influence upon the electro-deposition of nickel, secured a patent for "the electro-deposition of nickel by means of a solution of the salts of nickel containing boric acid, either in its free or combined state. The nickel salts may be either single or double." Mr. Weston affirms that the presence of boric acid prevents the deposit of sub-salts upon the articles in the bath, which is apt to occur if the bath is not in proper working condition; he claims, furthermore, that its addition in either the free or combined state to a solution of nickel salts diminishes the liability to the evolution of hydrogen when the solution is used for the electro-deposition of nickel, and increases the rapidity of deposition, by permitting the use of a more intense current, and improves the character of the deposit by rendering it less brittle and increasing its adhesion.

The results of extended practical trials of Mr. Weston's formula, made by the writer, have convinced him of the substantial correctness of the claims of this inventor. Where the double sulphate of nickel and ammonium is used, the addition of boric acid in the proportion of from 1 to 3 ounces to the gallon of solution gives a bath less difficult to maintain in good working order, and affords a strongly adhesive deposit of nickel. The deposited metal is dense and white, approaching in brilliancy that obtained from the solution of the double cyanide.



In 1880 J. Powell, of Cincinnati, patented an electro-depositing solution "composed of the pyrophosphate of soda, phosphate of nickel, the bisulphite of soda, and citrate of nickel and ammonia."

In the same year C. G. Pendleton, of New York, patented the use of an acid solution of the acetate of nickel. The inventor emphasizes the caution that this solution must always be kept acid. The metallic strength of this solution is fully maintained by the dissolving of the anodes, and the bath consequently requires no additions of fresh salt.

An interesting suggestion is that patented in 1880 by Mr. Powell, and which covers the use of benzoic acid in nickel-plating solutions. In describing his improvement Mr. Powell calls attention to the fact (?) that simple salts of nickel cannot be used on account of their failure to yield a reguline deposit. He claims to have discovered that the addition of benzoic acid to any of the nickel salts, arrests in a marked degree the tendency to an imperfect deposit, and prevents the decomposition of the solution, and, consequently, the formation of sub-salts. The amount of benzoic acid necessary to be added to the bath for this purpose is said to be  $\frac{1}{8}$  ounce to the gallon of solution. He, therefore, claims "an electro-depositing solution consisting of a soluble salt of nickel, its solvent and benzoic acid." This bath is reported to give very satisfactory results.

In the same year Mr. J. H. Potts, of Philadelphia, was granted a patent for an improved solution for the electro-deposition of nickel "consisting of the acetate of nickel and the acetate of lime with the addition of sufficient free acetic acid to render the solution distinctly acid." Mr. Potts prepares his bath as follows: He precipitates the carbonate of nickel from a boiling aqueous solution of the

sulphate by the addition of bicarbonate of sodium, filters and dissolves the well-washed precipitate in acetic acid, with the aid of heat.

The acetate of calcium he prepares by treating caustic lime, or the carbonate (marble-dust) with sufficient acetic acid to dissolve it with the aid of heat. The solution of these salts is acidified, slightly but distinctly, with acetic acid.

This solution, which we have worked with under a variety of circumstances, we have found to be in many respects an excellent one. It gives satisfactory results, without that care and nicety in respect to the condition of the solution and the regulation of the current which are necessary with the double sulphate solution. The metallic strength of the solution is fully maintained, without requiring the addition of fresh salt, the only point to be observed being the necessity of adding, from time to time (say once a week), a sufficient quantity of acetic acid to give a distinctly acid reaction. The Potts solution is rather more sensitive to the presence of a large quantity of free acid than to the opposite condition; as the former condition is apt to produce a black deposit, while it may be run down nearly to neutrality without notably affecting the character of the work. The deposited metal is characteristically bright on bright surfaces, and requiring but little buffing to finish. It does not appear, however, to be as well adapted for obtaining deposits of extra thickness, as the commonly used double sulphate of nickel and ammonium. On the other hand, its stability in use, the variety of conditions under which it will work satisfactorily, and the trifling care and attention it calls for, make it a serviceable solution for nickeling.\*

\* From experiments of the writer, there would seem to be grounds for the belief that a double acetate of nickel and calcium is formed in the

## FORMULÆ FOR NICKEL-PLATING SOLUTIONS.

*No. 1.*

Double sulphate of nickel and ammonium	5 to 8 parts.
Water . . . . .	100 "

Dissolve the nickel double salt in the above quantity of water with the aid of heat. Cautiously add ammonia, or the sulphate of ammonium, until the solution is neutral to test-paper. This solution should be maintained as nearly neutral as possible in use. This is commonly known in the United States as the Adams solution. It is in very general use by nickel-platers throughout the United States, and yields, when properly managed, excellent results.

*No. 2.*

Double sulphate of nickel and ammonium	10 parts.
Boric acid (refined) . . . . .	2½ to 5 "
Water . . . . .	150 to 200 "

(Weston's solution.) The superiority of this solution is generally acknowledged. The deposited metal, as previously remarked, is almost silver-white, dense, homogeneous and tenacious; and the solution maintains its excellent working quality very uniformly in long-continued service.

The nickel salt and boric acid may be dissolved separately in boiling water, the solutions mixed, and the volume brought up to that of the formula, or the two components may be dissolved together.

Potts solution. As prepared according to the formula given by the inventor, however, it contains a considerable excess of the acetate of calcium beyond that required for the formation of a double salt, the presence of which renders the determination of the fact very difficult.



## No. 3.

Acetate of nickel . . . . .	2 $\frac{3}{4}$ parts.
Acetate of calcium . . . . .	2 $\frac{1}{2}$ "
Water . . . . .	100 "

To each gallon of this solution add 1 fluidounce acetic acid 1.047 sp. gr.

To prepare this bath, dissolve about the same quantity of the dry carbonate of nickel as that called for in the formula (or three-quarters of that quantity of the hydrated oxide) in acetic acid, adding the acid cautiously, and heating until effervescence has ceased, and solution is complete. The acetate of calcium may be made by dissolving the same weight of carbonate of calcium (marble-dust) as that called for in the formula (or one-half that quantity of caustic lime), and treating it in the same manner. Add the two solutions together, dilute the volume to the required amount by the addition of water, and then to each gallon of the solution add a fluidounce of free acetic acid, as prescribed. (Potts's solution.)

## No. 4.

Sulphate of nickel and ammonium . . . . .	10 parts.
Sulphate of ammonium . . . . .	4 "
Citric acid . . . . .	1 part.
Water . . . . .	200 parts.

The solution is made with the aid of heat, and when small fragments of carbonate of ammonium should be added until the bath is neutral to test-paper.

## No. 5.

Sulphate of nickel . . . . .	6 parts.
Citrate of nickel . . . . .	3 "
Phosphate of nickel . . . . .	3 "
Benzoic acid . . . . .	1 $\frac{1}{2}$ part.
Water . . . . .	200 parts.

(Howell's solution.)

No. 6.

Phosphate of nickel . . . . .	10 parts.
Citrate of nickel . . . . .	6 "
Pyrophosphate of sodium . . . . .	10 "
Bisulphite of sodium . . . . .	1½ "
Citric acid . . . . .	3 "
Aqua ammonia . . . . .	15 "
Water . . . . .	400 "

(Powell's solutions.) These solutions yield good results, but their complex composition must debar them from general use.

No. 7.

Sulphate of nickel . . . . .	6 parts.
Aqua ammonia . . . . .	3 "
Water . . . . .	100 "

When the nickel is dissolved, add—

Aqua ammonia . . . . .	20 parts.
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This bath is similar to that recommended by Prof. Boettger; it is said to be well suited for the purposes of amateurs, inasmuch as it gives good results with a platinum anode. It is worked at a temperature of 100° Fah. with a moderate current. It requires renewal from time to time as it becomes impoverished in nickel, by addition of fresh nickel salt; it must also be kept alkaline by the occasional addition of ammonia.

No. 8.

Sulphate of nickel and ammonium . . . . .	10 parts.
Sulphate of ammonium . . . . .	1½ "
Water . . . . .	250 "

Dissolve in boiling water and allow to cool. These proportions are recommended for coating objects of cast and wrought iron, and steel.

## No. 9.

Sulphate of nickel and ammonium	. . .	10 parts.
Sulphate of ammonium	. . . . .	2 "
Water	. . . . .	300 "

Dissolve as above. Recommended for coating brass, copper, tin, Britannia, lead, zinc, etc.

## No. 10.

Sulphate of nickel and ammonium	. . .	6 parts.
Chloride of ammonium (sal-ammoniac)	. . .	3 "
Water	. . . . .	100 "

## No. 11.

Nitrate of nickel,	} equal parts.
Aqua ammonia	

When solution is complete, dilute with twenty or thirty times its volume of a saturated aqueous solution of bisulphite of sodium. (Roseleur.)

This is the solution employed by Roseleur (see *ante*).

The deposit has a dull, gray color.

Watt (*Electro-Metallurgy*, 7th ed., p. 94) recommends for ordinary purposes the following solution, which he affirms will give, in careful hands, very good results. "Take, say 2 ounces of pure nickel, dissolve in hydrochloric acid, taking care not to have an excess. A gentle heat will assist the operation. When dissolved, dilute the solution with 1 quart of cold water. Now add ammonia gradually, until the solution is quite neutral to test paper. Next, dissolve 1 ounce of sal-ammoniac (chloride of ammonium) in water, and mix this with the former solution. Lastly, evaporate and crystallize slowly." The resulting salt will be the double chloride of nickel and ammonium. It is one of the earliest solutions used for



nickel-plating by Smee and Gore, and is affirmed by these writers to give good results. According to Smee, the simple chloride of nickel will yield a deposit having a very brilliant lustre.

We can unqualifiedly confirm the statement of Gore (*Electro-Metallurgy*, 1877, p. 233) who remarks that the deposit obtained from a solution of the double cyanide of nickel and potassium "is said to be nearly equal in whiteness to silver." We have obtained deposits with this solution of such extreme whiteness and beauty as to deceive even an expert on casual inspection into the belief that they were silver. The solution, however, rapidly loses its activity because of imperfect conductivity, and runs down in strength because of the difficult solubility of the anode in the electrolyte, and is so difficult to manage that it is impracticable for general use. This, at least, is the opinion we have reached after many trials of it. We are informed, nevertheless, that it is successfully used on a large scale in certain nickel-plating works in this country though we have not been able to substantiate the fact.

To prepare this bath, take a solution of any salt of nickel, and add cyanide of potassium solution so long as a precipitate continues to be formed, being careful to avoid adding an excess. Then remove the liquid either by decantation or filtration; and after several washings dissolve the precipitate almost to saturation in a cyanide of potassium solution; or make a completely saturated solution, to which add a quantity of free cyanide of potassium. The brownish-red solution is then ready for use.

It may be added, in conclusion, that the double sulphate of nickel and ammonium is the solution most generally used by electro-platers with nickel.

*General Observations.*—Where the double sulphate of nickel and ammonium is used, it is important that the

operator should bear in mind the caution to maintain the bath ~~as nearly neutral~~ as possible. There is a diversity of opinion among nickel-platers upon this point, some preferring to operate with a slightly acid bath, while others prefer the opposite condition. Experience has shown that the solution will give satisfactory results either when slightly acid or slightly alkaline, and as the chemical character of the bath during electrolysis is constantly being modified, it is manifestly impossible for the operator to do more than to keep his solution approximately in the right condition. A strongly acid solution will fail to give a deposit. When the bath therefore is found to be in this condition, the addition of sufficient ammonia to restore its neutrality will bring it to working condition.

It is only by accident or carelessness, however, that the solution will become inoperative from this cause, as the chemical changes which occur in the double sulphate of nickel and ammonium, under the influence of the electrical current, and under the conditions in which it is commonly used in the plating bath, are such as to cause it to gradually assume an alkaline character. This is due to the fact that not simply sulphate of nickel, but to some extent also sulphate of ammonium, undergoes decomposition into its proximate constituents. The sulphuric acid set free by the decomposition of the ammonium sulphate will form an equivalent quantity of sulphate of nickel by solution of the anode, while the ammonia will remain free, and gradually, as it accumulates, will impart a decided alkalinity to the bath. The more intense the current employed, the more pronounced will be the decomposition of the solution and the liberation of free ammonia. As this change progresses, the quality of the work is more or less unfavorably influenced. Accompanying this change, especially where the current employed is irregular and at times too intense,



there is also a precipitation of some of the nickel, probably in the form of basic salt, by which the metallic strength of the bath is impaired, and which necessitates the addition of fresh quantities of the double sulphate from time to time. Where a current of only moderate intensity is used, and which is uniformly maintained, these difficulties will be reduced to a minimum, and the solution will maintain itself in good working order for a long time, requiring only the occasional addition of a little sulphuric acid to correct any pronounced alkalinity that may be exhibited, when tested, as it should be at frequent intervals, with test-paper. As metallic nickel is with difficulty soluble, the use of comparatively large anode surfaces is necessary, because the nickel dissolves so slowly that if the anode surface exposed in the depositing vat is not considerably larger than that of the objects on which the deposit is made, the solution will not keep saturated.

From the preceding remarks it will be unnecessary, perhaps, to add that the double sulphate solution commonly used by nickel-platers presents greater difficulties in its employment than the acid solutions of Pendleton, Potts, and others. By carefully observing the above-named precautions, however, much trouble and annoyance will be avoided.

Again, the strength of the current should be carefully regulated according to the surface of the articles in the bath, or the work will be apt to "burn;" that is, the metal will be precipitated as a dark-gray or black deposit, which discolors and renders it useless. This is evidence that the current is too strong. To obviate this difficulty, which is apt to manifest itself when small articles are first placed in the bath, the plan is generally adopted, by careful operators, of suspending a plate of nickel, presenting considerable surface, at both ends of the rod from whi



the articles are suspended in the bath. By thus diverting the current, the "burning" of the work is prevented.

As a general rule it is well to observe that, other things being equal, the slower the rate of deposition, the more adherent and tenacious the coating of deposited metal will be. Where the metal deposits too rapidly, the deposit is apt to be brittle, and to exhibit, especially in the case of a heavy coating, a tendency to split and flake. This is due to the liberation of hydrogen at the cathode, and which is occluded by the electro-deposited nickel. To obtain satisfactory results it is important that the articles should be "struck," that is, receive a uniform coating immediately after they are immersed in the bath. This is an indication that the articles have been properly cleaned, and are in good condition to receive the deposit, and so that the bath is in working order. After this first layer has been deposited, the subsequent rate of deposition is much slower, for the reason that the deposit of nickel on nickel does not take place as readily as upon a foreign metal, and this rule holds good of all metals.

Nickel solutions are feebler conductors of electricity than those of gold, silver, and copper, which is one of the reasons why its electro-deposition is attended with more difficulties than are experienced with the metals named. On this account, also, it is necessary to employ stronger depositing solutions than those used for gold and silver, and also a stronger current. To make up for this want of conductivity it is advantageous to use a much larger anode surface than is customary with other metals, and it is necessary to place an anode on both sides of an article to be plated. The usual arrangement with a large vat is to have two rails of brass the whole length of the vat, resting on the edges of the same, from which two rows of cast or rolled nickel anodes (to which copper wires are

soldered) are suspended. Between these outer rods is placed a similar one also running the whole length of the vat, and from this, by means of suitable slinging wires, the articles to be plated are suspended in the bath. The ends of the rails nearest the battery, or dynamo, are suitably connected therewith in the usual order. The work thus hangs between the two rows of anodes.

Watt (*Electro-Metallurgy*, 7th ed., 104 *et seq.*) very properly calls the attention of the operator in this connection to the importance of having the wire supports from which the articles are hung in the depositing vat, of a gauge suited to the character of the work. Small articles will require but a very thin wire, while larger ones will require correspondingly thicker slinging wire. On the same point he cautions the operator that the difference of conductivity in the metals to be plated is to be considered, "for, whereas, a steel, brass, or copper article would become readily "struck," even if suspended from the conducting-rod by a thin wire, articles of lead, Britannia-metal, pewter, or even cast iron, would not receive the deposit so readily." It is obvious, therefore, that, in suspending articles in the plating bath, the operator must be guided in the matter of the thickness of his slinging wires, by the nature of the articles, as well as by their dimensions.

It cannot be too strongly impressed on the operator, that the attainment of success in nickel-plating depends very largely upon the perfect cleansing of the articles before they are immersed in the bath. Important as we have found this operation to be in plating with other metals, it is even more important in the case of nickel. Gilding, silvering, bronzing, etc., are usually effected with solutions having a decidedly alkaline character (reference is made here to the double cyanide solutions commonly

used), and the presence of minute traces of oxide from careless exposure to the air after cleansing, or of grease from the fingers, etc., on the surface of the articles to be plated, is not necessarily fatal to the success of the work, as the free cyanide present in those baths, being a solvent of greasy substances, and of metallic oxides, may remove trifling quantities of such impurities. With nickel, however, the case is different. The solutions employed for its deposition are either neutral, or only weakly alkaline or acid. This chemical character is such, therefore, that they can have little or no solvent effect on the grease or oxide left on the articles by careless cleansing, or improper handling, or exposure before immersion; and if such articles are plated, the nickel coating at the unclean places will be found to have little or no adherence to the metal beneath, and will almost certainly flake or strip at these places, in the subsequent operation of polishing. Unless the surfaces to be coated are *chemically* clean an adherent deposit of nickel is simply impossible.

On account of the hardness of the deposited metal, nickel-plated articles cannot be burnished. In order therefore to obtain upon the finished work that superb metallic lustre which characterizes this metal, it is necessary to polish the surface of the articles upon the buffing-wheel before immersion in the plating bath, in order that the deposited metal may be as smooth as possible; thus reducing to a minimum the amount of subsequent buffing required to finish the plated articles.

The operation of cleansing articles differs somewhat in various establishments; the following methods, however, are those usually followed.

For copper, brass, Britannia-metal, tin, pewter, etc., the articles are first steeped for a few minutes in boiling potash solution to remove greasy matter; they are then re-



moved, rinsed in water, dipped for an instant in cyanide of potassium solution, of moderate strength, again rinsed, then thoroughly brushed with the finest pumice powder (precipitated chalk, Vienna lime, and other fine powders are also used), again rinsed in water, dipped again for an instant in the cyanide, well rinsed, and then hung at once in the nickel bath. The time of immersion in the boiling potash solution will depend on the strength of the alkali, and the amount of greasy matter present. Tin, Britannia, pewter, etc., however, should be left in it as short a time as possible, as the alkali exerts a solvent action on tin and alloys containing this metal. When rinsed in water after removal from the potash, the water should wet the surface uniformly; should any cloudy patches be visible, these indicate that the grease has not been completely removed, and the article must be immersed again in the boiling potash.

Steel articles are first cleansed in the potash bath, rinsed in water, scoured with pumice powder (or its equivalent), rinsed, dipped for a moment in dilute hydrochloric acid, again rinsed, and at once hung in the depositing vat.

Cast iron is first placed in the potash bath to remove greasy matter, well rinsed, then allowed to remain for some time in a pickle of dilute sulphuric acid to partially dissolve off and partially soften the scale that covers it, rinsed, then thoroughly brushed with pumice, rinsed, dipped for a moment in dilute hydrochloric acid, again rinsed, and immediately placed in the nickel bath.

Many operators vary the above methods of cleansing somewhat, but they are followed substantially as given, by the majority of nickel-platers. With Britannia-metal, pewter, and other compositions of comparatively low conducting power, it is to be recommended to give them a pre-

liminary coating of copper, for which purpose the cyanide bath is commonly employed. Many operators prefer also to copper articles of iron and steel preparatory to nickel-plating. The advantages secured are a better conducting surface upon which to lay the nickel, and a more tenacious deposit, having, in the case of a heavy coating of nickel, less tendency to flake. Where a substantial and durable nickel deposit is required on iron and steel, and especially where the articles are to be exposed to the atmosphere, or will be subjected to much handling, a preparatory coating with copper is almost indispensable. In the earlier days of nickel-plating, it was the almost universal practice to first copper all iron and steel articles.

The enormous extension of nickel-plating of late years has caused its application to an endless variety of articles of trifling value merely to enhance their beauty, and this, together with the severe competition amongst those in the business, has combined to cause a very general deterioration in the quality of nickel-plated work. The necessity of doing cheap work is responsible for the fact, therefore, that thousands of articles are turned out of the nickel-plating works with the merest wash of nickel. The want of durability exhibited by these inferior goods has had the consequence that many have formed a low estimate of the utility of nickel as a protective coating for metals, an unfavorable judgment which it is far from deserving.

It is important that the work should be examined very shortly after it has gone into the nickel bath, to observe whether it has been "struck," and its general appearance. Should dark streaks exhibit themselves upon the work, they may indicate either that the current is too intense, or that the work has not been properly cleansed. Such streaks will often be observed, starting from joints, seams, or rivets, where the grease from the buffing-wheel

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may have secured lodgment, and from which it is difficult to perfectly remove it. In such cases the work must be removed and given another thorough pumice brushing and rinsing, and again immersed in the depositing vat.

As has already been briefly noticed, the hardness of electro-deposited nickel renders it impossible to finish the plated articles by burnishing. It is therefore necessary to prepare the surfaces of the articles to receive the nickel deposited before they are plated in order to reduce the subsequent finishing operations as much as possible. On this account it is customary to polish the surfaces of articles to be plated on buffing wheels. In case the surface is very rough, as is sometimes the case with articles of iron or steel, it may be necessary to grind it smooth upon the emery wheel. The work when it is removed from the nickel bath is dipped for a few moments into boiling water, and then rapidly dried in sawdust. It is now ready to be polished on the buffing-wheels, when the work is finished.

The length of time required to produce a sufficiently heavy deposit of nickel will depend on the strength of the current, the condition of the bath, and the character of the articles. Brass and copper articles usually receive a sufficiently heavy coating in half an hour; for wares on which an extra heavy coating is desired the time of immersion is extended to an hour or even longer. Iron and steel, Britannia-metal, pewter, etc., require a longer time of immersion than brass or copper, even though given a preparatory coating of copper, because of their comparatively inferior conductivity. A good coating of nickel, properly laid on, possesses great durability, and with ordinary usage will last for many years.

Old nickel-plated work, which it is desired to replat, should first be "stripped," as is found necessary with the

precious metals. For this purpose a mixture of sulphuric and nitric acids is commonly employed. Watt (*Electro-Metallurgy*, 7th ed., 114 *et seq.*) recommends the following mixture as the most generally serviceable, viz: "4 pounds strong sulphuric acid, 1 pound nitric acid, and about 1 pint of water." By volume, these proportions would be, approximately: Strong sulphuric acid, 2 parts; nitric acid, 1 part; water, 1 part. The acids should be added to the water with constant stirring. This stripping liquid may be used either cold or slightly warm. It acts promptly, removing a light coating of nickel in less than a minute, and a heavy one in a few minutes. To avoid contaminating the solution as little as possible with the metal of the wares, the operation should be closely watched and the articles removed from the acid just as soon as the nickel has been dissolved. The preparation of the stripped articles for re-nickeling should be the same as for new work. Articles may be stripped in the nickel bath by the ordinary artifice of connecting them as anodes, but the practice is injudicious, as the purity of the bath will thereby become impaired by the solution of the metals composing the wares. Where the current is used for the purpose, therefore, a separate solution should be used, and for this purpose we approve Watt's recommendation to use as a stripping solution dilute sulphuric acid which will dissolve nickel readily without appreciably affecting brass. Under all circumstances, however, the articles should be looked at from time to time, and removed as soon as they are free from nickel. It is important, however, that the nickel be thoroughly cleaned off, to prevent the peeling of the subsequent nickel deposit.

*Plating with Nickel by Immersion.*—Stolba describes the following simple process for nickel-plating without the battery, which may be usefully applied in the case of



small objects. He dilutes a concentrated solution of chloride of zinc with twice its volume of water. This mixture he boils in a copper vessel, adding a few drops of muriatic acid should there appear a precipitate of basic chloride of zinc. He thereupon adds a small quantity of powdered zinc. This addition causes a deposit of zinc upon the vessel. Thereupon sufficient chloride, or sulphate, of nickel is added to the bath to give it a distinctly green color, and the previously cleansed articles are then immersed in the liquid in contact with zinc, and allowed to remain there for about fifteen minutes, the temperature being maintained at boiling during the operation. If the coating is found to be insufficient the articles are again immersed until a deposit of sufficient thickness is obtained. In this way he claims to be able to coat satisfactorily articles of zinc, cast and wrought iron, steel, and copper. (*Journal Chemical Society*, xi. 465.)

By an analogous process described by C. Mène, it is affirmed that metallic articles may be plated with nickel by immersing them in contact with zinc, in a boiling neutral solution of chloride of zinc, in which is contained fragments, or a plate, of nickel. Should the solution be acid, the plating, it is asserted, will be dull. By this procedure the author claims to be able to coat articles of iron, steel, copper, brass, zinc, and lead. (*Chemical News*, xxv. 214.)

Where electrotypes of type or engravings are to be printed with colored inks, that are disposed to become chemically affected by contact with the usual copper surface (as for example, vermilion, which becomes brownish), it is customary to give the usual copper electrotype a thin coating of nickel in the usual manner. This nickel coating renders the electrotype proof against the above-named difficulty that printers experience with electrotypes not so protected.

By methods and solutions analogous to those described for nickel, electro-deposits of *cobalt* may be obtained. The electro-deposits of this metal, which we have seen, equal, if indeed they do not surpass, those of nickel in whiteness and brilliancy of lustre. The rarity and costliness of this metal, however, exclude it from any practical uses in plating.

## CHAPTER XLVI.

### DEPOSITION OF ZINC.

#### ELECTRO-ZINCING—ZINCING BY CONTACT WITH ANOTHER METAL.

**ZINC** is easily deposited by the wet way and with the aid of the battery. Its dead lustre is gray bluish-white.

By precipitating a soluble zinc salt with ammonia, and then redissolving the precipitate in an excess of alkali, a bath is obtained which gives quite satisfactory results.

It is also possible to obtain satisfactory results with a bath made by dissolving any salt of zinc in cyanide of potassium, or in a soluble sulphite.

These zinc deposits obtained in the humid way, have nothing in common, either as regards the mode of operation or in point of durability, with such as are obtained by the method called *galvanizing*, by which cleansed iron, or other metallic objects, are plunged into a bath of molten zinc, and, receiving a substantial, adherent coating of this metal, become protected against oxidization for a long time. Electro-deposited zinc, in comparison with that deposited by "galvanizing," is much inferior as a protective coating. A few gilders employ deposits of this

metal, the dead lustre of which imitates chased aluminium; but it tarnishes entirely too soon to be of much service in the arts.

It may be useful, nevertheless, to give some of the most promising formulæ which have been proposed for obtaining electro-deposits of this metal:—

Winckler (*Handb. d. Metallüberzügen*, 256) proposes the following for a cold electro-zincing bath:—

Alum . . . . .	10 parts.
Hydrated oxide of zinc (freshly precipitated)	1 part.
Water . . . . .	100 parts.

The well-cleansed articles are immersed in this bath, which is worked with a large cast zinc plate as anode, and a weak current. Copper thus coated assumes the color of brass by subsequent heating. This bath gives good results with iron, for which it is specially recommended.

[This solution is identical with that of MM. Person and Sire (*Chem. News*, ii. 275). The zinc, according to these authors, is deposited as readily as copper, and takes place on all metals, on platinum, as well as on copper and iron.]

For the same purpose (*i. e.*, electro-coating iron with zinc) this author also recommends an aqueous solution of sulphate of zinc, using 1 part of zinc salt to 4 of water (or an equivalent proportion of the chloride may be used instead of the sulphate). The bath should be used moderately warm, and with a zinc anode. The articles soon coat themselves with a bluish-white film of zinc, which may be burnished.

Dr. Elsner (*Id.*, 257) recommends, for coating cast iron objects, a solution prepared by dissolving in the necessary quantity of rain water—

Chloride of zinc . . . . .	5 parts.
and Sal ammoniac. . . . .	4 “



The bath is worked at ordinary temperature, and with a zinc anode. With this solution Elsner has obtained zinc deposits of the thickness of writing paper.

Watt obtained, in 1855, a British patent for forming a solution for the purpose of coating iron or steel with zinc by galvanic agency. The patentee prepares a solution in 10 gallons of water, of 200 ounces of cyanide of potassium, to which he adds 80, by measure, of the strongest aqua ammonia. He then fills several large porous cells, with a solution containing 16 ounces of cyanide of potassium to the gallon, and immerses these cells partly in the latter solution. In these cells he places sheets of copper and of iron, to act as cathodes, and in the outer solution he places pieces of zinc as anodes, and with the current, charges the latter solution with about 60 ounces of zinc from the anodes. He then removes some of the zinc solution, dissolves in it 80 ounces of carbonate of potassium, and turns it to the zinc solution, in which condition, after decantation of the clear liquid from the sediment, it constitutes his zincing bath. He employs anodes of zinc, and a moderate current. The addition of a little cyanide and aqua ammonia is occasionally necessary. Of this solution Watt says it gives exceedingly beautiful results, and the metal deposited is tough and reguline.

Zinc may also be deposited by contact with another metal, by one or the other of the following methods, viz: Weil (*Ann. de Chim. et de Phys.* iv. 374) immerses copper, or articles that have been copper-coated, in a nearly boiling solution of caustic soda or potassa in contact with metallic zinc. The zinc coating obtained is said to be adherent and brilliant.

A process prepared by Dr. R. Boettger may be found useful (Gmelin, *Handbook of Chemistry*, i. 501). He immerses articles of copper or brass, cleansed in hydrochloric

ric acid, in contact with zinc, in a boiling solution of sal ammoniac or zinc chloride. The articles take a brilliant coating of the metal after a few minutes. A modification of this procedure, proposed by the same authority (*Bay. Ind-u. Gewerbeblatt.*, 1870, 152), consists in adding to a concentrated solution of sal ammoniac some powdered zinc, and immersing the copper or brass articles in contact with zinc, for a short time, in this liquid at or near the boiling point. The zinc deposited is brilliantly white and adherent.

The process of "galvanizing," however, which is described in a subsequent chapter, so completely answers the industrial requirements for a cheap, durable, and beautiful deposit on all metals by simple immersion in molten zinc, that it is practically the only process for zincing at present employed. The electro-deposition of zinc alloys will be found fully described in Chapter XI., p. 130 *et seq.*, of this work.

## CHAPTER XLVII.

DEPOSITION OF IRON—ALUMINIUM—ANTIMONY—BISMUTH—LEAD—ELECTRO-CHROMY.

### *Deposition of Iron.*

KLEIN, who has made a special study of the electro-deposition of iron, describes at length the results of his work in the *Bulletin de la Société d'Encouragement* (2<sup>e</sup> sér. tome xv. 288) from which we abstract the following useful memoranda:—

His object was chiefly to cover copper printing plates with a coating of "steel" to increase their wearing qualities in the press. His first solution was the double chlo-

of ammonium and iron, to which he added a small quantity of glycerine. He found, however, that the deposited metal was obstinately disposed to develop surface scales, and that it was also very brittle. As the result of his endeavors to overcome these objectionable features, he adopted the following methods to give good results where they are used with proper precautions:—

1. He uses either the double sulphate of iron and ammonium, or the sulphate of iron and chloride of ammonium. For the baths of the first kind he prepares either by making a concentrated solution of the crystals of the double sulphate or by mixing a concentrated solution of the two in their equivalent proportions; or by precipitating iron sulphate of iron by means of carbonate of ammonium, and dissolving the precipitate in sulphuric acid by which an excess of acid is avoided. He prefers the last of these methods for the preparation of the best sulphate baths.

2. For solutions with chloride of ammonium, he prepares them by mixing together in their equivalent proportions solutions of sulphate of iron and chloride of ammonium; or by dissolving in a solution of the sulphate of iron at ordinary temperature, as much chloride of ammonium as it will take up. In each case the solutions employed should be as highly concentrated and as neutral as possible. He uses an iron anode having a surface area eight times as large as that of the recipient, and a moderate current. [The electro-deposited metal, as it is, when first removed from the bath is as hard as steel, and very brittle, but may be tempered by annealing.]

3. Another bath described by the same author consists of a neutral solution of the double sulphate of iron and ammonium, worked with a feeble current.



Boettger (*Dingler's Polytech. Jour.*, xcix. 298) recommends a bath similar to one of those of Klein, namely, 2 parts of sulphate of iron (free from ferric oxide), and 1 part of sal ammoniac in a saturated aqueous solution. Medinger (Wagner, *Handb. d. chem. Tech.*, 124) proposes substantially the same solution for "steeling" copper printed plates.

Ryhiner prepares a bath by electrolyzing a solution of 20 parts of sal ammoniac in 100 parts of water, with a wrought-iron plate as an anode, and a similar one as a cathode. The point of proper saturation will be determined when, by substituting a copper article at the cathode, it takes a rapid and bright deposit (*Dingler*, ex. 422).

Electro-deposits of iron may also be obtained from a diluted solution of the sulphate to which a few drops of sulphuric acid have been added (Gore), or from a perfectly neutral solution of the proto-chloride (Roseleur).

All of these solutions, however, are difficult to manage, and they rapidly become unfit for use, by reason of their tendency to pass into the condition of per salts of iron (ferric salts) by absorption of oxygen from the air, from which it is desirable to shield them as much as possible by keeping the bath covered. Klein's suggestion to use glycerine to retard this alteration of the ferrous compounds seems, from all accounts, to be of some service. The ferric salts do not give a metallic deposit, and the energy of the current is expended in reducing them to the condition of ferrous salts.

Finally, it may be noticed, that all the advantages possessed by coating copper printing surfaces with an electro-deposit of iron, are practically gained by the use of a nickel coating, so that much of the importance attached to the electro-deposition of the former metal for this purpose, by earlier writers on electro-plating, has been lost.

*Deposition of Aluminium.*

[www.libtool.com.cn](http://www.libtool.com.cn)

Bertrand (*Comptes Rendus*, lxxxiii. 854) has succeeded in obtaining electro-deposits of aluminium from solutions of the double chloride of aluminium and ammonium (analogous to those which he employs for obtaining deposits of antimony and bismuth, see *ante*). With the aid of such a solution, worked with a strong current, he obtains upon copper or brass a gradual deposition of reguline white metal, which takes a brilliant polish under the burnisher.

Urquhart (*Electro-Plating*, 196) who has experimented with Bertrand's process, asserts that hydrogen is freely liberated and but little metal is deposited. He adds, however, that the deposit is improved by concentrating the solution and working it at a boiling temperature. The same author claims to be able to obtain white deposits of aluminium from a saturated solution of the sulphate, slightly acidulated with sulphuric acid, working at a temperature of about 150° Fah., and with an aluminium anode. The current must be strong. He adds that the results obtained are not always certain. Other salts of aluminium have been proposed and used by different inventors and experimenters, but none of those processes appear to be of sufficient importance to warrant mention.

Aluminium, in fact, does not seem to us to possess any qualities that would make it advantageous as an electro-deposit upon other metals. The deposition of alloys of aluminium, if it could be successfully accomplished, would appear to offer some desirable advantages, but though some efforts have been made in this direction (consult J. B. Thompson's claims for depositing aluminium bronzes, *Chem. News*, xxiv. 194), they have not as yet been made entirely practical.



The Pennsylvania Nickel Works, in Philadelphia, have lately announced a new alloy for electro-plating, as a substitute for nickel, composed of aluminium and nickel, to which they give the name, alu-ni; but we cannot learn that it possesses any advantages over nickel-plating, either in respect to lustre or durability, while the present high price of aluminium must place the suggested alloy at a decided disadvantage. A practical method of depositing the various aluminium bronzes, with their beautiful tints, green, yellow, and golden, would no doubt be of service in the arts.

Bertrand (*Comptes Rendus*, lxxxiii. 854) affirms that electro-deposits of *magnesium* may be obtained with an aqueous solution of the double chloride of magnesium and ammonium. This solution is readily decomposed, and with a strong current yields upon copper and its alloys, after a few minutes, a strongly adherent and homogeneous coating, which accepts a good polish.

*Cadmium*, he proposes to deposit from an acid solution of the sulphate, which gives a white coherent coating capable of taking a fine polish. He obtains good results with a solution of the bromide slightly acidulated with sulphuric acid. Smee (*Elem. Electro-Metall.*, 1st Am. ed., 212) obtained the best results with the ammonio-sulphate, formed by adding ammonia to the sulphate, until the precipitate is redissolved. Other experimenters recommend the double cyanide of cadmium and potassium. Neither of these metals is of any importance to the electro-plater.

#### *Deposition of Antimony.*

Electro-deposited antimony possesses all the brightness of polished cast-iron. Its dead lustre is a slate-gray, and it may be easily scratch-brushed and polished; during the last operation, however, the tool slides as upon a slightly



greasy substance. It gives a surface resembling black platinum and "oxidized" silver, and may advantageously take the place of either in many cases.

Roseleur deposits this metal by boiling, for about one hour, and in a porcelain dish, or enamelled cast-iron vessel—

Water	. . . . .	100 parts.
Carbonate of soda	. . . . .	10 "
Sulphide of antimony, finely powdered	. . . . .	5 "

The boiling solution is filtered through paper or a fine cloth, and, on cooling, deposits a reddish-yellow powder of *oxy sulphide of antimony*, the Kermes mineral of the shops. This powder is again boiled in the same liquid, and the resulting solution is the antimony bath. It is, therefore, necessary to keep the bath constantly boiling when in use. For the anode either a plate of antimony, or a platinum wire is used.

Gore (*Electro-Metallurgy*, 100 *et seq.*) recommends the chloride of antimony, dissolved in water acidulated with hydrochloric acid, as a good solution for depositing antimony. It is a good conductor, and with a moderate current freely yields a bright reguline metal.

The same author refers to the mixed chlorides of antimony and ammonium as forming a very good depositing bath. This liquid may be made either by passing the current through a bath composed of equal parts of a saturated solution of sal-ammoniac and muriatic acid, using a large antimony anode, or, by mixing equal measures of a saturated solution of sal-ammoniac and commercial chloride of antimony. This bath is preferable to that of the simple chloride.

The same author made the singular observation that if, while the deposit of antimony is going on, it is removed and struck gently or rubbed with any hard substance,

such as metal or glass, it explodes sharply with evolution of light and heat. (*Philos. Mag.*, 1855, p. 73.)

A. Bertrand (*Comptes Rendus*, tome lxxxiii, 854), obtains a galvanic deposit of antimony on metal surfaces with the use of a solution of the double chloride of antimony and ammonium, in water slightly acidulated with hydrochloric acid, in which the double salt is soluble without decomposition. Precipitation of the metal is easily effected with a weak current. The bath should be used at the ordinary temperature. This process is substantially the same as that just described.

Gore (*Electro-Metallurgy*, 100) gives the preference over all others, to a solution of the potassic-tartrate of antimony (tartar emetic) in water acidulated with hydrochloric acid. The following are his proportions:—

Potassic-tartrate of antimony . . . . .	8 parts.
Hydrochloric acid . . . . .	4 "
Water . . . . .	2 "

This liquid dissolves the tartrate freely and forms a solution which conducts well, gives a coating of any desired thickness, and is not injured by long-continued service.

The acid solution of chloride of antimony is decomposed more or less readily by all the more electro-positive metals, which therefore coat themselves with antimony by simple immersion. A boiling solution of this salt is sometimes made use of for the purpose of imparting a lilac color to articles of brass, and for bronzing gun barrels; while the metallic powder precipitated from its chloride solution with zinc, is used for giving the appearance of gray cast-iron to plaster casts.



*Deposition of Bismuth.*

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Bertrand (see p. 404) proposes for obtaining electro-deposits of bismuth, a solution of the double chloride of bismuth and ammonium, a white, crystalline compound, soluble in water weakly acidified with hydrochloric acid. This bath is analogous to that which he proposes for antimony, and is used in the same manner. The solution he prefers contains 250 grains of salt to the pint of liquid.

When the operation is finished, the objects—brass or copper—will be found to have a blackish tint on the surface, below which, however, the bismuth, which adheres firmly, will be found with its characteristic lustre, and slightly pinkish color. It takes a fine polish. From trials we have made of this process, the conditions to be observed appear to be, to use very dilute solutions and a feeble current. The deposited metal has a distinctly pinkish tint, and is very little affected by atmospheric influences. Many experiments have been made to produce bismuth deposits by galvanic means, but none appear to answer the purpose so well as that above described.

*Deposition of Lead.*

Deposits of lead may be obtained by means of the plumbate of potassium or sodium, which is prepared by the protracted ebullition of 1 part of protoxide of lead (litharge), in 10 parts of caustic potassa or soda, dissolved in 200 parts of distilled water.

The electro-deposition of this metal has no importance in the arts. Its deposition upon certain metals, from the state of igneous fusion, has lately acquired some industrial importance, and will be referred to in the chapter on GALVANIZING.

By means of suitable lead solutions, and the proper



manipulations, it is possible to produce those magnificent iridescent colorations upon metals called the *colored rings* of Nobili, and from which has sprung a distinct industry known as—

#### *Metallo-Chromy.*

*Metallo-Chromes.*—These superb metallic colorations are produced by the electro-deposition of coherent, but exceedingly thin films of metallic oxides upon metal surfaces. The oxide of lead seems to possess to an eminent degree the property of separating from its solution in caustic soda or potassa, in the state of peroxide. The chromatic effects produced on polished surfaces of metal are frequently very beautiful. These effects were first fully noticed and described by Nobili (*Poggendorff's Annalen*, ix. 183, x. 392), after whom they have been named "Nobili's rings." They were subsequently carefully studied by Gassiot (*Proc. Elect. Soc.*, 1839), and by Becquerel (*Comptes Rendus*, tome xvii. 1, 55), through whose suggestions the phenomenon has been turned to useful account in producing very beautiful decorative effects upon metal surfaces. To exhibit these colored rings, prepare a saturated solution of acetate of lead, in a shallow dish, in which place a polished plate of steel. A wire from the positive terminal of a battery of moderate strength is then caused to touch the plate, while the negative wire is held in the solution above the plate. A small tinted circle makes its appearance on the polished surface beneath the wire, and rings of color of the most brilliant hues rise from the centre and expand to the circumference. The colors commence with silver-blond and progress onwards to fawn-color, and thence through various shades of violet to the indigoes and blues; then through pale blue to yellow and orange; thence through lake and bluish-lake to green and green-

ish-orange; thence through greenish-violet and green to reddish-yellow and rose lake. Colored figures of varied character are obtained by modifying the shape of the electrode connected with the negative end of the battery; using instead of a point, a slip of metal, a disk, a ring, a convex or a concave disk, a cross or other pattern. By the employment of a large disk and small steel plates, and by very careful manipulation, a uniform tint may be given to each plate and the chromatic scale of 44 colors may be obtained. For this purpose each experiment must be timed by a pendulum, and one second being given to the first plate, the duration for the rest must increase by one second for each. (Walker, *Electrotype Manipulation*, Part II. 2d Amer. edition, 47 *et seq.*). As these colors do not adhere closely to the metallic plate, the latter should be washed in boiling distilled water and then varnished.

Wagner (*Handb. d. Chem. Tech.*, 125) gives the following procedure, based substantially upon Becquerel's method. Prepare a completely saturated solution of litharge in caustic potassa as above described. Introduce into this the article to be treated, at the anode, and opposite to it attach a plate of platinum at the cathode.

When the circuit is closed peroxide of lead will be deposited on the anode, the color of which will depend on the thickness of the film deposited. As soon as the desired coloration is attained, the article is at once removed from the liquid and washed. If a point of the cathode is presented to the object, the well-known colored rings of Nobili are produced. To avoid this, the electrode must be kept in constant motion, and should be held a certain distance away from the surface of the article. "Metallochromy," according to the same authority, is used to produce decorative effects upon objects of copper, tombac, and



brass, previously treated to a thin electro-gilding. The principal color is green or purple-red, which passes over into bright-red, blue, violet, or yellow. Instead of the lead solution, one may be prepared with sulphate of copper and rock-candy, saturated with caustic potassa.

The production of these colorations demands careful manipulation. With too strong a current, the tints assume a uniform dark brown or black color. The coating is very adherent, and if the article has been well prepared, they will sustain the action of the burnisher (Walker).

The proportions of Becquerel's lead solution are as follows: Caustic potassa, 20 parts; litharge, 15 parts; water, 200 parts. Dissolve the caustic potassa in water, then add the litharge, and boil for half an hour, then allow to cool, and after decanting off the clear liquid, dilute it with an equal volume of water. Use cold, and replace by a fresh solution when it shows signs of exhaustion.

Roseleur recommends the plumbate of sodium bath, used for the electro-deposition of lead (see p. 405), for the production of colored effects, and affirms that with the usual disposition of the battery *inverted*, the operator may, at will, coat a given metallic surface with the richest colors of the rainbow, and successively transform the colors obtained through all the tints of the solar spectrum. His *modus operandi* is as follows:—

After allowing the bath of plumbate of soda to cool off, the metallic, or metallized object, connected with the positive pole, is immersed in it. Then the platinum wire, communicating with the negative pole, is gradually introduced into the bath without, however, touching the article. The latter will at once become colored with various shades; of these, yellow is the predominating color, but all of them become darker, or are entirely transformed,



according as the platinum wire is more or less submerged. We may thus vary *ad infinitum* this play of colors, which is due to the variable thickness of the deposited peroxide of lead. Too much intensity in the current will conceal these various tints under a uniform coating of dark brown.

When an article is unsatisfactory in its coloration, it is rapidly dipped into aqua fortis, which dissolves the oxide of lead, and restores the metallic surface to its primitive state.

A few years ago, Roseleur applied the metallo-chromic processes to the decoration of stoneware and porcelain previously coated with platinum, as indicated in the chapter on SIMPLE IMMERSION GILDING. The results were sufficiently satisfactory to find their application in the production of a number of ceramic wares.

Watch-dials and hands are thus colored in Switzerland, and bells, etc., in France. A skilful operator might, by the same processes, impart to certain productions of bronze the natural colorations of the objects represented, as for instance, scarabæi, and other insects exhibiting iridescent colors.

While the article is colored by the oxide, a part of the lead in metallic form is deposited upon the anode in the shape of small cubical crystals, which have no adherence either to each other or to the platinum wire. This want of adherence is explained by the very small volume of the anode as compared with the iridized surfaces.

Roseleur's procedure differs from that of Becquerel in that his solution is very much more dilute. Should the work not appear satisfactory it will be advisable to increase the concentration of the liquid rather than increase the intensity of the current.

## CHAPTER XLVIII.

REDUCTION OF OLD AND SPENT BATHS—RECOVERY OF GOLD,  
SILVER, PLATINUM, COPPER, AND NICKEL—ASHES—COM-  
MENTS ON RECOVERY OF GOLD AND SILVER.

### *Reduction of Old Baths.*

BEFORE passing to the study of the galvanoplastic art proper, we shall indicate the most economical and practical processes for separating from spent baths, or solutions spoiled from any cause, the precious metals they contain, and in such a state of purity that they may be used for the preparation of new baths.

We shall also explain the treatment of spent acids, washwaters, and other liquids generally considered as waste, and which require great attention, since in many works they represent a value equal to one-fourth or one-fifth of that of the precious metals employed.

### *Recovery of Gold from Old Solutions.* (*Roseleur's Methods.*)

All the liquids which contain gold (*excepting cyanide solutions*, which will be separately considered) are strongly acidulated with sulphuric or hydrochloric acid, unless they are already acid, and then largely diluted with water. The precious metal is then precipitated by a solution of sulphate of protoxide of iron (green vitriol, copperas), and, after a few hours' waiting, it is well to ascertain that the liquid contains no more gold, by a fresh addition of sulphate of iron, which should produce no turbidity.



The gold, which is precipitated in the form of a red or brownish powder, is collected upon a filter, washed, and dried to dryness in an iron pan with equal weights of *borax*, *saltpetre*, and *carbonate of potassium*.

The fritted mass is then gradually introduced into a refractory crucible heated to a white heat in a suitable furnace. When all the substance is introduced, the heat is increased, to cause perfect fusion, in order that the metal shall collect well at the bottom of the crucible. After cooling, a button of pure gold will be obtained, which, being dissolved in aqua regia may be used in the preparation of fresh gilding solution.

Should it be desired to dissolve in aqua regia the pulvulent gold left on the filter, it will be necessary to wash it several times with a diluted solution of sulphuric acid, in order to remove the sulphate of iron with which it is still impregnated.

This mode of reduction is well adapted for impure chloride of gold, to the simple immersion baths with the carbonate or pyrophosphate of sodium, and also to the dilute liquors used for ungolding; but it only succeeds imperfectly with *cyanide* solutions, which never completely dissolve, by this process, with all the gold they contain.

The best manner of treating *cyanide* solutions consists in evaporating them to dryness in a cast-iron kettle, and heating the residue to a white heat in a clay crucible. A small proportion of borax or saltpetre may be added as a flux, but generally this may be dispensed with.

The button of gold separated at the bottom of the crucible is red when saltpetre has been employed, and green when borax; these differences of coloration, however, have nothing to do with the purity of the metal, but simply indicate different conditions of molecular aggregation. (See *Comments* at close of this chapter.)



Gold may also be separated from solutions which contain no cyanide, by treatment with an excess of protochloride of tin, which produces a precipitate of purple of Cassius (stannate of gold), from which the gold is easily reduced by heat to the metallic state. Sulphurous acid will also reduce the gold. But in the latter case, the liquid should be heated.

Granulated gold is obtained by running the molten metal in a thin stream, from a certain height, into a large quantity of cold water.

*Recovery of Silver. (Roseleur's Methods.)*

Old solutions which contain silver in the form of a *simple salt* are very easily treated. It is sufficient to add to them, in excess, a solution of common salt or hydrochloric acid, when all the silver will be precipitated in the state of chloride of silver, which, after washing, may be employed for the preparation of new baths, or reduced to the metallic form by one of the processes about to be described. Solutions of nitrate of silver, desilverizing acids, etc., fall in this category.

Common salt, on the other hand, is without action upon solutions containing silver in the state of a *double salt*, and will rather facilitate solution than precipitation. The double tartrate of potassium and silver (whitening bath) - the double sulphite of sodium and silver (immersion bath), etc., belong to this category. Before employing common salt with such solutions, the liquids should be strongly acidulated with sulphuric acid, which restores the silver to the state of a simple salt, readily precipitated by common salt. Hydrochloric acid, however, precipitates silver well from these solutions.

Solutions which contain silver, as *cyanide*, form another exception; and in order to recover all the metal, we must

again have recourse to the process employed for similar combinations of gold; that is to say, evaporation to dryness, and reduction of the mass in a crucible, with an addition of carbonate of sodium and powdered charcoal. The silver is then obtained as a fused button at the bottom of the crucible. (See *Comments* at close of this chapter.)

When the silver has been obtained in the state of the chloride of silver, it may be reduced to the metallic state by many processes, the principal of which are:—

1. Well-washed chloride of silver (water does not dissolve a trace of it) is placed in a stoneware dish with two or three times its weight of zinc, and the whole is covered with water strongly acidulated with sulphuric acid. As soon as they are in contact, these substances react upon each other: the sulphuric acid and the zinc decompose the water into its elements, the oxygen of which oxidizes the zinc, which then combines with the acid to form sulphate of zinc (white vitriol or white copperas), a very soluble salt. On the other hand, the hydrogen seizes upon the chlorine of the silver, transforming it into hydrochloric acid, also very soluble in water. The silver is left behind in the form of an impalpable powder, and when all the zinc is dissolved the contents of the dish may be filtered. The silver, which remains upon the filter, must be thoroughly washed with pure water, and may then be dissolved in pure nitric acid to form a pure nitrate of silver.

2. The chloride of silver, freed from foreign metallic salts by washing, is mixed with four times its weight of crystallized carbonate of sodium, and half its weight of pulverized charcoal. The whole is made into a homogeneous paste, which is thoroughly dried, and then introduced into a strongly heated crucible. When all the material has been introduced the heat is raised, to promote



complete fusion, and to facilitate the collection of the separate globules of silver into a single button at the bottom of the crucible, where it will be found after cooling.

If granulated silver is wanted, pour the metal in a thin stream, and from a certain height, into a large volume of water, as in the case of gold.

This method is almost exclusively employed in electro-gilding and silvering works.

During this operation, the carbonic acid of the carbonate of sodium having disappeared, the oxygen of the soda unites with the carbon of the charcoal forming gaseous products, which escape. In its turn, the sodium combines with the chlorine of the chloride of silver, forming chloride of sodium, while the metallic silver is set free. The fact is worthy of remark, that the chloride of sodium, which is decomposed by a silver salt in aqueous solution, is reconstructed by igneous fusion in the presence of chloride of silver.

3. Lastly, we may employ in many cases a plate or sheet of copper for separating silver from its salts; but it is quite difficult to free the deposited metal entirely from traces of copper.

#### *Recovery of Nickel.*

To recover nickel from old solutions, Urquhart proposes to (*Electro-Plating*, 165) take advantage of the observation of Unwin (see Chapter XLV., p. 376), that the double sulphate of nickel and ammonium is almost insoluble in a concentrated solution of sulphate of ammonium.

He makes up a saturated solution of ammonium sulphate in warm water, and adds it to the old nickel-plating solution, with constant stirring, and after the lapse of a few minutes, a granular precipitate of the double sulphate will begin to separate. The addition of ammonium sulphate



should be continued, from time to time, until the liquid is colorless. The precipitated salt is very pure, and may be used directly in making a new bath.

*Recovery of Platinum. (Roseleur.)*

This process is very simple, and consists in first acidulating with hydrochloric acid any solution of platinum, unless it be already acid, and then immersing in it for some hours a well cleansed bar of iron. The platinum is reduced in the form of a black powder, which is washed, and then calcined to a white heat. By dissolving it in aqua regia we reconstitute the chloride of platinum necessary for the preparation of the platinizing baths.

Platinum solutions may also be reduced by evaporating them to dryness, and strongly calcining the residue, which is then washed upon a filter in order to remove the soluble salts, and again submitted to a white heat. The platinum thus obtained is soluble in aqua regia.

*Recovery of Copper. (Roseleur.)*

In works where great quantities of copper are operated upon, it is advantageous to recover the metal dissolved in the cleansing baths, which are allowed to go to waste with the rinsing water, by the majority of gilders, silver electro-platers, and galvanoplastic operators. The recovery of such copper is an easy and inexpensive process. All the liquids holding copper are collected in a large cask filled with wrought or cast-iron scraps. By the contact of the copper solution with the iron, a chemical reaction immediately takes place, by which the iron is substituted for the copper to make a soluble salt, while the copper falls to the bottom of the cask as a brown powder.

The cask should be sufficiently large to hold all the

liquids employed in a day's work. The liquids are decanted every morning.

The old iron scrap is generally suspended in a willow basket near the top of the liquid, and, by occasionally moving it about in the liquid, the metallic powder of copper alone falls to the bottom of the cask.

The same method is employed for recovering the copper from old cleansing acids, or from spent galvanoplastic baths. The copper thus obtained is quite pure, and, by calcining it in contact with the air, a black oxide of copper is obtained which is serviceable for enriching and neutralizing galvanoplastic baths too strongly acidified.

*Utilization of Other Wastes. (Roseleur.)*

Nothing whatever should be allowed to go to waste in well-conducted works. Sweepings, sawdust, residues from the bottoms of scratch-brushing tubs, filters, papers, rags, etc., should be carefully collected, mixed, and burned in a furnace adapted for the purpose. The resulting ashes are finely pulverized, sifted, and sold to certain operators called "sweep smelters," who extract the precious metals from them.

The method in vogue in France, as described by Roseleur, and which is a very equitable one, is as follows:—

The purchaser is called in, and, after having thoroughly mixed the heaps of ashes, several samples are taken with a sampling-gauge, which is a rod hollowed out laterally. The various samples are then mixed, and divided into two parts, one for the buyer and the other for the seller, each of whom has one assayed for gold and silver. From the comparison of the two assay certificates, the buyer takes the lot at its bullion value, after deducting a certain sum for the expense of the operation and his profit.

The sweep-smelter, in turn, pulverizes and sifts the



ashes again, either reduces the metals himself, or disposes of the material to the smelter and refiner.

The gold and silver are obtained together, and to separate them the metal is granulated, and treated with nitric acid free from chlorine, which dissolves the silver, and is without action upon the gold. The latter metal, in the shape of a black or brownish powder, collects at the bottom of the vessel, and, after thorough washing with distilled water, which removes the nitrate of silver with which it is impregnated, is obtained in a pure state.

When an ingot contains little silver and much gold, it previously melted with a certain proportion of the former metal, otherwise the gold will so envelop the silver as to prevent its complete solution by the acid.

Ingots of silver and copper are treated in cast-iron kettles by boiling with concentrated sulphuric acid, which transforms the copper into soluble sulphate of copper, and silver into sulphate of silver, but slightly soluble. The separation of the two may be partly effected by washing, but, generally, the silver is precipitated by plates of copper. The alloy, previous to its solution, should be finely laminated.

#### *Utilization of Spent Acids. (Roseleur.)*

The list of acids, or cleansing solutions which the galvanoplastic operator renders useless for further service, is as follows:—

1. Preliminary cleansing pickel (sulphuric acid, more or less diluted with water);
2. Nitric acid (aqua fortis), with salt and other additions;
3. Acids used for bright or for dead-lustre dipping, and composed of mixtures in various proportions, of sulphuric and nitric acids, with the addition of soot or of salt;



4. The desilvering solutions, used for removing silver from copper and its alloys ;

5. The ungilding solutions, composed of mixtures of sulphuric acid, nitrate of potassa (saltpetre), and chloride of sodium (salt), which have been used to remove gold from gilded copper ;

6. And last, spent acids of batteries.

On the principle that nothing should be lost in industrial operations, we indicate herewith certain methods by which these several liquids may be utilized.

The preliminary cleansing pickle of sulphuric acid saturated with copper, is treated with scrap iron, which separates the copper in pulverulent form. The supernatant liquid contains sulphate of iron of little or no commercial value, but which may be discharged wherever its disinfecting qualities may be serviceable.

Old nitric acid (or aqua fortis) saturated with copper, and no longer of service, is treated by the addition of more or less concentrated sulphuric acid, which decomposes the extremely soluble nitrate of copper, transforming it into the sulphate, which is crystallized out and separated by decantation. These crystals are sold to the chemical manufacturers under the name of gilder's verdegris (*verde-gris de doreur*). The supernatant liquid, which consists of aqua fortis still more or less charged with copper, and with sulphuric acid, is used for the whitening baths employed by varnishers. (See Chapter II. Aqua fortis for Bright Dipping and Whitening Bath.)

The spent acids used for bright or "dead" dipping are commonly mixed with spent aqua fortis. The effect is practically the same as the addition of sulphuric acid in the case just named ; that is to say, crystals of sulphate of copper are deposited, and the supernatant liquid is

utilized for the preparation of a new bright dipping bath, or the whitening bath.

Solutions used for *disilvering* are diluted with four or five times their weight of water, with the addition of common salt or of hydrochloric acid, which precipitates the silver in the state of insoluble chloride.

Solutions used for *ungilding* are diluted with five or six times their volume of water, treated with an excess of sulphate of iron (copperas), and allowed to remain undisturbed for some time. The gold collects in the condition of a brownish powder at the bottom of the bath, and is recovered either by decantation or filtration. The recovered gold after several washings may either be fused and cast into an ingot, or dissolved in aqua regia to form perchloride.

Finally, the spent nitric acid of batteries is disposed of by the manufacturers of dyes, who, after removing the mercury, should it contain any, convert it into nitrate of iron, which is used for dying black and various dark shades.

The sulphuric acid in which the zincs of the battery have been immersed are commonly thrown away as of no value. Nevertheless, the firms that operate on a large scale have begun to dispose of it to the chemical manufacturers, who saturate it, hot, with oxide of zinc, metallic zinc, or the dross of this metal, producing a sulphate of zinc, dense or crystallized. This salt is employed at the present time in considerable quantities in the manufacture of strong glue. It is also used for disinfecting purposes.



## COMMENTS ON THE FOREGOING METHODS.

*Precautions Necessary—Modifications Suggested.*

For the treatment of old, spoiled, or spent *cyanide* baths, either of gold or silver, it will be noticed, Roseleur prefers the method of fusion to that of precipitation. This preference is unquestionably proper, unless the bulk of solution to be evaporated is very great, for the dry method requires much less manipulative skill than the wet, the chances of loss of the precious metals by imperfect precipitation, etc., are avoided, and the operator is not incommoded by the disengagement of poisonous vapors of hydrocyanic acid. It is possible, however, that the reduction of the precious metals by fusion of the dry residuum in the manner described, may not be perfectly accomplished, and that the slag from which the button or particles of metal are removed may still contain a small quantity of metal. To be assured that no precious metal is lost in this form, it will be prudent to lixiviate the mass in hot water, pour off the wash waters, and test them for silver or gold. For silver, by the addition of hydrochloric acid, which will produce, if any is present, a precipitate of chloride of silver; and for gold, by first acidulating the liquid with hydrochloric acid, heating it to boiling, and introducing some fragments of metallic zinc—which, after some time, will precipitate the remaining traces of gold.

It should be noticed that *cyanide gilding solutions*, in which articles of silver, copper, brass, etc., have been gilded for a long time, will contain notable quantities of both of these metals. The metal obtained by the above-described method of fusion will, therefore, contain, in addition to gold, also silver and copper. To separate these metals the simplest procedure is to digest the metal—



lic button or residuum with aqua regia, which will dissolve the gold and the copper as chlorides, and leave the silver as chloride, in which condition it can be separated by filtration, and reduced in the manner previously described. The gold may be separated from the copper by the addition of proto-sulphate of iron.

Similarly, *cyanide plating solutions* that have done long service in plating articles of copper, bronze, or brass, will contain a notable quantity of copper, which, in recovering the silver by the method of fusion will contaminate the reduced silver. The mode of purifying the silver is described above.

As it may sometimes be found inconvenient to use the dry method of reduction for the recovery of gold and silver from old or spoiled cyanide solutions, as where the volume of liquid to be evaporated is very considerable, or for other reasons, we append a brief description of the most approved wet methods for that purpose, for which we are indebted to Elsner (Winckler, *Handbuch d. Metallüberzügen*, 206).

*Recovery of Gold from Old Cyanide Gilding Baths (Wet Process).*—The solution containing gold, silver, and copper is acidulated with hydrochloric acid, which causes a disengagement of hydrocyanic acid (this gas is *extremely poisonous*, for which reason the operation should be carried on in the open air, or where there is good draft or ventilation to carry off the fumes). A precipitate consisting of the cyanides of gold and copper, and chloride of silver, is formed. This is well washed, and boiled in aqua regia, which dissolves the gold and copper as chlorides, leaving the chloride of silver behind. The solution containing the gold and copper is evaporated nearly to dryness, in order to remove the excess of acid, the residue is dissolved in a small quantity of water, and the gold precipitated therefrom as a brown metallic pow-

der, by the addition of sulphate of iron (copperas). The copper remains in solution. (See *Recovery of Copper*, p. 415.)

The silver chloride is reduced by fusion with carbonated alkali as previously described. It should be noticed, however, that by Elsner's process the separation of the gold is not perfect, since the original solution from which the metals were precipitated by hydrochloric acid still contains a little gold.

These remaining traces of gold may be best removed by strongly acidulating the original solution, heating it to the boiling point, and introducing therein some fragments of zinc, which will remove the last traces of gold. After the solution of the zinc, the precipitated gold may be collected and added to the principal portion.

*Recovery of Silver from Old Cyanide Plating Solutions (Wet Method).*—Strongly acidulate the solution with hydrochloric acid, as above (observing the precaution to provide for the effectual carrying off of the hydrocyanic acid liberated). Remove the precipitated chloride of silver and cyanide of copper by filtration, and, after thorough washing, transfer it to a porcelain dish and treat it, with the aid of heat, with hot hydrochloric acid, which will dissolve the cyanide of copper. The resulting chloride of silver is then reduced to the metallic state in the manner previously described.

Other processes, wet and dry, have been described by various authors, for recovering gold and silver from old baths (consult Elsner, *Winckler's Handb.*, 205 *et seq.*; Bolley, *Id.* 205; Elsner, Hessenberg, *Jour. f. prak. Chem.*, xxxvii. 477; xxxviii. 169, 256; Huber, *Dingler's Polytech. Jour.*, clxviii. 384; Boettger, Varrentrapp, *Winckler's Handb.*, 207); but the methods above given, when intelligently applied, will be found to give very satisfactory results.

## PART II.

### GALVANOPLASTIC OPERATIONS PROPER.

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#### THICK METALLIC DEPOSITS.

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#### CHAPTER XLIX.

##### OBJECTS OF THE GALVANOPLASTIC ART.

ONE who will have practised the operations described in the first part of this work, will find no difficulty whatever in the manipulations which follow. The GALVANOPLASTIC ART proper calls for baths less complex in their composition; the causes of failure from too much or too little intensity in the electric current are less frequent; and in the majority of cases the operations are inexpensive.

Although plating with gold and silver and other metals with the aid of electricity is a branch of the *galvanoplastic art*, it is customary to confine this term to *those deposits having sufficient thickness to form a resisting body, which may be separated from the object serving as a mould, and which, at the same time, will preserve the shape and dimensions of the model.* To be more explicit, let us give a few examples:—

A medallion of bronze being given, we may superpose upon one of its faces an electro-deposit, which, being separated from its matrix or mould, reproduces with mathe-



metrical accuracy all the parts of the model save that the sunken portions appear in relief, and conversely.

A statue of plaster of Paris, a carving in wood, an impress in wax, or in gutta percha, a fruit, etc., may, after certain preparations, be covered with an electro-deposit say, of copper, and it will be possible to destroy the mould and to preserve in this deposit a fac simile of its form and its dimensions.

The galvanoplastic art may even impart a certain degree of resistance and unalterability to materials essentially ephemeral in their nature. Thus, ornaments and utensils of crystal, porcelain, clay, or wax, may be preserved against rapid destruction by a metallic coating which will respect all the minutiae of their forms. It will also be easy to keep destructible objects, like small animals, plants, insects, and flowers, indefinitely, which will leave their exact imprint on the durable deposit of metal with which they have been covered.

There can be no more striking proof of the accuracy of galvanoplastic impressions, than to say that the electro-deposit of copper upon a daguerreotype will reproduce it with all its shadows, tints, half tints, etc. The copy will be in some respect even superior to the original, since the image will be in the right position, and less susceptible to atmospheric and photodynamic influences.

In galvanoplastic operations, copper is almost exclusively employed. This metal is easily separated from its combinations, is very malleable, and not very oxidizable; and, as it permits of being perfectly cleansed in the wet way, no difficulty is encountered in gilding, silvering, and platinizing it.

We must not confuse galvanoplastic deposits proper with the thin ones described in the first part of this work, and which are merely adherent films of metal. The

copper galvanoplastic deposits are generally obtained from simple salts (sulphate of copper). The thin electro-deposits, on the other hand, are produced from double salts.

It is possible also to obtain galvanoplastic deposits entirely of silver and gold; but these operations are exceptional, on account of the cost of the materials and of the difficulties of the operation. We shall, nevertheless, mention them after we have passed entirely over the ground of copper galvanoplastic deposits, which have been, and are still, of eminent service in the arts.

The galvanoplastic operator will have presented to him the following cases:—

1. He will be required simply to apply upon a metallic surface, which is consequently a conductor of electricity, a deposit of copper adhering to the underlying metal.

2. Or, the operation being completed, it will be necessary to separate the two metals in such a manner that they will furnish two identical productions, one of which will be a relief, and the other an intaglio. (Casts of medals, bass reliefs, etc.)

3. Or, he will be required to apply an electro-deposit upon materials not naturally conductors of electricity, but rendered so by a preliminary process of metallization. The object will be entirely or partly covered with the metallic deposits. (Copper deposits upon ornaments of plaster of Paris, wax, glass, porcelain, etc., or upon leaves, fruits, insects, etc.)

4. Or, after obtaining the deposit, he will be required to separate the non-metallic mould in order to have a perfect copy of the original in copper. (Reproduction of printing type in moulds of wax, stearine, gutta percha, gelatine, typographic clichés, electrotypes, etc.)

5. Or, if he cannot apply the electro-deposit of copper



directly upon the object, he will be obliged to make a mould of it, from which a greater or less number of copies may be obtained. (This is the most frequently occurring case: an impression of the original is taken in some plastic substance, which is rendered a conductor of electricity, and upon the surface thus metallized the galvanoplastic deposit is effected.)

The above five cases embrace all the possible applications of the galvanoplastic art; the same bath answers for all, and its composition is very simple.

## CHAPTER I.

### THE BATH.

1. INTO a vessel that will be unacted upon by sulphuric acid, such as glass, stoneware, porcelain, gutta percha, or lead, a certain quantity of water is introduced, to which is added about 8 to 10 per cent. of sulphuric acid, say 8 to 10 volumes of acid to 100 volumes of water.

The acid must be poured into the water with constant stirring, as otherwise the former, being much denser than water, falls to the bottom, and, slowly combining with the surrounding water, may cause an increase of temperature sufficient to break the glass or melt the gutta percha. Whatever be the nature of the vase, it is always wise to add the acid by small quantities at a time, and to stir the liquid with a glass or wooden rod.

2. Dissolve in this acidulated liquid as much sulphate of copper as it will take up at the ordinary temperature. If the crystals of sulphate of copper are placed directly in the liquid, they fall to the bottom, and dissolve very



slowly, for the reason that the layer of water in contact with them soon becomes saturated, and, being denser than the liquid above, does not mix with it, but forms a saturated solution surrounding the crystals. In this case it is, therefore, necessary to agitate the liquid frequently with a glass or wooden rod, in order to mix the dense and saturated layers with the lighter ones which have dissolved little or no sulphate. But it is preferable to operate in a different manner; thus, the crystals of sulphate of copper may be placed in a perforated ladle of copper or stoneware, or in a bag of cloth, suspended near the surface of the liquid. With this arrangement, as soon as a portion of the liquid has become saturated with sulphate of copper, it becomes denser and flows downward, while a lighter layer takes its place, and becomes saturated in its turn. When the liquid refuses to dissolve any more of the crystals, it is said to be saturated, and marks about  $25^{\circ}$  of Baumé's hydrometer for liquids heavier than water.

Water, without the addition of sulphuric acid, will dissolve the sulphate of copper equally well, and may be used to form a galvanoplastic bath. But, if the water is not distilled, and contains, as is nearly always the case where ordinary water is used, bicarbonate of calcium, the solution is rendered turbid by the precipitation of carbonate of copper.

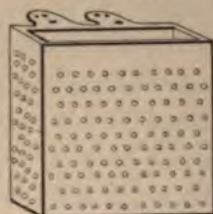
Baths of water and sulphate of copper only are rarely employed, because they are poor conductors of electricity, and because the deposited copper is irregular, granular, and brittle. It is possible to replace the sulphuric acid by other acids or salts which increase the specific gravity of the liquid, and increase its electric conductivity; such are acetic, tartaric, citric, etc., acids, or the bisulphates of potassium and sodium, the alums, and sul-

phate of aluminium. But, in the arts, sulphuric acid is nearly always employed.

To sum up, a galvanoplastic bath consists of water, more or less acidulated with sulphuric acid, and saturated with sulphate of copper at the ordinary temperature.

Baths of sulphate of copper, while working, must always be kept saturated; that is to say, new supplies of sulphate

Fig. 132.



of copper must be furnished to the bath to replace that decomposed to form the metallic deposit. This result is simply accomplished by suspending to the top of the vessel, so as to dip in the upper portion of the liquid, bags of cloth or hair, or perforated baskets of gutta percha (Fig. 132), kept always provided with crystals of sulphate of copper.

One cannot be too particular about the choice of the sulphate of copper, of which three very distinct varieties are found in the market. The first, which is the best, is produced from the treatment of copper, or its oxide, with sulphuric acid, more or less concentrated. This sulphate comes in the form of rhomboidal crystals, semi-transparent, and of a fine blue color. Its solution is also a pure blue.

The second variety is produced from the spontaneous oxidization of natural copper sulphides, or pyrites. As these ores contain a large percentage of arsenic and other metals, the resulting sulphates are very impure, and often exhibit veins of white and green.

The third is the product resulting from the treatment by sulphuric acid of the dipping liquors employed for cleansing copper and its alloys. These sulphates are mixed with those of zinc and of other metals entering into

the composition of bronzes, brasses, or other alloys. Besides they still retain a certain proportion of nitric acid, which is injurious to the operation.

We shall give in the third part of this work (CHEMICAL PRODUCTS), the best and readiest methods for ascertaining the purity of the sulphate of copper.

The galvanoplastic baths are always employed in the cold, and are kept in vessels of various shapes, according to the wants of the operator. Stoneware, porcelain, and glass are the best materials for the purpose; but as it is quite difficult to find in the trade such vessels sufficiently large, it is also customary to employ wooden troughs, vats, covered inside with a layer of gutta percha, marine glue, various resinous substances, or with sheet lead, which may be coated with a layer of varnish.

Zinc, iron, and tin must, manifestly, be excluded from the bath on account of the chemical reactions taking place between these metals and the sulphate of copper.

The working of galvanoplastic baths remains satisfactory, when the specific gravity is retained between 20° and 25° Baumé.

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## CHAPTER LI.

MODES OF OPERATING—DEPOSITS BY SEPARATE CURRENT—  
SIMPLE APPARATUS—THE SAME FOR THE “AMATEUR”—  
LARGE PLANT.

### *Modes of Operating.*

It has been stated that copper can be reduced by two distinct methods, viz: by the separate current process, employing either the voltaic battery or the dynamo-

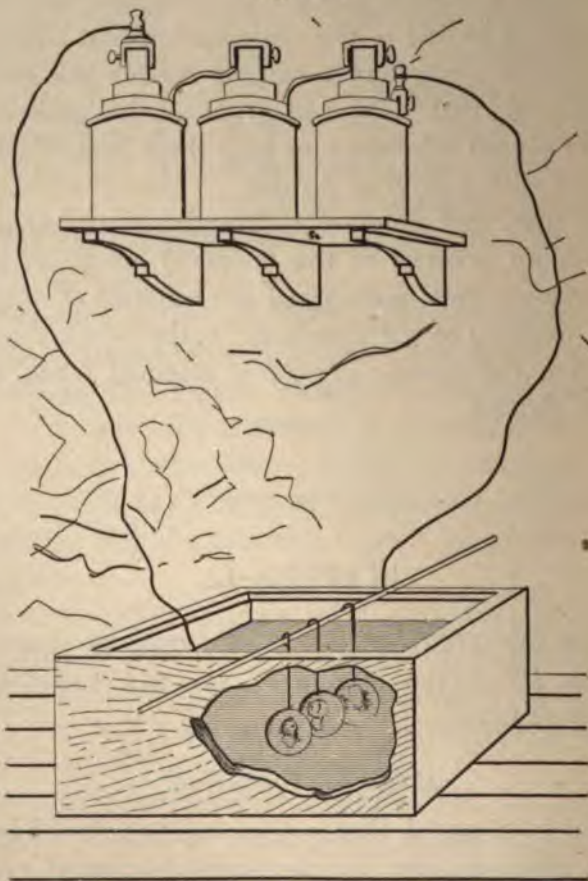


machine, or by a modified procedure in which the object to be covered constitutes the positive pole. We shall describe these two processes.

*Separate Current Process.*

The solution of sulphate of copper having been prepared and disposed as above described, the object which is to receive the deposit is connected (Fig. 133) with

Fig. 133.



conducting wire attached to the negative pole of the battery or dynamo, and immersed in the solution. On the other hand, to the conducting wire leading from the positive pole (carbon or copper) is attached a sheet or plate of copper, and this anode is placed in the liquid parallel to the object connected with the other pole. The plate should have a surface at least equal to that of the article to be covered. The deposit begins immediately, and its progress may be observed by removing the object now and then from the solution.

To operate upon a clean metallic surface, the deposit of copper will be formed instantaneously on every part of the surface. On the contrary, if the surface is only a mediocre conductor of electricity (as plumbago or graphite), the deposit begins at the points nearest by the conducting wire and from which it spreads over the surface from one

Fig. 134.



side to the other. Thus, for instance, a medal of silver covered with plumbago (Fig. 134), and joined at one end alone with the conducting wire, will receive a

deposit beginning at the periphery, and radiating towards the centre. After a variable length of time, the whole surface will be covered ; but, evidently, the thickness of the deposit will be greater at the edges than at the centre. This is at times very objectionable, and to avoid it, the metallization of the mould is resorted to, as will be explained further on. (See, also, the chapter on ELECTROTYPING, Knight's process.)

With a little practice it is easy to ascertain whether the intensity of the current bears the proper relation to the surfaces to be covered. The operation is slow with a weak current, but there is no other inconvenience associated with this, unless the substance of the mould is alterable, like gelatine. Too intense a current results in a granular deposit, the particles of which have little cohesion, and no adherence to the mould.

#### *Simplified Apparatus.*

A modified process, which is capable of yielding galvanoplastic deposits, employs substantially a solution of sulphate of copper, in which is immersed a diaphragm or porous cell filled with some liquid capable of dissolving iron or zinc placed in it. The iron or zinc is connected by a conducting wire with the object in the bath which is intended to receive the deposit.

It is scarcely necessary to explain that the nature, shape, volume, and disposition of this apparatus may be varied *ad infinitum*, to suit the purpose of the operator and the shape of the moulds.

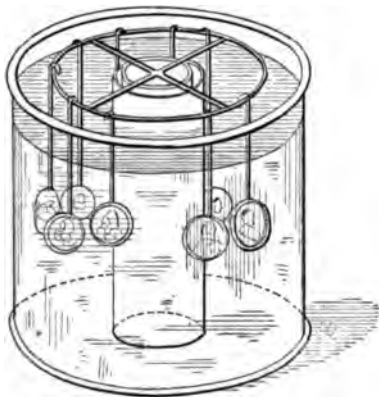
The most convenient form of this apparatus is that in which the surfaces of the zinc are nearly equivalent, and, as far as practicable, parallel to those of the mould. This latter condition is, in most cases, very difficult to fulfil.



*Simplified Apparatus for Amateurs.*

Beginners will have no difficulty in arranging an inexpensive apparatus, which will suit perfectly for depositing copper upon small flat surfaces, or upon medals, or small articles in bas-relief by conforming to the following directions. The solution of sulphate of copper may be kept in a stoneware, earthenware, or porcelain vessel, in the centre of which stands a porous cell filled with water acidified with 2 or 3 per cent. of sulphuric acid, and 1 per cent. of amalgamating salt. This liquid surrounds a cylinder of zinc (Fig. 135), which supports a circle of brass wire, the two

Fig. 135.



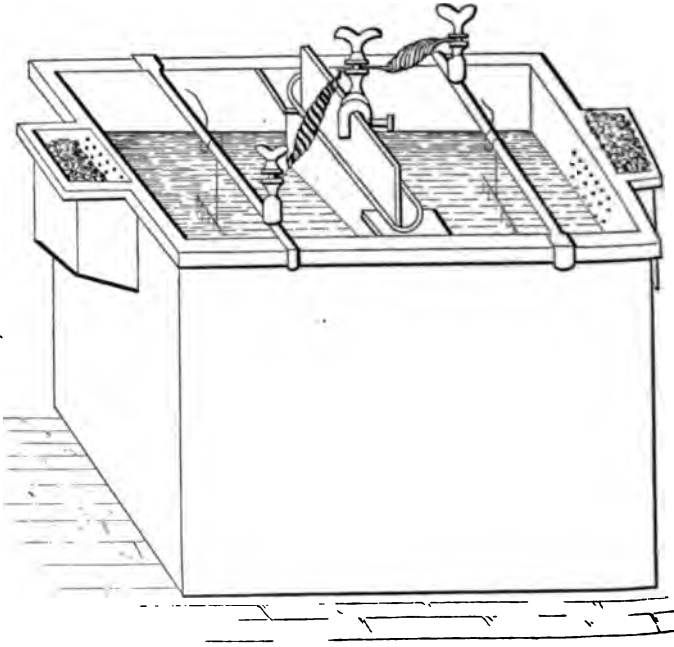
crossed diameters of which are soldered, or simply fixed, in four notches to the top of the zinc cylinder.

In this manner it will be easy to suspend from this circular framework a certain number of objects or moulds, which will be immersed in the liquid in such a manner that the faces to be covered shall face the diaphragm. Two small bags of hair, filled with sulphate of copper, are attached to the upper edge of the vessel.

Fig. 136 represents a simple apparatus for amateurs,

devised by M. Roseleur, which may be easily transported, and is not liable to be broken. It is a rectangular trough

Fig. 136.



of gutta percha in the centre of which are two grooves for holding in position a flat or oval diaphragm (Fig. 137). At the two extremities, and at the top, two small trays are fixed, which serve as handles for moving the apparatus and communicate with the interior of the vat by numerous small holes. These trays are filled with crystals of sulphate of copper. The porous cell contains acidulated water and a plate of amalgamated zinc (Fig. 138). The connections are made by means of double binding screws placed upon the zinc plate and the supporting rods (Fig. 139). The metallic wires are twisted in spirals, so as

allow of the rods supporting the articles being approached to or removed from the diaphragm.

Fig. 137.

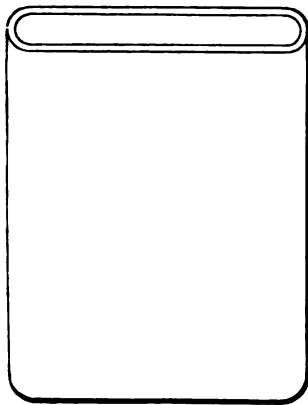
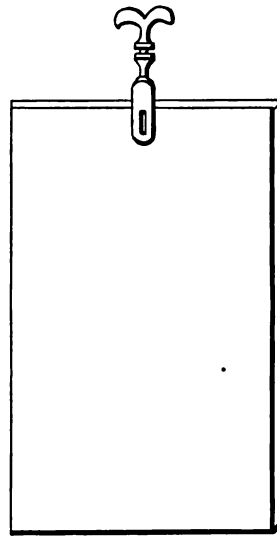
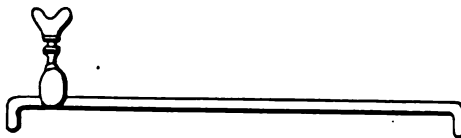


Fig. 138.



With this disposition of the apparatus each side of the cell may be used for operating upon a medal or bas-relief;

Fig. 139.



but if two cells are arranged in the vat, one at each end of the apparatus, and with the supporting rod between them, the deposit on objects in high relief—a small statue, for instance—may be effected on all sides at once.

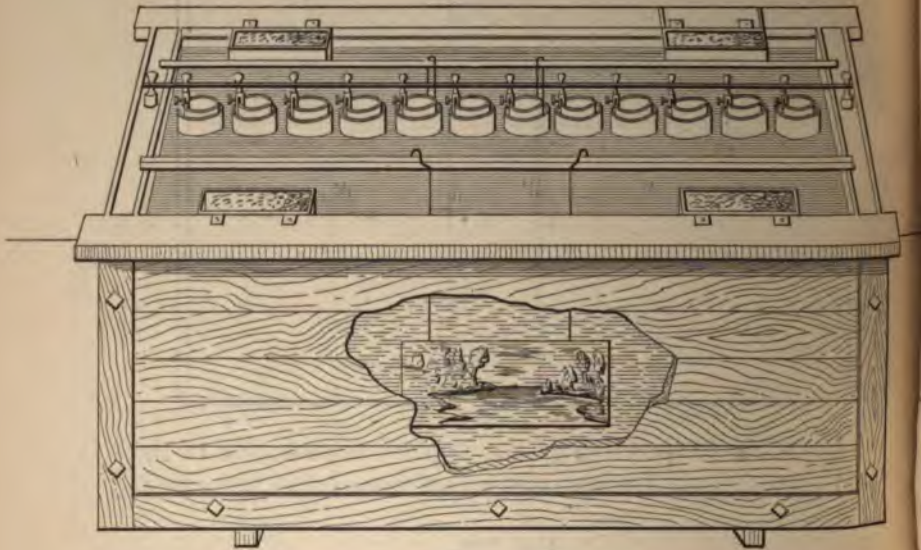
#### *Large Plant.*

For covering large surfaces, Roseleur describes the following disposition. The bath will be contained in a large



wooden depositing vat (Fig. 140), lined inside with gutta percha, or lead, or any other substance unacted upon by the bath. In the middle of the trough and in the direction of its length he disposes a row of cells close to each other, each provided with its zinc cylinder. A thin

Fig. 140.



metallic ribbon is connected with all the binding screws of the cylinders, and is in contact at its extremities with two metallic bands on the ledges of the depositing vat. The metallic rods supporting the moulds are in contact with the metallic bands of the ledges, and therefore in connection with the zincs.

With such a disposition of the supporting rods on each side of the depositing vat, the entire surface of the zincs is utilized. It will be easy to double the effect by employing two rows of cells instead of one (Fig. 141); thus, a surface will be covered on each side of the trough, and

two other surfaces placed back to back, in the interval between the two rows of cells.

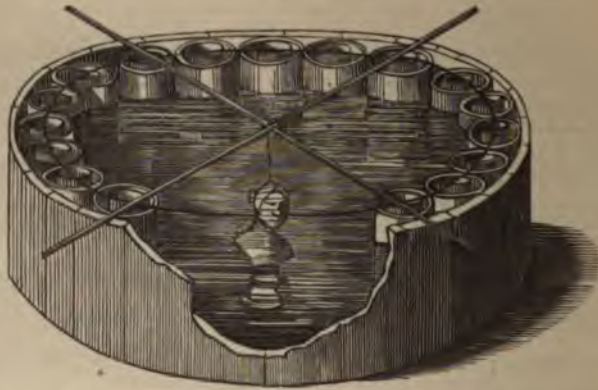
Fig. 141.



If, instead of nearly plane surfaces, it is required to operate upon objects in high relief, he has recourse to the circular depositing vat (Fig. 142), in which the cells form a circle, and the mould to be covered is in the centre. Whatever be the shape of the mould, its position should now and then be changed, that is to say, the upper portions should be made the lower ones, and conversely. This is necessary, because the lower layers of the bath give the more abundant deposits, which is explained by the difference of specific gravity of the layers more or less charged with sulphate. In fact, a solution may contain very little sulphate at the surface, and be saturated with it at the bottom. This explains the practice of keeping the tray with sulphate at the top of the bath, instead of allowing the crystals to lie at the bottom.

Formerly, a certain apparatus, quite inconvenient, and called an *electrotype*, was used for the reproduction of

Fig. 142.



medals. It was composed of a cylindrical glass vase, with a wooden cover (Fig. 143), to which was fixed a support

Fig. 143.



in the shape of a T, with two holes each supplied with binding screws. The wooden cover had a circular open-



ing through which passed a truncated cone of glass (Fig. 144), open above and closed below with a piece of bladder. For working this apparatus, the mould was fixed upon a metallic disk, dipping into the solution of sulphate of copper, and connected by a bent wire with the top support. Another wire, bent twice at right angles, passed through the second hole of the support, and carried a disk of zinc dipping into acidulated or salted water contained in the truncated cone of glass. By this disposition the mould and the zinc plate were kept horizontal and opposite each other, but separated by the bladder.

Fig. 144.



This apparatus, the manipulation of which was tedious and difficult, has been simply mentioned, because it was the first in use. It has been superseded by apparatus in which the cell and the moulds are placed vertically, which allows of the rapid removal and examination of the objects. It should, however, be mentioned that this latter disposition favors the production of striæ upon the deposits, should the operator neglect to change, now and then, the position of the articles. These striæ are mainly due to convection currents formed by liquid layers of unequal saturation which traverse the surface of the object, and they are the more numerous as the intensity of the current is greater. They may be avoided by frequently agitating the bath, or the objects.

As far as practicable, the liquids in the bath and in the cells should be maintained at the same level; and it is even more prudent to have that of the bath slightly above that of the cell, in order to prevent the solution of zinc from mingling by exosmose with the copper solution. The converse is preferable, although the zines become blackened by a pulverulent deposit of copper.

## CHAPTER LII.

DIAPHRAGMS OR POROUS CELLS—KEEPING THE BATTERY IN ORDER—AMALGAMATING SALT—ACID BATHS.

*Diaphragms or Porous Cells.*

By this name we designate vessels made of materials capable of containing liquids, and, at the same time, of allowing them to ooze out slowly through their pores, especially under the influence of electricity. Pipe clay, pasteboard, bladder, gold-beater's skin, and parchment, certain tissues, especially sail-cloth, and certain kinds of woods, may be employed for diaphragms. But nothing answers the purpose so well as porcelain clay, or kaolin, submitted to a certain heat, which hardens the paste without destroying its porosity. Vases made with this material are just porous enough, and resist the action of the most corrosive acids. It is this latter quality which renders the kaolin cells so much superior to all the other substances indicated above.

It is often quite difficult to obtain cells of dimensions and shape suitable to our wants. The largest generally found in the trade do not exceed 4 inches in diameter, and 14 inches in height. And, as it often happens that we are required to effect deposits upon surfaces, the height of which is at least double that stated, we shall indicate the manner of remedying this inconvenience. Diaphragms of about 28 inches in length may be made as follows: Saw off carefully the bottom of a large cell, and grind well to match the top of another. Then heat the



two ground ends, place them one on the other with an interposed film of varnish, and wrap the joint with a ribbon of gutta percha, which is kept firmly in place by a screwed collar of copper. Heat the collar again slightly in order to soften the gutta percha, and screw up the collar to make the joint tighter. Lastly, cover the copper collar entirely with varnish, or, preferably, melted gutta percha (Fig. 145).

Fig. 145.



When the dimensions of the diaphragms are too great to allow of the employment of kaolin, we must have recourse to sail cloth, fixed with copper nails upon a frame of oak. The seams are covered with coal tar, and the cloth lasts longer than would be supposed. Diaphragms are also made of well-joined boxes of thin and porous woods. But there is nothing that answers so well as the kaolin cell.

*Keeping the Battery in order.*

It has already been explained that the electric current was produced by the action of certain liquid excitants which slowly dissolve zinc, and that this liquid was commonly water with two or three per cent. of sulphuric or hydrochloric acid, or simply a solution of common salt. It is evident that, after a greater or less length of time, the action will be arrested by the saturation of the acid or of the salt; we must therefore maintain, or revive, the action by additions of the exciting liquid, for which purpose the procedure is as follows:—

The battery, charged as described, will work well for twenty-four hours; and, for four consecutive days, it will be sufficient to add small quantities of acid and amalga-



mating salt, in proportion governed by the capacity of the cells, stirring the liquid with a glass rod.

On the fifth day, all the exciting liquid is poured off, and a fresh charge is substituted, as, without this precaution, the zinc salt will be found to accumulate to such an extent as to crystallize upon the zincs, clog up the cells, and by arresting the osmotic action, interrupt the current.\*

It is useless to allow the corrosion of the zinc, except on the surface that faces the article to be covered; therefore, it is well to varnish the insides of zinc cylinders. This method, however, will succeed only with the employment of amalgamating salt.

Cast-zinc, though it answers the purpose, is far inferior as regards durability and economy, to rolled zinc, which is more dense and homogeneous, and which will be uniformly corroded instead of being perforated by the acid.

It sometimes happens that the zinc is scarcely attacked, even by concentrated liquids, and that a multitude of small cavities make their appearance on its surface. It becomes covered also with a grayish-black crust, and the flow of electricity at length ceases. These phenomena take place when the zinc is rich in lead.

All commercial zincs contain lead, in greater or less proportion, but when the proportion of lead is too great, the above difficulties ensue. In zinc rolling mills where

\* A diaphragm or cell may become clogged in two different ways: By the sulphate of zinc which, having an insufficiency of water, crystallizes in its pores. In this case it is sufficient to boil the cells in water acidulated with sulphuric acid, to restore its porosity; or, by deposits of copper caused by bad working. It is then necessary to dip the cells in aqua fortis until all of the copper is dissolved, and to rinse in plenty of water afterwards.

It is also possible to clean cells by keeping them filled with water, which, escaping through the pores, discharges the substances with which they are clogged.

a great quantity of zinc is melted at once, the phenomenon of *liquation* takes place by which nearly all of the lead goes to the bottom of the containing vessel. It results from this that when the upper portions of the molten metal are ladled out to form the slabs for rolling, the zinc obtained is quite pure; while that taken from the bottom parts is rich in lead. The latter is very good for roofing and many other purposes, but it should be avoided by galvanoplastic operators.

#### *Amalgamating Salt.*

The great majority of operators, in order to avoid the solution of the zinc when the apparatus is not working, cleanse it in diluted hydrochloric acid, and then amalgamate it by rolling the cylinders in a trough filled with mercury. This method necessitates the employment of a large quantity of mercury, which, not only does not form a uniform coating, but renders the copper connections brittle. Instead of metallic mercury, Roseleur uses a compound of this metal, made for the purpose, and introduced into the cell itself in the form of a liquid. By this means, only that part of the zinc which dips into the liquid receives the mercury deposit, and the amalgamation is continued during the solution of the zinc.

The salt which he employs is prepared by boiling an aqueous solution of mercuric nitrate, with an excess of a powder composed of equal parts of mercuric chloride and mercuric sulphate, and the resulting liquid, as above stated, is added in suitable quantity to the acidulated water in which the zincs are immersed. Its use is, of course, confined to those batteries in which two fluids and a porous cell are employed.

*Acid Baths.*

We have said that when a bath becomes impoverished, that is to say, contains too weak a solution of sulphate of copper, the electro-deposit is pulverulent, black, and irregular. The same inconvenience occurs when the baths become too acid, in which case they do not dissolve enough of sulphate of copper.

While it is true that, in baths working with separate batteries, the copper of the anodes is dissolved and combines with the sulphuric acid set free at the other pole, and thus maintains the solution without a great excess of free acid, it is not so with the modified form of apparatus here described. In this case the acid set free by the deposited metal remains uncombined, and will soon accumulate sufficiently to render the bath too acid, and to this cause of excessive acidity we must add the transudation of the liquid through the diaphragm. It is, therefore, necessary that this inconvenience should be now and then corrected, otherwise the electro-deposits will be worthless, or at least very brittle.

Roseleur recommends the following remedies: When the bath is too acid, add carbonate of copper until effervescence no longer takes place. In this reaction, the free sulphuric acid decomposes the carbonate of copper, and forms sulphate of copper, and the carbonic acid escapes in gaseous form. The bath should then be acidified anew in order to increase its conducting power. The carbonate of copper may be replaced by the oxide of the metal, which dissolves without effervescence. Many galvanoplastic operators prepare the oxide by calcining at a red heat all the copper wastes of their operations. By the combined action of heat and of the oxygen of the air the



copper is transformed into a black oxide of copper, which readily dissolves in acid baths. If the entire quantity of copper has not been transformed into oxide, the operation is repeated as often as may be necessary.

If, after very long use, and by transudation from the cells, a bath becomes overloaded with free acid and sulphate of zinc, there is no other remedy but to prepare a fresh one.

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### CHAPTER LIII.

#### DISPOSITION OF THE PIECES IN THE BATH—GALVANOPLASTIC DEPOSITS UPON METALS (WITH ADHERENCE).

##### *Disposition of the Pieces in the Bath.*

WE have said that the pieces or moulds were placed vertically, and, as nearly as practicable, parallel to the copper anodes or to the cells. The depth of the bath should be sufficient to have a few inches of liquid above and below the moulds. It often occurs that the moulds are lighter than the solution of sulphate of copper, and it then becomes necessary to ballast them with pieces of lead covered with varnish or gutta percha, or with stones, glass stoppers, or other convenient objects that are non-conductors of electricity.

When the object to be covered is metallic, and unacted upon by the solution of sulphate of copper, it is sufficient to attach the conducting wire to any part of its surface, and it will be rapidly covered with a uniform electro-deposit. On the contrary, if the mould is a non-conductor of electricity of itself, and has been covered

Fig. 146.



with some conducting substance, such as *plumbago* (or *graphite*), *bronze-powder*, or *reduced silver*, it is important, as far as practicable, to multiply the points of contact of the electrode. Roseleur accomplishes this object by attaching to the principal conducting wire (Fig. 146) a number of fine copper wires, like those employed for scratch-brushes, and causing their bent extremities to touch the mould at various places. The copper is deposited first at these points of contact, from which it radiates in every direction, until the whole surface is covered. This method likewise has the advantage of a

greater rapidity of operation, and of a practically uniform thickness of deposit. It is especially serviceable in the case of moulds having deeply indented surfaces. As soon as the surface is entirely covered, these supplementary wires may be removed.

Knight's plan of securing a thin copper deposit on the surface of black-leaded moulds, which is described in the chapter on ELECTROTYPING, will be found applicable in many cases; and is a simple and efficient remedy for the difficulty here alluded to.

It often happens that only one face of the mould is intended to receive the electro-deposit; in this case it will be easy to protect the other surfaces against the action of the bath by the use of a "stopping-off" varnish melted beeswax, or softened gutta percha. The same precaution should be taken with the suspension wire

which should be covered their whole length, except at the points of contact.

*Galvanoplastic Deposits upon Metals (with Adherence).*

The simplest case the operator will meet in his practice is that of covering a metal with a coating of copper in such a manner that the object and the deposit shall form a single body.

All the metals are not equally qualified to receive the galvanoplastic deposit; and there are some which are naturally unfit for it. For instance, wrought and cast iron, steel and zinc, as soon as immersed in the solution of sulphate of copper, and even without the action of the galvanic current, decompose the salt, and become covered with a muddy, non-adherent precipitate of copper. When operating with these metals it is, therefore, absolutely necessary to give them a previous, and quite thick, coating of copper in the bath of double salts described in the first part of this work, before submitting them to the action of the sulphate of copper bath. Tin, although presenting these inconveniences to a much less degree, nevertheless reacts upon the sulphate of copper, blackens, but finally receives a deposit of slight adherence. It should also be copper-plated in the solutions of double salts before going into the galvanoplastic bath. The same observations hold good also for lead.

On the other hand, when the metal to be covered is unacted upon by the bath, it is sufficient to cleanse it well, and to submit it then to the action of the current in order to obtain a rapid and uniform deposit, which adheres more or less perfectly. The copper deposits obtained under these circumstances should not be too thick, otherwise the surfaces may have a coarse appearance, which will not satisfactorily reproduce the finer outlines of the mould.



With a bath in good condition, and a well-regulated electric current, the delicacy of the pattern will not be impaired by a copper coating having the thickness of a sheet of stout writing paper. A bright lustre will be imparted to the deposited surface by simply scratch-brushing and burnishing; or by a passage through aqua fortis and soot, and afterwards through the acid mixture for bright dipping.

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## CHAPTER LIV.

### DEAD-GILDING BY GALVANOPLASTIC DEPOSIT.

ALTHOUGH we have already described *in extenso*, in Chapter XXVI., the galvanoplastic process of dead-gilding, it may be of interest to repeat the method here, and to generalize upon it by describing its application to all the metals and their alloys, as well as to non-metallic substances.

Adherent galvanoplastic deposits furnish us the means of obtaining cheaply a very handsome dead-gilding which equals, if not in durability at least in appearance, that obtained with mercury, which was described in the first part of this work.

Roseleur conducts the operation in the following manner: After having carefully cleansed the object if metallic, or rendered it a conductor, if non-metallic, immerse it in the sulphate of copper bath, and allow the deposit to acquire a dead lustre slightly in excess of that desired. After this operation, which may last from two to six hours, remove the article from the bath, rinse in plenty of water, and pass it rapidly through the compound acid mixture

for bright dipping, which diminishes the dead appearance of its surface. Next rinse in fresh water; steep in quickening solution, rinse again; and, lastly, immerse in an electro-gilding bath made of—

Distilled water . . . . .	1000 parts.
Phosphate of sodium . . . . .	60 “
Bisulphite of sodium . . . . .	10 “
Cyanide of potassium . . . . .	2 “
Gold (or its equivalent of chloride) . . . . .	1 part.

At first the current is rendered sufficiently intense by submerging the platinum anode deeply; afterwards the intensity is diminished by partly withdrawing the anode until the desired shade of gold is obtained. This gilding requires but little gold, since the frosty dead lustre is derived from the copper. When the lustre of the copper is very fine and velvety, we may dispense with the dipping in the acid mixture, but a rapid passage through the quickening solution is always desirable.

If the deposited gold be not uniform, or appears partly cloudy, it is proof of an imperfect deposit in the bath, or of an insufficient passage through the acid mixture for bright dipping. The piece should then be removed from the bath, washed in a tepid solution of cyanide of potassium, rinsed in fresh water, “quicked,” and electro-gilded anew. This gilding bears burnishing well, but acid waters and soap, which will produce a red tint, must be avoided, and saliva only, or fresh solutions of linseed, or of marsh-mallow, be used. The tone of the gilding thus obtained is richer, deeper, and more durable than that produced upon frosted silver, which last may be recognized by the green color of the burnished parts.

This method is employed for dead-gilding the ornamental parts of cigar-cases, tablets, medals under glass for paper-weights, and especially chandeliers, clocks, and



other articles of ornament or utility, which, at the present day, are sold much more cheaply than formerly. Many articles of plaster of Paris and wood are also gilded by this process.

These adherent galvanoplastic deposits likewise give us the means of imparting a uniform appearance to objects composed of heterogeneous substances. For instance, a clock may have a base of copper and ornaments of lead; and the whole may be made to appear like bronze after a thin galvanoplastic deposit.

To conclude: this form of deposit may be employed for binding together substances simply placed side by side, since the electro-deposited covering will form one continuous body. Certain kinds of mosaic work are thus made, of which the different pieces are simply placed side by side and united by, or set in, a galvanoplastic deposit.

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## CHAPTER LV.

### NON-ADHERENT GALVANOPLASTIC DEPOSITS UPON METALS— GALVANOPLASTIC COPIES OF DAGUERREOTYPES.

#### *Non-adherent Galvanoplastic Deposits upon Metals.*

THE second galvanoplastic problem consists in depositing a coating of copper upon another metal, and in such a manner that, the operation being completed, the deposit may be easily separated from the object that has served as a mould, preserving at the same time, with mathematical accuracy, the shape and dimensions of the model, and possessing a considerable solidity.

This method is used for reproducing medals, bas-reliefs, etc., with great perfection.



We cannot give a more striking example of the capabilities of this method of procedure than the interesting experiment which we have already mentioned, of reproducing, with its aid, a daguerreotype with all its minutiae. The manipulations, which are very simple, are as follows: Take a daguerreotype plate and coat its back and edges with varnish, then hold it by a corner and pour upon it a small quantity of alcohol, and rinse it in fresh water. After having connected it with a brass conducting wire, hang it for six or eight hours in the bath of sulphate of copper. The four edges are then cut with strong shears, and, by raising a corner with a pen-knife, or visiting card, the two sheets will easily separate, and will furnish two images, one as perfect as the other.

Returning to the general method of non-adherent galvanoplastic deposits of metals upon other metals, it will be necessary, as has been said, to cover zinc, iron, or tin with a previous coating of copper in the baths of double salts before submitting them to the simple electro-bath.

In this condition, or in the case of a metal unacted upon by the bath, we proceed as follows:—

After a thorough cleaning of the object to be copied, it is rubbed with a brush charged with plumbago, or, what is better, with a soft brush slightly passed over a tallow candle. By this means, an imperceptible film of fatty substance, which prevents the adherence of the deposited copper, is left on the surface. This latter method is quite as good, and cheaper than that of covering with gold and silver, sometimes employed to prevent adherence.

It will be understood that the deposit will represent an inverted image of the pattern, in which the raised parts are seen as hollows, and conversely. This inconvenience is remedied by performing the same operation anew, using

the deposit as a mould, and this second deposit will be an accurate reproduction of the original. A great number of copies may be made from the first or reverse matrix obtained.

## CHAPTER LVI.

### ELECTRO-DEPOSITS UPON NON-METALLIC SUBSTANCES.

THERE is simply an artificial, or indirect adherence between a deposited metal and a non-conducting mould. Metals are generally, and by the usual methods, welded or soldered only to metals. When we speak of metallic deposits adhering to non-metallic substances, therefore it will be understood that, either the non-metallic material is completely enveloped by the metallic deposit, or that the mould is undercut, or held by several points of adhesion.

In either case, when the artificial support is removed, the metallic and non-metallic surfaces separate.

It is by this process that we are enabled to cover with galvanoplastic deposits the surfaces of porcelain, crystal, plaster of Paris, and other plastic materials, wood, flowers, fruits, animals, and the most delicate insects.

But the first difficulty to be overcome in these various operations is the absence of conductive power for electricity which characterizes these materials. It is, therefore, absolutely necessary, and before anything can be done, to render them conductors by the procedure known as *metalization*.

## CHAPTER LVII.

METALLIZATION—PLUMBAGO—RENDERING OBJECTS IMPERVIOUS TO LIQUIDS—METALLIC POWDERS—METALLIZATION BY THE WET WAY.

*Metallization.*

THE metallization of a non-conducting substance consists in covering all the parts, which are destined to receive the galvanoplastic deposit, with a coating of some material which will conduct electricity as well, or nearly as well, as a metal. This coating should be imperceptible in thickness, so that it may not sensibly fill up the finest details of the surface of the object.

Many methods are known for imparting the power of conducting the electric fluid to substances which do not possess it naturally. Unfortunately, however, none are perfect, and many are so expensive and difficult to apply as to forbid their employment. We shall, nevertheless, enumerate those in common use, and which produce results with which we are obliged to content ourselves.

*Plumbago—Gilt Plumbago—Silvered Plumbago—Coppered Plumbago.*

The substance generally employed as a metallizing material is *plumbago*, also called black-lead, or graphite. In a majority of cases its conducting power is sufficient; and it may be applied in films thin enough not to impair the sharpness of the mould.

Commercial plumbago is rarely pure, being contami-



nated with earth, iron, and sometimes with the sulphides of this metal. The impurities may be removed by digesting for twenty-four hours with hydrochloric acid a paste made of plumbago and water. Several washings with water, and a slow drying in a stove finish the operation. In its pure state, plumbago is simply a peculiar variety of mineral carbon. For the purpose here described, only the very best should be used, and it should be in the finest possible state of division. An extra quality is prepared and sold expressly for the galvano-plastic operator.

Plumbago is satisfactory for the metallization of moulds of a certain nature and shape, but will not suit for others. Generally, the conducting power of this substance is sufficient when the surfaces are not deeply indented. At the same time, the object should be rough enough, or sufficiently fatty or greasy to permit of the adherence of the plumbago.

Roseleur has lately prepared plumbago with a conducting power much greater than that of the ordinary substance, by incorporating with it gold or silver.

*Gilt Plumbago* is prepared as follows: In 100 parts of sulphuric ether he dissolves 1 part of chloride of gold, and thoroughly mingles with it from 50 to 60 parts of good plumbago. The whole is then poured into a shallow porcelain vessel, and exposed to the action of air and light. After a few hours the ether is completely volatilized, and the powder is now and then stirred with a glass spatula. The desiccation is finished in a stove, and the product is ready to use.

*Silvered Plumbago* is obtained by dissolving 10 parts of crystallized nitrate of silver in 200 parts of distilled water, and mixing with this solution 100 parts of good plumbago. The whole is dried in a porcelain dish, and

en calcined at a red heat in a covered crucible. After  
oling, the product is powdered again, and sifted.

Plumbago thus metallized conducts electricity nearly as  
ll as a metal surface. Knight's process of coppering  
n-conducting surfaces is very generally applicable,  
ough especially serviceable in electrotyping, and consists  
applying on the mould, after black-leading, a solution  
sulphate of copper, then dusting thereon from a pepper-  
x some impalpably-fine iron filings, and gently going  
er the surface with a soft brush. A uniform and con-  
uous precipitation of pure metallic copper is thus pro-  
ced, which covers the entire surface of the mould with  
excellent conducting medium. A process devised by  
r. Adams, for accomplishing the same object, consists  
applying finely-powdered tin to a wax mould, with a  
ft brush, until the surface presents a bright, metallic  
pearance.

*Rendering Objects Impervious to Liquids.*

Certain objects, before-being coated with plumbago, are  
bmitted to a preparatory operation, for the reason that  
ey are porous, and will be injured by the solution of sul-  
ate of copper which penetrates them. Objects of car-  
nate of calcium (chalk and marble), sulphate of calcium  
laster of Paris), wood and other spongy materials, fall  
to this category. It is therefore necessary to render them  
pervious before metallization, by covering them with a  
at of varnish, or by saturating them with wax, tallow,  
, still better, with stearine.

Let us take a plaster cast, and describe this procedure:  
fter having cut a groove on the rim of the object, con-  
ct to it a brass wire in the manner shown (Fig. 147),  
d long enough to facilitate the operation. The plaster  
st, previously dried, is then dipped into a bath of molten

stearine kept at a temperature of about 175° to 212° Fah. There will be an immediate and copious disengagement of bubbles from the escape of air and moisture which the stearine replaces.

Fig. 147.



When the production of air bubbles has considerably diminished, the cast is removed from the bath, and almost immediately dries, by the absorption of the last portions of stearine.\*

When the cast has become nearly cold, it is dusted with the finest plumbago, and allowed to cool off entirely. Then, after breathing upon it, it is rubbed thorough

\* If this operation has been effected with great care and cleanliness (upon adam plaster, Keene's cement, pâtre aliné), it is sufficient to rub with a woollen rag, and afterwards polish the stearined cast, to impart to it a species of translucency. Thus are made those religious emblems fixed upon velvet and framed in ebony, which so well imitate ivory. In this case, the stearine employed must be very pure, or contain only a small proportion of spermaceti, and it should be melted on a water bath in glass or porcelain vessels. The plaster of Paris may receive, by absorption, various colors before it is introduced into the bath of stearine.



with a brush covered with plumbago; and as upon this operation depends the regularity of the deposit, care must be taken to render the surfaces completely black and lustrous, without gray or whitish spots.

A process of black-leading moulds by the wet way, which gives very superior results, has been devised by Mr. S. P. Knight. He uses an emulsion of finest plumbago and water, and forces the same by means of a pump and a travelling fine-rose nozzle over the surface of the moulds, which are placed upon suitable supports. The surplus liquid is returned and used over again. The process is specially intended for electrotypers' use.

When the model is very indented or undercut, it becomes difficult to employ plumbago, and, in such case, the entire mould, or at least the cavities, are metallized by the wet way, about to be described.

It is generally believed that soft brushes should be employed for spreading the plumbago upon moulds. This *is* a mistake which prevents many from succeeding; Roseleur uses watchmakers', and even blacking brushes, with which he obtains sufficient friction to cause the adherence of the plumbago without injury to the mould. Artists' modelling wax alone requires soft brushes.

The metallization of stearined objects succeeds well with alabaster, plaster of Paris, wood, etc. For the latter, however, Roseleur prefers a protracted steeping in fatty oil, or simply in linseed oil. The object must be rubbed dry before the plumbago is applied.

When the substances to be metallized are not porous, they are covered with a thin coating of varnish, which, when nearly dry, receives the plumbago. This method applies to glass, porcelain, stoneware, horn, and ivory.

It is by analogous processes, that M. Oudry has succeeded in producing, on the commercial scale, those great

galvanoplastic works which contribute so largely to the decoration of the streets, public gardens, and squares of Paris. Such are the monumental fountains and candelabra for gas lights, which this inquiring and indefatigable worker has succeeded in coating with a copper deposit sufficiently uniform to respect the beauty of the ornaments, and durable enough to withstand shocks and friction, and the action of the atmosphere, and capable of assuming the appearance of various bronzes. These products are generally made of cast-iron. Many trials had been made to coat them with a sufficient thickness of copper; but all these attempts, which were conducted in the same manner, that is to say, a previous cleansing of the cast-iron in acid pickles, a first coating of copper in the bath of double salts, and then the finishing out in sulphate of copper, proved to be failures on account of the imperfections of the material operated upon. Cast-iron is always porous, full of cavities, and exhibits on its surfaces particles of sand, carbon, and other impurities; therefore the deposit of copper presented similar imperfections, and was not continuous. The result was that moisture soon penetrated between the two metals, the iron was oxidized, and the copper coating detached.

Avoiding the errors of his predecessors, M. Oudry, instead of cleansing the cast-iron, covers it with a thin layer of fat varnish, very plastic and resistant, and, at the same time, sufficiently elastic to adapt itself to the expansion and contraction of the metal without cracking. When this varnish is nearly dry, it is covered with plumbago, and the object is immersed in the depositing vat. Such is the process by which are coppered, and then bronzed, a multitude of objects of wrought and cast-iron intended to withstand the action of the atmosphere. M. Oudry thus manufactures a great variety of garden benches,



fountains, vases, statues, railings, etc., and could cover the entire hull of a ship with a continuous copper sheathing, if he had a depositing vat large enough to contain it.

*Metallization of Ceramic Wares.*

For ceramic wares, other processes are employed, which give more rapid results.

After having varnished the portions of the piece to be coppered, they are covered with very finely laminated sheet lead, which readily adapts itself to the contours of the object; then a brass conducting wire is connected with the lead, and the article is suspended in the copper bath, where the copper is immediately deposited upon the metallic parts. By similar methods, glass flasks and retorts, tubes, dishes, and other culinary vessels of glass, stoneware, earthenware, or porcelain, are coated with a continuous coating of copper. Unfortunately it is found that owing to the unequal expansion and contraction of the article and of the copper deposit, the adherence between the two surfaces is soon destroyed.

Nevertheless, the decorative arts have made good use of this species of deposit, and we have crystal vases entirely covered with copper, upon which have been successively deposited other layers of gold and silver. The chaser may then penetrate with his tool to different depths, and uncover one after the other, and at determined places, first the layer of silver, next that of copper, and at last the crystal itself. The vase will appear as if set in a network of various colors. A goblet, a paper weight, and any analogous article may, of course, be treated in the same manner.

M. Chablin, a skilful electrician and artist, ornaments porcelain, ceramic, and crystal wares on a large scale, by



galvanoplastic processes. His method of metallization is quite different from those described, inasmuch as he simply uses as a conducting metal the coating of gold which is applied upon porcelain by the old and well-known processes. The fineness of the details can scarcely be surpassed, and the durability and firmness of the deposit are remarkable. Let us suppose that a plate of porcelain is to receive in its centre an ornament or initials in metals and in relief: the device in leaf gold is first attached to the surface with the pencil, and fixed in the usual manner by heating the plate in a muffle. The metallic film thus obtained is made to serve as the basis of a galvanic deposit. It is connected with a very thin conducting wire, and the whole immersed in a galvanoplastic bath of copper, silver, or gold, where the deposit takes place in the same manner as upon an ordinary metallic or metallized surface, and the adherence is as perfect as that of the film of gold upon the porcelain. The deposit is afterwards polished, chased, or ornamented on the lathe. Nothing can exceed the beauty of this species of ornamentation, and the numerous specimens seen in our jewelry stores often puzzle the beholder to understand how they have been produced.

#### *Metallic Powders.*

We have said that when a metal is immersed in the bath of sulphate of copper, the entire surface is immediately covered—in the case of a surface metallized with plumbago; on the other hand, the deposit starts from the points of contact of the conducting wire, and radiates from these slowly in all directions. It follows, therefore, that while the metal is an excellent conductor of electricity, plumbago is relatively a poor one.

It has, therefore, been attempted to replace plumbago

by metals in the state of exceedingly fine powders; and bronze powders, shell-gold, silver reduced by copper or hydrogen, antimony, and bismuth, in impalpable powder, have been successively tried without good results, either from a want of adherence, or from the solvent action upon them of the copper bath. Some operators, however, continue to use a mixture of bronze powder and plumbago, and claim to be satisfied with it; but Roseleur prefers the gilt or silvered plumbago, prepared in the manner already described. These are doubtless excellently adapted for galvanoplastic work on the small scale, but for large operations, and for electrotyping, will be altogether too expensive. (See our remarks on the processes of Knight and Adams).

*Metallization by the Wet Way.*

Although the results obtained by the mechanical application of various metals in impalpable powder are not entirely satisfactory, such is not the case with the metallization produced by the reduction, upon the object itself, of certain metallic salts. Silver, gold, and platinum, thus reduced from their solutions, have an excellent conducting power, for the reasons, probably, that they are not acted upon chemically by the bath, and because they form a layer more nearly continuous.

Silver is generally preferred, and for this purpose a solution of the nitrate is made, and this solution is applied with a pencil upon the object to be operated on, and allowed to dry, and the operation repeated two or three times. Lastly, the object is exposed to the action of sunlight, or of a current of hydrogen. A convenient plan is to subject it, in a hermetically-sealed box, to the vapors of a concentrated solution of phosphorus in bisulphide of carbon contained in a porcelain evaporating dish.



After a few hours this solution will have completely evaporated, and will be found to have reduced to the metallic state the nitrate of silver covering the object, which has become entirely black, and is ready for the galvanoplastic bath.

To metallize wood, porcelain, and other resisting substances, Roseleur recommends the following procedure, viz: Dissolve 1 part of nitrate of silver in 20 parts of distilled water. With fatty or resinous materials, which are water repellent, we employ aqua ammonia, which dissolves the nitrate of silver in all proportions. Lastly, with very delicate articles, which will not bear a long manipulation, alcohol, which evaporates rapidly, is employed as the solvent. Concentrated alcohol dissolves nitrate of silver but slightly; nevertheless, enough will be dissolved for metallizing flowers, leaves, mosses, lichens, etc., especially if the solution is assisted by trituration in a glass or porcelain mortar.

We have recourse also to metallization by silver (reduced by phosphorus in bisulphide of carbon) of those deeply indented parts of certain moulds which cannot be reached by even the slenderest pencil charged with plumbago. In this case, the mould is plunged entirely into the solution of nitrate of silver, then allowed to dry, and lastly exposed to the phosphorus fumes in the manner indicated.

This process of metallization is so perfect, that a silk cocoon thus prepared may be unspun, and the resulting fibre will possess a conducting power sufficient to immediately deflect the needle of a galvanometer, when it is used as a conductor between the instrument and the battery.

Roseleur makes allusions to laces and mousselines, which were coppered, gilded, and silvered, and which had scarcely, or not at all, lost their primitive softness.



was even possible to burnish certain parts, and thus produce contrast of dead and bright lustres.

It is important to remark that if we fix the conducting wire to the mould before metallization, the wire must be of gold, silver, or platinum, since the other metals rapidly decompose the solution of nitrate of silver. On the other hand, brass or copper wires may be employed when the metallization is completed, that is to say, after the reduction by phosphorus has been effected.

The solution of phosphorus in bisulphide of carbon is prepared as follows: Half fill with this liquid a wide-mouthed flask with a tightly fitting ground glass stopper, then gradually introduce the phosphorus, gently dried with blotting paper, and shake the bottle now and then until no more dissolves. The preparation of this solution requires the exercise of great care, because in drying upon combustible materials it takes fire spontaneously.

A piece of paper or of cloth moistened with it, takes fire after a few moments' exposure to the air.

It is not impossible to obtain galvanoplastic deposits, without previous metallization, upon a non-conducting substance, of which Roseleur gives the following instructive illustration: If we bind a cameo of agate with a copper wire, and hang it in the bath, the wire alone will receive the deposit, and its volume will increase in every reaction. If, now, we cover with an insulating varnish the exterior of the deposit, repeating the operation as it flows, it will continue to increase only on the periphery, and by and by it will cover the whole of the cameo. After separation, the reproduction will be all the more perfect from the fact that no foreign substance has been interposed. It is from a similar expansion of the deposit that the non-metallized parts of moulds often become coated.

## CHAPTER LVIII.

MOULDING—MOULDING WITH PLASTER OF PARIS—WITH STEARINE—WITH WAX—WITH MARINE GLUE—WITH FUSIBLE METAL—WITH GELATINE—WITH GUTTA PERCHA.

*Moulding of the Pattern.*

IN cases where the original objects are used as patterns or moulds, even where they have flat or not-undercut surfaces, and with copies of medals or bas-reliefs of plaster, bronze, wax, etc., there is a risk of damaging them if we effect the galvanoplastic deposit directly upon them. Moreover, we thus obtain a reversed copy of the object in which the reliefs are sunken, and *vice versa*, and, in order to reproduce a fac-simile, we are obliged to make a second deposit upon the first, which is double work.

These considerations have naturally induced galvanoplastic operators to begin by taking a mould from the pattern or object itself, with the aid of some plastic or fusible material, and to submit this mould to the subsequent operations. If from a bronze metal in relief, we have taken a cast in plaster of Paris, this casting will be a hollow mould, which being filled afterwards with the copper deposit, will exactly reproduce the relief of the original medal. In this operation we run no risk of damaging a rare and valuable object, and have the advantage of being able to reproduce it many times and with the same accuracy, since we can make as many casts or moulds from the original as may be desired.

There are many substances which may be employed

for making moulds, but all are not equally well adapted, and it is important to know how to apply them in the manner best adapted to each special case.

*Moulding with Plaster of Paris.*

Plaster of Paris stands first, not in the order of merit, but as having been the earliest to be employed for this purpose. It is convenient for taking casts from plaster of Paris itself, from stucco, marble, alabaster, metals, and wood. The mode of procedure is as follows: Given, a plaster medal in relief, from which we desire to obtain a hollow mould which will furnish the true relief of the original in copper. After the original has been thoroughly soaped or black-leaded, wrap around the rim a piece of sufficiently stout paper, or of thin lead foil, and attach it in such a manner that the face of the medal to be copied is at the bottom of the receptacle thus formed. It is desirable to sink this box to a certain depth in a layer of fine sand, which prevents the escape of the semi-fluid plaster of Paris between the rim of the medal and the paper. Then in a vessel filled with a sufficient quantity of water, sprinkle fine plaster of Paris until the last portions reach the level of the water. After waiting for one or two minutes, the mass is stirred, and the resulting thin paste must be employed immediately. Take up a small quantity of this paste with a pencil or brush and spread it in a thin film carefully and smoothly over the face of the medal, then pour on the remainder of the paste up to a proper height, and allow it to set. After a few minutes the plaster heats and solidifies. Then remove the surrounding paper, scrape off with a knife what has run between the paper and the rim of the medal, and carefully separate the plaster cast from the model.

If, instead of applying the first layer with a brush, the



whole of the plaster were run at once into the recess, there would be great risk of imprisoning bubbles of air between the model and the mould, which would consequently be worthless.

We have seen that moulds of plaster of Paris cannot be introduced into the bath of sulphate of copper without having been previously rendered impervious. This difficulty prevents the more frequent use of this substance for moulding, and galvanoplastic operators, for this reason, give the preference to other materials which are unaffected by the bath, and which it is sufficient to metallize if they are non-conducting; such are stearine, wax, fusible-metal, marine-glue, and, especially, gelatine and gutta-percha.

*Moulding with Stearine, Wax, and Marine Glue.*

Stearine is applied in the same manner as plaster of Paris, with this difference, that the former is melted with the aid of heat, and poured upon the model when it is about to congeal. When stearine is too new or dry, it crystallizes in cooling, and this impairs the beauty of the cast. In such case it should be mixed with a few drops of olive oil, or with tallow. On the other hand, if it be too fat, it remains soft and is difficult to separate from the mould. It should then be mixed with beeswax or spermaceti.

As stearine contracts considerably in cooling, its employment should be avoided when the copies from the model are required to be mathematically accurate reproductions of the original.

When we desire to make a cast with stearine of a plaster model, it should be thoroughly saturated with water or stearine beforehand, as explained in our description of galvanoplastic deposits upon plaster. It should also be thoroughly coated with plumbago before the melted

substance is poured upon it, otherwise the two stearine surfaces will stick together, and it will not be possible to separate the cast from the model.

Wax is also employed in the same manner, but its price and want of hardness considerably interfere with its application.

Marine glue may be used in the melted state, like wax ; or, after having been softened in hot water, may be impressed upon the object and allowed to harden. This material is now seldom used.

### *Moulding with Fusible-Metal.*

This metal, also known under the name of Darcet's alloy, is a good conductor of electricity, and therefore well adapted to the production of homogeneous deposits of uniform thickness. Nevertheless, it is seldom employed on account of its crystalline texture, and the difficulty of avoiding the presence of air bubbles.

Several formulæ for this alloy are given herewith :—

I. Lead . . . . .	2 parts.
Tin . . . . .	2 “
Bismuth . . . . .	5 “
Fusible at 212° Fah.	
II. Lead . . . . .	5 parts.
Tin . . . . .	3 “
Bismuth . . . . .	8 “
Fusible from 176° to 194° Fah.	
III. Lead . . . . .	2 parts.
Tin . . . . .	3 “
Bismuth . . . . .	5 “
Mercury . . . . .	1 part.
Fusible at 158° Fah.	
IV. Lead . . . . .	5 parts.
Tin . . . . .	3 “
Bismuth . . . . .	5 “
Mercury . . . . .	2 “
Fusible at 127.5° Fah.	

For the alloys without mercury, the component metals may be melted together; on the contrary, when mercury is employed, the other metals of the alloy should be fused together, and the mercury added at the moment of removing them from the fire. In order to insure a thorough mixture, the alloy should be stirred with an iron rod, or remelted and cast several times.

There are several methods of employing the fusible metal: Some run the metal into a small dish, remove the oxide with a card, and then apply the model, and give it a few taps just as it is on the point of setting; others place the model in the dish, and pour the clean alloy upon it. Roseleur finds the following method to be the most satisfactory: Place the medal at the bottom of a small box of iron or copper, and bury it to about half its thickness in plaster of Paris; then, covering the medal with the cold fusible alloy, apply heat until it is melted, when it is allowed to cool off. It is easy to separate the medal from the fusible alloy, since the portion protected by the plaster of Paris may then be grasped.

A well-made cast of fusible alloy is the best mould for galvanoplastic operations with silver and gold.

It must not be forgotten that fusible alloys containing mercury should not be used for taking casts of metallic medals (iron excepted), as these will amalgamate with the mercury, and be injured. Moreover, copper deposits obtained upon such alloys are very brittle, an evidence of the combination of the mercury with the deposited copper.

Sulphur, which melts at a temperature of about 230° Fah., yields very neat and sharp casts, and would prove very useful were it not that it is almost impossible to metallize it, and that it transforms the deposit of copper into sulphide.



*Moulding with Gelatine.*

[www.libtool.com.cn](http://www.libtool.com.cn)

The different substances above indicated are employed for moulding those objects, the surfaces of which present no curves, sinuosities, or undercut parts, which would prevent the separation of the original from the mould.

Under certain circumstances the elasticity of gelatine and gutta percha allows of the possibility of their removal from such curved, sinuous, or undercut parts of the model, when they reassume the shape and position they had before removal therefrom.

This valuable property is found in gelatine to a higher degree than in gutta percha, but this material requires that the deposit shall be made rapidly, otherwise it will swell, and be partly dissolved by too long an immersion in the solution of sulphate of copper. Without this inconvenience, which is most serious, no other moulding material would be more convenient for galvanoplastic operations.

To make good gelatine moulds, proceed as follows: Place a sufficient quantity of sheets of white gelatine (cabinet-maker's glue) in cold water, and let the substance swell there for about 24 hours; then drain off the water, and heat the swollen mass in an ordinary glue pot until it has become of a syrupy consistency, when it is ready to be poured upon the object, which has been encased for the purpose in a box of pasteboard or of sheet lead. After cooling for about 12 hours, the gelatine cast is separated from the object.

Many attempts have been made to render the gelatine impervious; or, at least, to enable it to bear, without alteration, a longer immersion. The several receipts here appended are among the best for the purpose:—

1. Dissolve 20 parts of the best gelatine in 100 parts of

hot water, and add  $\frac{1}{2}$  part of tannic acid (tannin), and the same quantity of rock candy; then mix the whole thoroughly, and pour it upon the model in its case. After a few hours the gelatine forms a kind of semi-transparent leather, which may be easily separated from objects in high relief, of which it is an exact counterpart.

2. A mould having been made with gelatine alone, an aqueous solution of 10 per cent. of bichromate of potassium is poured upon it, and, after draining, the mould is exposed to the action of the sun.

3. Beat into a quart of distilled water the whites of two eggs, filter, and cover with this liquid the entire surface of the gelatine mould. After drying, operate with the solution of bichromate of potassium, as in No. 2. The solar action renders the coating impregnated with bichromate insoluble.

4. Cover the gelatine mould with varnish of some kind, drain carefully, and let it dry. The best varnish for the purpose is a solution of caoutchouc in benzole, or, still better, in bisulphide of carbon.

The mould finally must be metallized, and, when in the bath, submitted to a strong galvanic current at the beginning. When the entire surface is covered with the copper deposit, and when swelling is no longer to be feared, a weaker current may be used.

#### *Moulding with Gutta Percha.*

Gutta percha, the discovery of which was nearly contemporaneous with that of Jacobi, is a species of gum, being the coagulated sap of a peculiar plant. It is entirely insoluble in water, in weak acids, and the copper bath. It possesses the peculiar property of softening under the influence of heat, to the point of becoming nearly fluid, and of re-acquiring, on cooling, its hardness and previous



properties, and this quite an indefinite number of times. From its tenacity and flexibility it derives the name of *vegetable leather*. It is much less elastic than gelatine, and there is more difficulty in separating it from objects finished in high relief; nevertheless, with a little practice, results truly surprising may be attained.

The following is the method of operating with this substance: After its purification, by softening and kneading in boiling water, in order to separate the dirt, sticks, and other impurities it contains in the crude state, it is formed into sheets and lumps of various thicknesses and sizes. A quantity sufficient for the intended mould is cut from these plates or lumps with a hot knife, or, what is better, with a shoemaker's knife, and put in cold water, which is gradually heated. The gutta percha is now and then moved about, until it is soft enough to be kneaded with the fingers like dough. It is then ready to be used in one of the following modes:—

After having stretched the gutta percha in every direction, the edges are turned in so as to form a hollow hemisphere, the convex and smooth surface of which is applied upon the middle of the object. Then, with a vertical pressure of the palm of the hand, the gutta percha is spread over the surface and forced to penetrate into all the details of the object. The kneading is continued as long as the material remains sufficiently soft, when it is allowed to cool. When nearly cold, the gutta percha is separated from the model, and dipped into cold water, when it hardens, and may then be handled with impunity.

This method is very imperfect in operation and in results, and its smallest inconvenience is that the casts are seldom free from cavities due to air bubbles or drops of water. It is only practised by amateurs who do not possess the utensils necessary for the three methods, about



to be described, *i. e.*, moulding with the press; moulding in the stove, or by sinking; and moulding by hand, or by kneading.

*Moulding with the Press.*—The object to be moulded, carefully coated with plumbago or tallow, is placed square and firm upon the bed, and surrounded with a ring or frame of iron, which should be slightly higher than the most elevated parts of the object. A piece of gutta percha, of a thickness at least double that of the pattern, is cut so as to accurately fit into the ring or frame of iron, and is then heated, on one of its faces only, before a bright fire.

To prevent the gutta percha from running, it is now and then turned about. When about two-thirds of its thickness have been softened, it is placed, soft portion downwards, in the iron ring or frame, followed by a tightly fitting metal block or follower. The screw of the press is now made to act, at first slowly, and then more strongly, as the gutta percha becomes harder and more resisting. Percussion presses are very good. The gutta percha being imprisoned between the pattern and the metallic follower as in a pair of dies, is forced to penetrate the most intricate and delicate parts of the object.

*Moulding with a Counter-mould.*—It will be obvious that when the gutta percha is compressed between a highly wrought pattern and a flat metallic follower, its thickness at different places is very variable. This is very objectionable, because these various thicknesses do not set with the same rapidity which often prevents a good mould from being obtained. To counteract this difficulty many intelligent operators use a *counter-mould*, which they prepare in the following manner: After having cast in sand a thick block of lead, they hollow out approximately

with a graver the places corresponding to the reliefs of the pattern, and conversely, observing carefully at the same time the desired thickness of the gutta percha. By using the lead as a follower it is possible to obtain a mould of gutta percha of the same thickness in all parts. This process produces excellent results. It is even possible to dispense with the softening of the gutta percha, if it be thin, but the pattern and counter-mould should be heated up to about 212° Fah. There is, however, danger of overheating, in which case the gutta percha will adhere to one or other of the surfaces.

*Moulding in the Stove, or by Sinking.*—Moulding with the press, just described, is confined to those objects which are comparatively flat, and which will bear pressure. Moreover, it requires the employment of a costly screw press.

The method of moulding about to be described does not require a press, and is convenient for many brittle articles of plaster of Paris, marble, alabaster, and other analogous substances. The pattern is placed upon a dish of iron or earthenware, or simply upon a piece of sheet-iron, the edges of which have been turned up. Then a ball of gutta percha is placed in the middle of the object to be moulded, and the whole is placed in a stove, where the temperature is sufficient to melt, but not high enough to burn it. Ovens furnished with a series of shelves, especially those of glazed earthenware, are very good for this purpose. Large operators employ special arched ovens with the fireplace at the bottom, and all of the space is traversed by iron bars for the support of the iron trays which hold the pattern and the gutta percha. In this manner, it is easy to watch the operation and avoid too much heat. The gutta percha gradually softens, and penetrates all the details of the pattern; when it has



sunk completely, it is removed from the stove, and when sufficiently cooled is separated from the pattern. The spherical or globular shape is given to the gutta percha in order that it may expel, as it sinks, the air which otherwise would become imprisoned between it and the surface of the pattern.

*Moulding by Hand or by Kneading.*—The foregoing process is unsuited for preparing moulds from objects that will not bear the heat of the stove, though they will support the contact of softened gutta percha, in which category we may class sulphur, wood, statuary, pasteboard, etc. With these materials the gutta percha should be slowly heated in one of the above-described stoves, or otherwise until it becomes a semi-fluid paste, of which a sufficient quantity is turned out upon the pattern previously placed in an iron frame or ring. After waiting a few minutes, the plastic material is kneaded with moistened, or, what is preferable, with oiled fingers, to make it penetrate into all of the details of the pattern, and until it yields to pressure with difficulty. This last process is employed by the majority of amateurs, and by many professional workers, and is decidedly preferable to the employment of gutta percha softened in boiling water.

Whatever the method followed, certain precautions are necessary to be observed for separating the mould from the pattern. First, we should cut off with a shoemaker's knife all the useless parts of the gutta percha, and especially those which may have passed under the pattern, and which consequently bind it. Then the proper position and shape of the covered pattern must be ascertained, because when it is undercut, either the pattern, if brittle, will be broken, or the gutta percha will be torn, if we remove it in the wrong direction.



In moulding with the press, gutta percha without mixture, but of the best quality, is generally employed.

For the other methods of moulding by sinking or kneading, the gutta percha is nearly always mixed with certain substances which increase its fusibility, such as linseed oil, lard, tallow, and beeswax. The proportions of such mixtures may vary *ad infinitum*, although they should never exceed one-third of the total weight. A mixture with linseed oil, for example, is made by heating in a kettle of iron, copper, or stoneware, 1 part of linseed oil, and when its temperature has reached about 175° or 212° Fah., adding gradually (and stirring with a wooden rod) 2 parts of gutta percha cut into small pieces. When the whole is in a pasty state, and begins to swell up and give out jets of dense vapors, the kettle is removed from the fire, and its contents emptied, with the aid of the wooden rod, into a large body of cold water, where, without loss of time, the paste is thoroughly kneaded and stretched. While still hot it is placed upon a slab of marble, or polished stone, and formed into lumps, plates, etc., which may afterwards be laminated between warm rolls.

Gutta percha may be used for an indefinite length of time. The old, up to a certain point, is preferred for certain casts, especially those of copper-plate engravings, since the impressions are finer and more delicate. After a great deal of use, nevertheless, gutta percha becomes dry, hard, and brittle, and envelops too much plumbago. An addition of fresh gutta percha restores its previous qualities.

Although it would seem, *à priori*, that gutta percha, on account of the heat necessary for its employment, is not very well adapted to the moulding of animal or vegetable substances, nevertheless masterpieces in this line, such as

[www.libtool.com.cn](http://www.libtool.com.cn)

very delicate insects and leaves, are reproduced in copper from gutta percha moulds.

Of other delicate objects, nettle leaves have been reproduced so perfectly that all the hairs on their surface were to be seen. The operation was conducted as follows. One of the sides of a fresh leaf was covered by means of a brush with a thin paste of plaster of Paris, and, after the drying of this first coating, other layers were applied until a resisting block had been obtained with the leaf uppermost. The free side was then covered with several coatings (always with a brush or pencil) of gutta percha dissolved in bisulphide of carbon, and lastly with the melted gutta. The mould was removed from the leaf, metallized, and immersed in the galvanoplastic bath.

Impressions have also been taken with India rubber (caoutchouc), and very fine specimens of such moulds have been made. Roseleur expresses surprise that this material is not employed more extensively, since, for certain works, its elasticity renders it much superior to gutta percha.

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## CHAPTER LIX.

### ELECTROTYPING.

As electrotyping was one of the earliest outgrowths of the galvanoplastic art, and is at once one of the most valuable and important of its branches, a somewhat detailed account of the process is herewith given for the use of those who may desire to be informed on the subject. We have already defined it to be the art of reproducing and duplicating printing surfaces, engravings or letter-press in

copper, by means of the galvanic current. The resulting electro-deposited metal is removed from the surface on which it is deposited, and is suitably prepared for use in the printing press.

The art of electrotyping, which has grown to the proportions of a great industry, indispensable to the printer and publisher, is by no means a simple one; on the contrary, many operators are required to produce a finished electrotype block ready for the printing-press, and the successful practice of electrotyping demands, not only manual dexterity, which can be acquired only by practice, but also careful attention to the various steps of the process, and to the quality of the materials employed therein.

*Arrangement of an Electrotyping Establishment.*—For operating on the large scale there will be required depositing vats, scouring and cleaning apparatus, batteries or a dynamo-electric machine, and a variety of machinery and apparatus for preparing the moulds and finishing the shell of copper obtained in the depositing vat, such as machines for taking the moulds, for black-leading the same, a furnace for melting metal used for “backing up” the shell, sawing, planing, and shaving machines for dressing and blocking the plates, etc. etc.

The best location for the depositing vats is on the ground floor, both on account of the nature of the work to be done, and the great weight of the vats and their contents. The depositing room should be provided, preferably, with a cement floor. It should be well lighted, drained, and ventilated, and provided with an abundant water-supply. The construction and arrangement of the depositing vats will be the same as those described in other portions of this work. Where batteries are employed, it will be found advantageous to place them in separate rooms. When the



dynamo machine is used its disposition will be governed by the location of the engine and shafting, but it should be so placed as to be conveniently accessible to the plater.

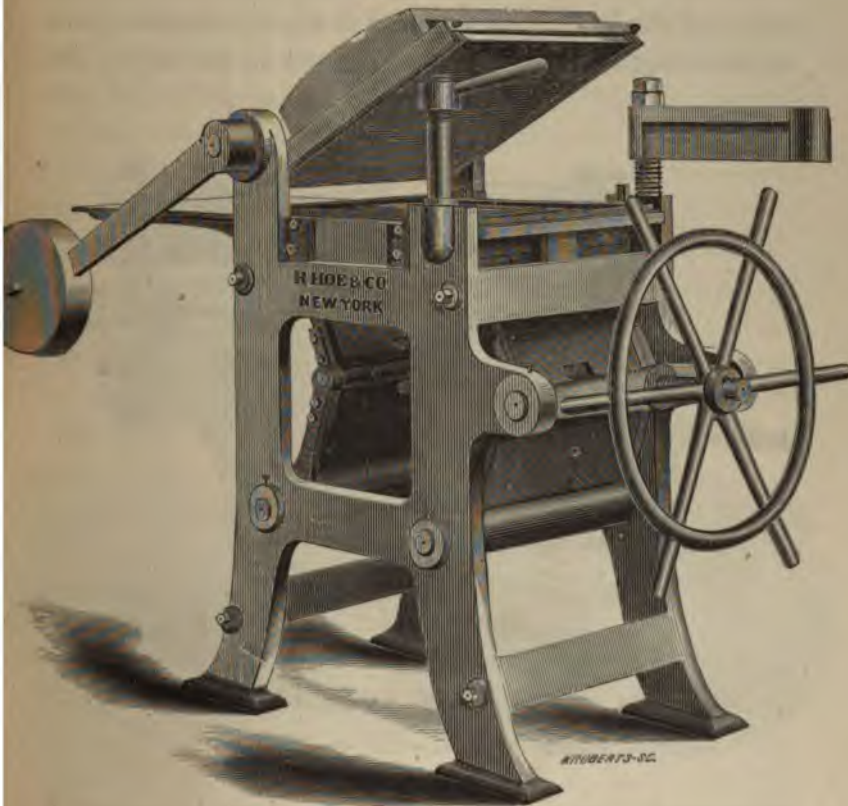
*The Process.*—The subject to be duplicated being, for example, a page of type properly locked up in a form, the operation is as follows: The first step is the preparation of the matrix which is to receive the impression of the page to be copied. For this purpose there is provided a "case," usually a rectangular pan of brass, about one fourth of an inch in depth. These cases are of various sizes, but average 12 × 18 inches, and are furnished with two flanges to engage with clamps on the moulding press. One of these is placed on the case-filling table with top levelled true, and the moulding composition, usually a mixture of wax and resin (or of wax and gunt turpentine), is ladled, from a pot in which it is kept melted, into the case. A jacketed melting-pot, heated by steam to avoid the risk of burning the moulding composition, is preferable. Gutta percha, spoken of by Roseleut, in his reference to this subject, is very little used in this country for taking the moulds.

The case being slowly filled with the melted composition, and any air bubbles appearing on the surface being removed, the contents is allowed to set or harden, when it should present a smooth and level surface. This surface is then black-leaded to prevent the sticking of the type in moulding, and it is then ready to receive the impression of the type to be copied. Previous to moulding, the form of type should be washed off with lye or benzine, if it be very dirty, or with clean water if not very dirty. For this purpose, a rubber pipe connected with the water-supply, and provided with a rose jet is usually employed. After drying, the face of the form of type is also thoroughly black-leaded, to prevent the adhesion of the form to the

wax. This is usually done with a soft hand-brush, and the black-lead is made to penetrate every crevice. While it is necessary, however, that the black-lead coating should be a continuous and perfect one, it is important that all superfluous black-lead be removed, so that the fine lines of the subject shall not be filled up. This is usually done with a small hand-bellows.

*Moulding.*—For making the impression of the form in

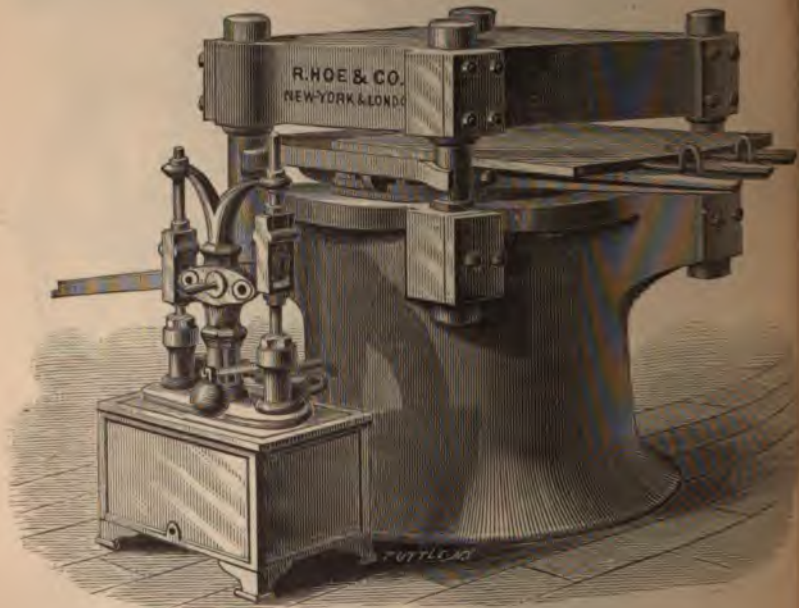
Fig. 148.



the moulding composition, which must be done with extreme nicety, a moulding press is used, which is capable

of giving a gradual and powerful pressure. The preceding figure (Fig. 148) represents a form of moulding press in common use, and known as the "toggle" press. It consists of a massive frame having a planed movable bed, over which is a head swung on pivots and counterbalanced by a heavy weight as shown, so that it can be readily thrown up, leaving the bed exposed, the black-leaded type-form being placed on the bed; the well black-leaded case is attached by clamps to the movable head, or the form (also black-leaded) is laid face down on the case, and the head is then turned down, and held in place by the swinging bar (shown turned back in the cut). All

Fig. 149.



being ready, the toggle-pressure is put on by means of the hand-wheel and screw, the result being to raise the bed of the press with an enormous pressure, causing the face

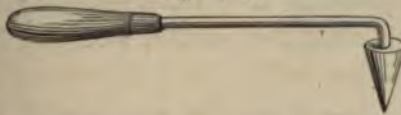


of the type form to impress itself into the exposed wax surface.

Figure 149 represents a form of "hydraulic" press, less commonly used than that just described. It is provided with projecting rails and a sliding plate, on which the form and case are arranged before being placed in the press. The pump, which is worked by hand, is supported by a framework on the cistern below the cylinder, and is furnished with a graduated adjustable safety-valve to give any desired pressure.

*Building.*—The proper depth of the impression to be taken can only be determined by practice. Supposing the impression to have been successfully taken, the mould is passed to a workman, who with a wide, thin-bladed knife shaves off the projecting wax ridges that have been forced up about the edges and low places of the mould by the press, and which, if not removed, would overlap and hold the copper shell, and make it difficult to remove the shell from the face of the mould when it comes from the battery. He then proceeds to the operation of "building" the mould, which is performed with an instrument like that shown in Fig. 150. The workman is provided with

Fig. 150.



several of these building irons, which are laid on a rack, in a small oven heated by a gas-jet. Taking one of these irons properly heated, and applying to it from time to time a thin strip of wax, he allows the melted wax to run from the point of the tool on to the open spaces or blanks of the mould. This operation is an important one, requiring a steady hand and a certain



copy of the original, and it will be useless to place the mould in the bath.

It should be noticed here, that the black-lead used in every stage of the electrotyping process must be of the purest description, and in the most minute state of division. An inferior material will injuriously affect the electrical conductivity of the surface of the mould, and the presence of any gritty particles will scratch and

Fig. 151.



deface it. The manufacturers of this material, therefore, prepare electrotypers' stock with special care. The best for this purpose is prepared from the purest selected Ceylon graphite, which is ground by rolling with heavy iron



balls until it is reduced to a dead-black, infinitely fine powder. It should be separated by air-floating, or by floating in a bath of dilute sulphuric acid, which will dissolve out its mineral impurities.

The operation of black-leading the moulds is performed either by hand, or, more commonly, by machines. The preceding cut (Fig. 151) shows one of the most practical of these machines with its cover removed to exhibit its construction. It has a travelling carriage holding one or more forms, which passes backward and forward under a laterally vibrating brush. Beneath the machine is placed an apron, which catches the powder, which is made to do service over again. (Several modifications of the dry black-leading machine have been devised, and an excellent one is described in *The Polytechnic Review*, vol. iv. p. 262, 1877.)

When the mould has been thoroughly dusted, it is removed from the machine, and the superfluous plumbago is blown out of the lines of the mould with a broad-nosed bellows, or brushed out, leaving the mould covered with a film of graphite of infinitesimal thickness, but very lustrous. If any loose particles of the dust are permitted by carelessness to remain, the result will be a faulty electrotype.

On account of the dirt and dust caused by the dry process of black-leading, and which cannot be avoided, owing to the impalpably fine condition of the black-lead powder, some electrotypers prefer the wet process, invented by Mr. Silas P. Knight, chief of the electrotyping department of the Messrs. Harper & Brothers, New York. This process is designed to work more quickly and neatly, producing moulds that are thinly, evenly, and perfectly covered, not omitting the dot of an *i*, nor allowing "bridging" over fine lines. In Mr. Knight's process

the moulds are placed upon a shelf in a suitable receptacle, and a rotary pump forces an emulsion of graphite and water over their surfaces through a travelling fine-rose nozzle. This process is pronounced to be rapid, efficient, neat, and economical.

*Wiring.*—After the above operation of black-leading has been properly performed, the workman takes one or several stout copper wires, the ends of which, after thorough cleansing, he heats for an instant, and imbeds in the wax on the side of the mould. The surface of this wire is carefully exposed, and, by way of precaution, the place is rubbed with black-lead with the finger, to restore the black-lead surface that may have been disturbed. Trifling as this circumstance of exposing the imbedded wire may appear, the galvanic deposit of the copper on the face of the mould would be impossible were it neglected, as the mass of wax being a non-conductor of electricity, a galvanic circuit could not otherwise be established. The exposure of the wire, therefore, is essential, in order that the surface of the mould may be rendered properly conductive to insure the uniform deposition of copper upon it. To confine the deposit of copper where it is actually desired, and to prevent it from unnecessarily spreading over the edges of the mould, the hot building-iron is run over it so as to destroy the continuity of the black-lead surface save where the deposit of copper is wanted.

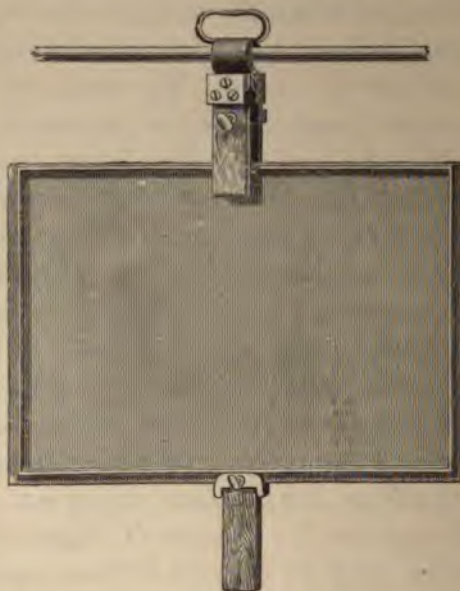
In order that the deposition of copper may be as nearly uniform in thickness as possible over the entire surface of the mould, it becomes necessary where a large surface is to be coated, to provide as much metallic surface as possible on which the deposit of copper may commence and spread. One method of accomplishing this is to attach one or more pieces of metal to the wax on the edges of



the mould, and connect them with the slinging wires by good metallic connections.

A very practical device in this connection is the "electric connection gripper" of Messrs. R. Hoe & Co., of New York, which is shown in Fig. 152.

Fig. 152.



This arrangement is designed to hold and sustain the moulding case, and at the same time to make an electric connection with the prepared conducting face of the mould only; consequently leaving the metal case itself entirely out of the current, so that no copper can be deposited on it.

*Metallizing the Moulds.*—On account of the comparatively inferior conducting character of the black-lead surface of the mould, several methods have been devised and are in use for improving its conductivity by metallization.



By this procedure, the mould is provided with a surface eminent conducting quality, by which the uniformity of the metallic deposit over its whole surface is insured. Without such preparation, the deposition of copper would commence at the suspension wires, and would gradually proceed from these over the surface of the mould. Those portions nearest the wires would, therefore, receive the thickest deposit, and those farthest therefrom, the thinnest. Gilt and silvered black-lead, prepared in the manner described on page 454, are occasionally used for this purpose. The coppering process of Mr. Silas P. Knight is, however, preferable, and is in general use for this purpose. The process in question effects in a few seconds the coating of the mould with a thin and uniformly distributed film of copper. It is performed in the following manner: After stopping out those portions of the mould that are not to receive a deposit, it is laid in a shallow trough, and a stream of water turned upon it from a rose jet to remove any particles of black-lead that may remain in the lines or letters. The workman then ladles out of a conveniently placed vessel some sulphate of copper solution, pours it upon the face of the mould, dusts upon it from a pepper-box some impenetrably fine iron-filings, and brushes the mixture over the whole surface, which thus becomes coated with a thin, bright, adherent film of copper. Should any portion of the surface, after such treatment, remain uncoppered, the operation is repeated. The excess of the copper solution is washed off, and the mould is then ready for the bath.\* The use of tinning in place of coppering

\* In experimenting with the Knight process, the writer accidentally made the observation that chemically pure iron, in the finest possible state of division (as prepared, for example, by the reduction of the oxide of iron by hydrogen) will *not* produce an adherent copper film

has also been recommended, in accordance with the patented process of Adams. (For description, consult R. Hoe & Co.'s Catalogue, page 91.)

Before the moulds are placed in the depositing vat, it is important to wash them thoroughly, which is done generally by directing upon their faces a strong stream of water from a rubber hose and pipe. When the moulds have been thoroughly washed out, they should be placed at once in the depositing vat, and connected.

*The depositing solution* is the same as that previously described and used for obtaining thick electro-deposits (*i. e.*, a saturated solution of sulphate of copper, acidulated with sulphuric acid, *vide* Chapter L.), and either the battery, or what is now commonly the case, the plating machine, is used to effect the deposit. The vat is provided with a series of large copper anodes, between which the cases containing the prepared moulds are suspended in the solution back to back, so that the moulds face the anodes. When the metallic connections are made, the mode of doing which has been repeatedly described in other portions of this work, the circuit is completed, and

upon the mould. In a number of trials with such chemically pure iron, the copper was invariably reduced as a non-adherent powder. The most probable explanation of this curious fact appears to be, that the reducing action of the iron on the copper salt is so energetic, that the solution of the iron and the precipitation of the copper are instantaneous, no time being afforded the copper to come in contact, in the act of precipitation, with the black-leaded surface. Where, on the contrary, iron filings are used, as is the case in practice, the particles of iron, though so minute as not to injure the face of the mould, are enormously larger, comparatively speaking, than those of the reduced iron, their action on the copper salt is much slower, and, as the precipitation of the copper is slowly taking place on the iron particles, as they are moved by the brush to and fro over the black-leaded surface, enough of it is transferred and adheres to the latter surface to give it a continuous metallic coating.



the copper at once commences to be deposited on the moulds.

The time required to obtain a shell of copper of proper thickness will vary according to the thickness desired and the strength of the battery current. For ordinary book or job work, the copper shell should be about as thick as good book paper, which will require an immersion of from three to five hours. For newspaper headings, and such other blocks as will be subjected to hard usage, a much thicker shell is made, requiring a correspondingly longer immersion in the bath.

To give an idea of the rate at which this class of work may be done, we may state that the Smee battery (zinc-silver couple with sulphuric acid as an excitant), of 26 pairs, 12  $\times$  12 inches, will copper from 6 to 6 $\frac{1}{2}$  square feet of prepared moulds in four hours. In this branch of galvanoplastic work, as in electroplating, the battery has, however, at least in the United States, been largely superseded by the dynamo-electric machine, and with the result of greatly increasing the capacity of the establishments, and of dispensing with the trouble and care which even the simplest batteries demand. As every such establishment requires to use steam-power in some portion of its work, and generally has at command more power than is actually required, the taking off of one, two, or even three horse-power additional for running a plating machine, in some cases, makes no appreciable difference in the expense account. A comparison of the relative economy of battery- and machine-plating is given in our chapter on the dynamo-electric machine.

*The Shell.*—When the mould has received a suitable deposit it is removed from the bath, and the copper shell removed from the wax. To do this the mould is placed in an inclined position, and a stream of hot water is poured



over the copper surface. This artifice softens the wax sufficiently to allow the shell of copper to be stripped off. This may be done by taking hold of one corner of the shell, and quickly lifting it as the hot water flows over it. In removing the shell, care should be taken to keep it straight, as otherwise it will be difficult to back and finish it properly.

The film of wax which always adheres to the copper, the quantity of which depends on the skill of the operator, is removed by laying the shell upon a wire-screen, and pouring a hot lye of potash over its surface from a ladle, until the adhering particles of wax have been dissolved, allowing the potash to run back again into the pot from which it was dipped. The shell is then thoroughly rinsed off in cold water.

The tinning of the back of the shell is the next operation, and has for its object to strengthen the union between the shell and the backing metal. For this purpose the back of the shell is cleansed by brushing with "soldering fluid" (made by allowing muriatic acid to take up as much zinc as it will dissolve and diluting with about  $\frac{1}{3}$  of water, to which sometimes some sal-ammoniac is added). Then, the shell, face down, is heated by laying it upon an iron soldering plate, floated on a bath of melted stereotype metal, and, when hot enough, melted solder (half lead and half tin) is poured over the back, which gives it a clean, bright metallic covering. Or, the shell, is placed downward in the backing pan, brushed over the back with the soldering fluid, alloyed-tinfoil spread over it, and the pan floated on the hot backing metal until the foil melts and completely covers the shell. When the foil is melted the backing pan is swung on to a levelling stand, and the melted backing metal is carefully poured on the back of the shell from an iron ladle, com-

cing at one of the corners, and gradually running over surface until it is covered with a backing of sufficient kness. The accompanying cut (Fig. 153) represents

Fig. 153.



venient form of backing pan and stand for this purpose. Or, after tinning the shell, as above described, it is allowed to take the temperature of the backing metal on the floating iron plate. The plate is then removed from the molten metal, supported in a level position on a stand having projecting iron pins on which it is rested, and the molten stereotype metal is ladled carefully to the proper thickness on the back of the tinned shell. This process is called "backing." The thickness of the metal-backing is about an eighth of an inch, enough to give the necessary rigidity to the shell to enable it to with-

stand the pressure to which it will be subjected in the printing press. A good composition for backing metal, which is warranted not to separate from the shell in the process of finishing is—

Tin . . . . .	4 parts.
Antimony . . . . .	5 "
Lead . . . . .	91 "

*Finishing.*—The plates thus prepared must now be finished, that is, they must be sawn apart, trimmed to remove rough edges, shaved down to take the roughness off the backs and make them of equal thickness, the printing faces brought to a perfect level, and then mounted.

In the finisher's department the plates go first to the saw table (Fig. 154), where the several subjects are roughly sawn apart by a circular saw, the eyes of the operator being protected from the flying metal cuttings by an interposed pane of glass.

After trimming all around to remove the rough edges, the plates are shaved to take off any roughness from the back and to make them of even thickness. In all large establishments this portion of the work, which is very laborious, is done with a power planing machine. With this machine, the plate is brought to very nearly proper thickness and almost true. The flatness of the plates is then tested with the straight-edge, and any unevenness is beaten down with a light hammer and planer. To bring up low places, the face of each plate is then tested by rubbing with a flat piece of willow charcoal, which will not blacken such parts as are depressed below the general surface, and these places are indicated on the back by marking with a suitable caliper. Turning the plate face downward, their marked places are struck with a ball-faced hammer which brings up the printing face opposite to the true level. These operations are repeated



en as may be necessary to obtain a true printing  
e.

Fig. 154.

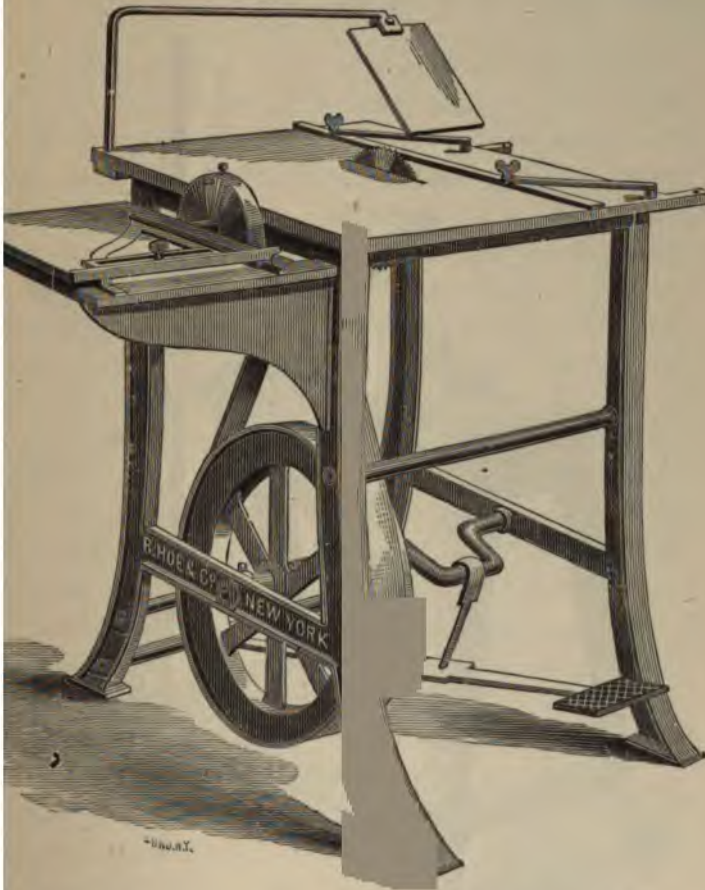


plate then passes to the hand-shaving machine (Fig. 155), where the back is shaved down to a proper finish, smooth and level. The edges of the plate are planed down square and to a proper size. The machine then receives the dressed and squared plates, and counts them type-high on a block of wood—cherry,

mahogany, walnut, or oak—true and square. This is the last stage of the operation, and the electrotype is now ready for the printing press. Book-work is usually not

Fig. 155.



mounted on wood, the plates being left unmounted and finished with bevelled edges, by which they are secured on suitable plate-blocks of wood or iron, supplied with gripping pieces, which hold them firmly at the proper height, and enable them to be properly locked up.

Finally, it may be mentioned that plaster of Paris may also be used in the place of wax as the material for taking the mould, and electrotypes made therefrom, after proper preparation by one of the several methods previously described.

*Stereotyping* is the name given to several processes involving the same object as electrotyping (*i. e.*, the duplication of printing surfaces, of engravings or type, to be used in place of the originals in the printing press). These methods, however, are purely mechanical, and do not involve the employment of the galvanic current. They consist, generally, in obtaining a cast in some metal directly upon the mould taken from the original, the mould being usually placed in a "casting-pan" of suitable shape and size, into which, after properly preparing it, melted stereotype metal is poured, and the whole subsequently submerged in a bath of the melted metal. According to the material used for making the mould, three processes of stereotyping are known, distinguished respectively as the *plaster*, the *clay*, and the *papier-mâché* method. The methods of preparation and casting differ somewhat with each. The first two are generally adapted for miscellaneous work, and the last is specially adapted for newspaper uses, where curved plates are required for the perfecting presses, though it is not confined exclusively to this class of work.

The operations involved in finishing the stereotype plate after it has been removed from the casting-pan, are very similar to those in use with electrotypes.

For a detailed description of the several processes of stereotyping, we must refer our readers to special works treating of it, as the subject is somewhat foreign to that of this treatise.

Very satisfactory descriptions thereof may be found in



*Stereotyping and Electrotyping*, R. Hoe & Co., New York, 1881, and *Stereotyping and Electrotyping*, by Fredr. J. F. Wilson, London, Wyman & Sons.

## CHAPTER LX.

GALVANOPLASTIC DEPOSITS ON PATTERNS WITHOUT DELIVERY (UNDERCUT), AND WHICH ARE SACRIFICED—LENOIR'S PROCESS—GALVANOPLASTIC METHOD FOR ARTICLES IN HIGH RELIEF WITH GUTTA-PERCHA MOULDS.

### *Galvanoplastic Deposits on Patterns without Delivery (Undercut), and which are Sacrificed.*

ROSELEUR describes the following ingenious method of obtaining a copper mould and a copy afterwards from originals so undercut that they must be sacrificed: A human head in plaster of Paris, for example, is rendered impervious, and then metallized.

Fig. 156.



After a galvanoplastic deposit of copper has been effected on its surface, the plaster is removed, breaking it away through some such unimportant part as the opening of the neck. The continuous mould of copper thus obtained is slightly greased inside, and serves as a depositing vat (Fig. 156), which is filled with the solution of sulphate of copper. Bags filled with crystals of blue vitriol are suspended to the edges, and with a separate current and copper anode, or with

a porous cell placed inside of the mould, which is connected with the zinc, another deposit of copper takes place in the cavity. When the thickness of the metal is sufficient, the mould or first deposit is peeled off, and we obtain the copper reproduction of the object in high relief. This process is expensive, but gives sure results with large patterns with parts in pronounced relief. With small, or narrow objects, or those of which the reliefs are very sinuous, Roseleur recommends sectional moulds, although the seams are always seen and require careful retouching.

*Lenoir's Process—Galvanoplastic Method for Originals in High Relief with Gutta-Percha Moulds.*

It is proper to insert in this place the galvanoplastic method for articles in high relief, with gutta-percha moulds, invented by Lenoir, to whom the arts are indebted for several valuable discoveries.

Lenoir had been impressed by the enormous labor required for finishing up a bronze coming from the foundry: retouching, filling up, scraping, smoothing, and chasing were as many causes for rendering the object accessible only to the favored few. Moreover, after a passage through so many hands, the reproduction was but the shadow of the work of the master. He was also well acquainted with the difficulty of soldering together the various parts of galvanoplastic productions, so as to form with them a bust, a group, or a statue.

The problem to be solved was to obtain from a perfect pattern as many galvanoplastic copies in one piece as desired, and with such accuracy that the artist to whom the model was due could not distinguish it from the reproduction.

We shall see by what series of processes, one more in-

genious than the other, Lenoir succeeded in solving the problem.

Let us take, for instance, a statue (Fig. 157). We begin by making with gutta percha a mould in several

Fig. 157.



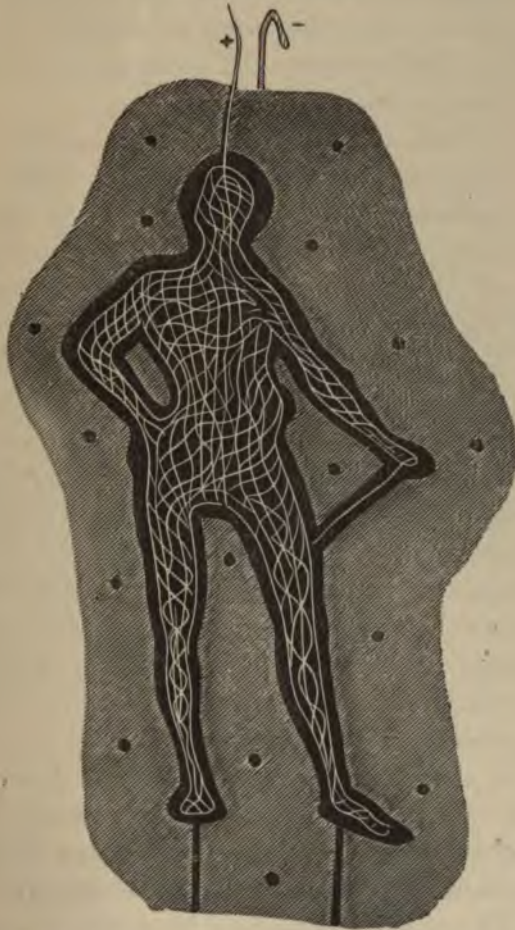
pieces, which, by means of proper marks, may be united together, and form a perfect hollow mould of the original. All these parts are carefully coated with plumbago.

This having been done, a skeleton (Fig. 158), is made with platinum wire, following the general outline of the model, but smaller than the mould, since it must be suspended in it without any point of contact.



If the skeleton thus prepared is inclosed in the metallized gutta-percha mould, and the whole is immersed in the galvanoplastic bath, it will be sufficient to connect the inner surface of the mould with the negative pole of the

Fig. 158.



battery, and the skeleton of platinum wires (which should have no points of contact with the metallized surface of the mould) with the positive pole, in order to decompose

the solution of sulphate of copper which fills the mould. When the metallic deposit has reached the proper thickness, the gutta-percha mould is removed by any convenient process, and a faithful copy of the original will be reproduced, which may be finished at a very small expense.

But though the explanation of the process is very simple, its execution is not so easy, for which reason we shall examine the precautions devised by the inventor to insure success.

Fig. 159.



First, it is very difficult to ascertain that the skeleton anode is nowhere in contact with the inclosing mould. In order to avoid such contact, Lenoir wraps with a spiral of India-rubber thread all the external parts of the platinum anode. This rubber coating prevents the contact of the metal with the mould. Fig. 159 represents the manner in which the spiral of India-rubber thread runs round the platinum wire.

Second, notwithstanding all these precautions, it was still possible that, with the increase of the deposit of copper, which would reduce the distance between the mould and the anode, the latter and the deposit would come in contact, and hence stop the operation without manifesting any exterior sign to attract the attention of the operator.

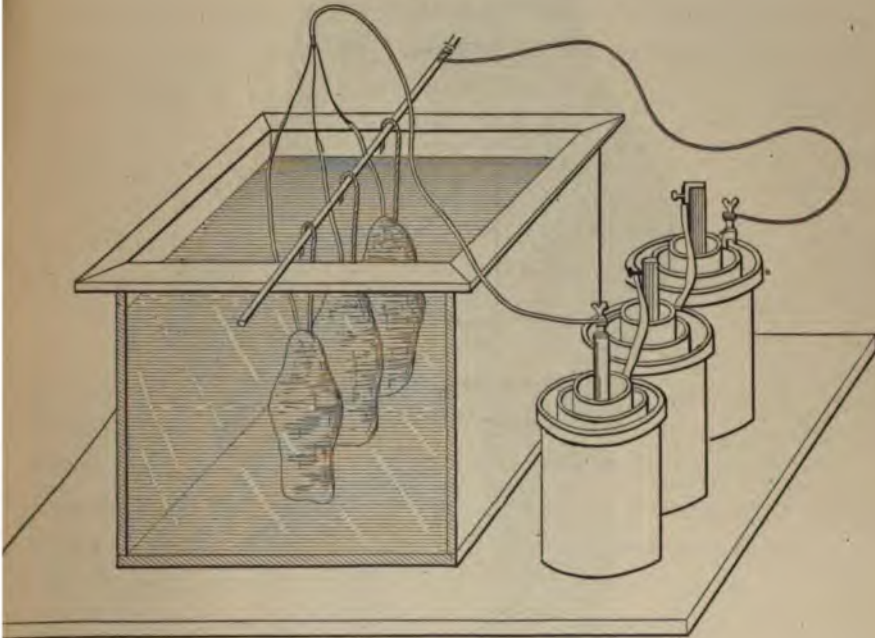
This was an objection sufficiently serious to render the whole process entirely useless. For, if in a vat holding many moulds, one point of contact were established between the two poles (mould and skeleton), the current of the battery would be short-circuited and escape at that place, and the deposition would cease entirely.

In order to obviate this possible inconvenience, Lenoir has devised the following process:—

All the moulds of the same bath are supported by hooks suspended from a metallic rod. These hooks have

no contact with the black-leaded surfaces of the moulds, which are connected with the negative pole by means of metallic wires terminated above the liquid by other *iron wires* as fine as hair. The connecting wires of the skeleton anode pass through the same opening as the negative conductor, but without contact, and are united to the positive pole (Fig. 160).

Fig. 160.



It results from this disposition that, as long as there is no contact between the skeleton and the interior of the mould, the electric current finds sufficient passage through the several slender iron wires which connect the moulds with the battery; but, if any contact takes place, the electricity escapes at that point, and, being too abundant for the small section of the iron wire, it heats and burns



it out rapidly. The galvanoplastic deposit is thus instantaneously stopped upon this mould, though it continues to the others. Moreover, the broken wire shows the operator the location of the defect.

The iron wire should be very short, in order to run out rapidly. A length of a few inches is sufficient.

Fig. 161.



Lastly, it will be understood that, in closed moulds and with an insoluble platinum anode, the solution of

te of copper will be rapidly transformed into sulphuric acid and water. Hence the necessity of allowing lower part of the mould (under the feet for instance), for two holes, through which and the opening at the top, left for the passage of the electrode, a free circulation of the liquid in the bath may take place (Fig. 161). When the operation is completed, the gutta-percha is removed, and the skeleton anode forcibly withdrawn.

We have then simply to close the three holes in the mould, and to file off the seams left at the junction of the different parts of the mould, in order to have an accurate copy of the model.

## CHAPTER LXI.

### DURATION OF THE OPERATION.

There are no precise rules for determining the length of time necessary for a galvanoplastic deposit. It depends on the thickness of the desired deposit, the intensity of the current, the dimensions, and the more or less irregular shape of the object. The article may be removed from the bath when the thin copper deposit has spread all over the mould; but in this case, the film is not sufficiently firm, and is often perforated. Nevertheless, a quantity of these thin and defective deposits are to be met with in trade, and an appearance of firmness is given by tinning these from the back, and strengthening them with tin or other solder. These strengthened deposits are sometimes returned to the galvanoplastic bath in order to cover the solder with a light layer of copper, and make it appear as though the thickness of

the deposit were considerable, whereas its solidity is simply due to the added solder.

The firm of Ch. Christofle & Co. employs a process for filling with copper solder (copper and zinc) galvanoplastic reproductions. By this process they are enabled to furnish to the trade an enormous quantity of perfectly finished and durable articles for furniture and cabinet-makers' use. Similar objects were previously made of cast bronze or brass, which required trimming, chasing, and other manipulations before being ready for use.

For filling galvanoplastic reproductions with brass solder, their exterior is first covered with clay, plaster of Paris, or Spanish-white mixed with charcoal dust, after which the whole is perfectly dried in the stove-room. This coating is intended to prevent the copper deposit from losing its shape and being oxidized by the action of a high temperature. The interior of the article is then filled with the softest brass solder to be found, and with powdered borax, which are melted by a gas jet or before the blowpipe. All the hollow parts are soon filled with the solder, which imparts to them at least equal firmness and durability as is to be found in cast articles.

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## CHAPTER LXII.

### REMOVING THE MOULD—FINISHING UP THE ARTICLES.

#### *Removing the Mould.*

THIS operation consists in separating the galvanoplastic deposit from the substance of the mould, and it is evident that there will be nearly as many methods of effecting this as there are substances employed.



With a metallic mould the operation is very simple, and it is sufficient, after having removed the useless portions of the deposits with a file, a saw, or otherwise, to pass a card or a blade of horn or ivory between the model and the deposit to effect their separation without injury.

The operation is about the same with moulds of plaster of Paris, porcelain, marble, glass, or wood; but it is very difficult to save a plaster mould which has been in the bath, and which is nearly always sacrificed and separated in fragments.

Moulds of wax, stearine, fusible metal, gelatine, or gutta-percha are heated in boiling water or otherwise; their separation, therefore, presents no difficulty.

#### *Finishing the Articles.*

The articles separated from the moulds are generally spotted with plumbago, grease, or other still adhering substances, from the moulds. It is usual to heat them, so as to burn out the impurities, and to cleanse them by a more or less protracted immersion in a pickle of diluted sulphuric acid. The heating presents the advantage of rendering the copper deposit softer and more malleable; on the other hand, it may result in injury to the minute details and the fineness of the copy. Therefore, for delicate reproductions, it will be preferable to clean with alcohol, turpentine, gasoline, or benzole, and to rub the surface with a stiff brush. We may finish with a paste of Spanish-white (levigated chalk) in water, which is allowed to dry upon the object before it is wiped off. In this case, should any Spanish-white still remain in the depressions, it may be dissolved in water containing one-tenth of its volume of hydrochloric acid, which does not corrode the copper. The operation is completed by rinsing in fresh water, and drying in sawdust, or otherwise.

When it is desired to anneal the articles without injury to their surface, we may plunge them into boiling colza, linseed oil, or simply grease, which will bear a heat sufficient for annealing, and will prevent the oxidizing action of the air. This annealing in fatty substances is especially to be recommended in the case of highly undercut moulds of gutta percha, which may have left part of the substance in the deep recesses of the galvanoplastic copy. The gutta percha is first softened, and then dissolved in the fatty material.

## CHAPTER LXIII.

### GALVANOPLASTIC OPERATIONS WITH GOLD OR SILVER—GALVANOPLASTIC BATHS FOR SILVER AND GOLD.

#### *Galvanoplastic Operations with Gold or Silver.*

WE have said that it is possible to obtain galvanoplastic deposits of gold or silver; but the processes known at the present time are more difficult and less effective than those for copper. The latter metal is obtained by the reduction of simple salts; whereas such operations with gold or silver require baths of double salts, such as the double cyanide of gold and potassium, or the double cyanide of silver and potassium. The sulphate of copper is very soluble and easily reduced; on the contrary, the sulphate of silver is but slightly soluble in water. The sulphate of gold exists only hypothetically. As for the nitrate of silver and the chloride of gold, which are the most soluble salts of these metals, they have been tried without success.

A very great disadvantage with the galvanoplastic baths

of gold or silver is their alkaline state, which prevents the use of many substances, especially of fatty materials, for the preparation of the moulds. Moreover, these baths are inferior in conducting power for electricity, and require a better metallization than that afforded by plumbago. We dare not use the reduced metals from solutions of nitrate of silver or chloride of gold, because they will be immediately dissolved. Therefore, in the case of somewhat deeply wrought moulds, we are obliged to get around the difficulty by the following artifice: After having deposited by the ordinary process a thin film of copper, the whole is immersed in the silver bath, which then deposits very well. After the separation of the copy from the mould, it is allowed to remain in a solution of ammonia or of very dilute nitric acid, which, after a certain length of time, dissolves the film of copper, and leaves the silver deposit alone.

Such a reproduction must necessarily be very imperfect, since there has been, between the mould and the precious metal, an intermediary layer of copper of unequal thickness. This is, however, the only process we know of, in operating upon non-conducting and undercut moulds. On the other hand, when the surfaces are plane, or but lightly in relief, we may employ moulds of lead, tin, or fusible metal, upon which silver or gold will deposit well and without adherence.

Roseleur describes the following process for employing non-conducting moulds for galvanoplastic operations with gold or silver: The pattern is covered with a foil of lead very thin and larger than the object, then the gutta percha is applied upon it, and the whole is subjected to pressure, as before explained. The lead foil, without being torn, follows all the details of the pattern, and may be separated afterwards with the gutta percha which it



has metallized. Instead of lead we may employ silver or gold leaf, which is so thin that the joints disappear by simple pressure. Roseleur recommends this method to amateurs, desirous of obtaining good deposits of silver or gold, as very simple and easy to acquire.

A somewhat thick sheet of very pure lead may be employed for taking moulds of engravings upon copper or steel. The lead and the engraved plate are passed between rollers, or simply subjected to pressure in a screw-press.

*Galvanoplastic Baths for Silver and Gold. (Roseleur.)*

The bath for galvanoplastic operations with silver is composed of—

Distilled water . . . . .	100 parts.
Cyanide of potassium . . . . .	20 "
Nitrate of silver (fused) . . . . .	7½ "

A more economical solution is obtained by using half of the above named quantities of cyanide and nitrate of silver for the same proportion of water.

The gold galvanoplastic bath is composed of—

Distilled water . . . . .	100 parts.
Cyanide of potassium . . . . .	15 "
Neutral chloride of gold . . . . .	5 "

These baths are generally operated with separate current and with anodes of the metal used in the solution. Nevertheless, the porous cells and zincs may be immersed in the bath itself, provided that the exciting liquid be a more or less concentrated solution of cyanide of potassium, or of common salt.

Green gold is obtained by mixing ten parts of gold bath with one of silver bath, or, what is preferable, by employ-

or a certain length of time a silver anode in the solution.

galvanoplastic deposits of gold and silver, after separation from the mould, should be heated and h-brushed; and it will be advantageous to give them desired tint by a short immersion in the ordinary gilding or silvering baths.

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## CHAPTER LXIV.

### GALVANIC ETCHING—THE FUTURE.

#### *Galvanic Etching.*

we have said that, with baths working by the battery system, the *soluble anode*, or plate of the same metal as in solution, was connected with the positive pole, and dissolved at the same time as the metallic deposit effected at the other pole.

From this phenomenon to galvanic etching is but a small step. Indeed, it is evident that, if certain portions of the anode be covered with some insulating material, the exposed parts will be dissolved slowly and more or less uniformly, and will form the hollows of an engraving, in which the reliefs will be the covered parts.

Galvanic etching is obtained by several methods, which differ but little one from another.

The most simple process consists in covering entirely a copper plate, for instance, with an insulating varnish, which is not acted upon by the bath, and then in tracing or drawing with a graver, which should penetrate through the coat of varnish, and expose the copper. By using this plate as the soluble anode of a bath of sulphate

of copper, and suspending another copper plate at the negative pole, the latter will receive the deposit, while the former will be eaten away at the places uncovered by the graver. The engraving produced will need only a slight touching up to be ready for use. |

Instead of using wax, varnish, or similar substance as an insulating material, we may employ a film of some metal that will not be dissolved in the bath. Let us suppose, for instance, that the copper plate has been strongly gilded with the aid of the battery, and that with a graver we trace a drawing deep enough to uncover the copper, this plate, being submitted to the same electric conditions as above, will be corroded where the graver has passed, while the gilded portions will remain entirely unacted upon, since the free acid liberated in the bath of sulphate of copper does not dissolve gold.

With the same ease it is possible to produce a drawing in relief, instead of countersunk, by making the drawing with some insulating material like varnish or a lithographic crayon. The uncovered portions surrounding the lines of the drawing will become eaten away, and the drawing will remain in relief. We may also make the drawing with the lithographic pencil or with varnish, and strongly gild the uncovered parts; then, if the varnish or the greasy lines of the pencil are removed, the etching will follow these lines, which will be countersunk.

The baths employed generally contain in solution the same metal as that to be engraved; thus, baths of sulphate of copper are used for etching copper plates, solutions of sulphate of zinc for zinc plates, and gold or silver baths for these metals.

Nevertheless, it is possible to engrave copper and zinc plates, with the aid of the battery, in baths of water simply acidulated with either nitric, hydrochloric, sul-



phuric, or acetic acid; and this process seems to be coming more and more into use.

Herewith is given a process, not for engraving, but for obtaining a mould of a design by substitution, from which galvanoplastic copies ready for printing may be obtained: Upon a varnished plate of copper a drawing is traced; this plate is dipped into a weak "quicking" solution, and then set perfectly level. By covering it with metallic mercury, this metal becomes fixed upon the lines traced by the graver, and takes the *meniscus* (curved) shape, that is to say, the relief is the greater as the engraved line is larger. Therefore, all the drawing is reproduced in relief by the mercury. We may now cover the plate with a thin paste of plaster of Paris, and when the latter has set, the two moulds may be separated, the mercury still adhering to the copper. The plaster mould will be treated by one of the above-described methods, either for preparing a counter mould from it, or for directly obtaining a galvanoplastic deposit after its metallization.

The following is another similar method which gives a mould immediately ready for the bath: The copper plate is varnished as above, and with the graving tool the parts which will produce the blacks of the engraving are uncovered. A solution of neutral protochloride of zinc is poured upon the plate, followed by a quantity of Darcet's metal, fusible at about 175° to 212° Fah. (see page 467), which is melted by means of an alcohol lamp moved about under the copper plate. The operation is facilitated by spreading the fused metal with a small iron rod all over the plate. The same result is obtained as with the mercury, except that the mould may be immediately reproduced by galvanoplastic methods.

*The Future.*

On the eve of finishing our descriptions of hydroplastic manipulations, let us say that the galvanoplastic art is open to an infinite number of applications which will be developed by the artist from time to time. Thus, by cutting an open pattern upon a sheet of copper, spreading it evenly upon another metallic plate, and dipping the whole into a bath of silver or gold, the empty spaces will be filled with the new metal, and the whole will form a kind of mosaic work which may be very rich and variegated. It is by an analogous process that, after having fastened by a thin coating of varnish precious stones, or other objects, upon a metallic plate, and the whole being steeped in the bath after metallization, it will be possible to *set* artificially different parts of an artistic production. A pattern may be hollowed out with a graver from a plate of ivory or mother of pearl, and the whole metallized and immersed in the galvanoplastic bath. After the entire surface has become covered with the metallic deposit, it is sufficient to grind and polish it until the reliefs of ivory or mother of pearl reappear, and the metal will form a variety of artistic incrustations. In fact, we may say that there is scarcely any industry in which the galvanoplastic art will not be found serviceable.

## CHAPTER LXV.

## TINNING BY IMMERSION IN MOLTEN TIN.

THIS method of securing upon metal surfaces, principally upon iron, and to a slight extent, also, upon copper, an adherent coating of tin of any desired thickness, is

the principal one employed in the arts for this purpose. The tinning of sheet-iron by this process is an industry of vast importance, and prodigious quantities of *tin-plate*—as sheet-iron thus coated is termed—are annually manufactured and consumed for a great variety of uses.

The objects sought to be accomplished by the tinning of iron, are, to protect the latter metal from oxidation, tin being very indifferent to atmospheric influences, and also to improve the appearance of the iron, and fit it for many uses for which in its ordinary condition it is quite unsuited.

The art of tinning by immersion in fused tin is a very ancient one. It is supposed to have been practised in Bohemia as early as the thirteenth century, from which country, which was then favored with the possession of rich mines of tin, it was introduced into Saxony in the year 1620. From Saxony, it was carried to Wales in 1670, in which country, in spite of some early vicissitudes, it has ever since flourished.

The question of the protective action of tin as a coating upon iron has some scientific interest.

It is a well-known fact that two dissimilar metals in contact with each other, in the presence of an exciting liquid, will form a galvanic couple; the conditions of the galvanic battery being thus practically established. Under these circumstances, precisely as in the galvanic battery, the electro-positive metal of the combination will be dissolved (corroded, oxidized) while the electro-negative metal will remain unaffected; and when thus coupled, the solvent or corrosive action of the liquid upon the electro-positive metal will be more energetic and rapid, than when it is exposed alone to its action. The energy of the galvanic action set up by two metals thus coupled, will be governed by their relative electro-chemical char-



acters. For instance, between two metals standing near to each other in the electro-chemical series, the galvanic action will be exceedingly feeble, but this will progressively increase, as they recede from each other in the electro-chemical series.

Applying these facts to the case of tin and iron, it will appear that they stand, relatively, considerably apart, and their union under the proper conditions will provide the elements for a galvanic current of some intensity. In such a combination, tin is the electro-negative element, and is therefore protected, and iron is the electro-positive element, and is therefore the metal which is chemically acted upon by the electrolyte or liquid excitant.

When exposed to atmospheric moisture which will play the role of the electrolyte, tinned iron must be *perfectly* coated with tin, in order that it shall not suffer rapid destruction. These facts are fully known, and the manufacturers spare no care and attention to coat the sheet-iron so perfectly that it shall be without a flaw. Wherever such a flaw exists, or wherever moisture finds its way between the two metals, galvanic action is at once set up, and the points in question become the foci from which the oxidation (or rusting) of the iron extends in all directions, like the continually-widening circles made by a stone cast into a pool of water.

So long, however, as the coating of tin remains intact, the tin by reason of its presence and its indifference to atmospheric influences, effectually protects the underlying iron, but it should not be forgotten that as soon as the continuity of the tin coating is destroyed, the rusting of the iron, when exposed to moisture, proceeds with greater rapidity than if it were uncovered. Where, however, the tin coating has been removed from a considerable space by the oxidation of the underlying iron, the exposed

surfaces of the latter metal behave to all intents and purposes as though the tin were absent, since it is only at the points of contact of the two metals that the galvanic action is maintained.

The above remarks will serve to explain why tinned vessels, or sheets, exposed to the damp or allowed to remain wet for a comparatively short time, are rapidly eaten through by the rusting of the iron; and also why it is important to completely dry such vessels at once after drying them, or to protect with a coating of paint or varnish tinned sheets that are exposed to the weather. The principles involved in the above considerations have, as we shall see, an equally important bearing on the behavior of galvanized (zinc) objects.

As the tinning of sheet-iron is the most important branch of the tinning industry, we shall proceed to describe it in detail.

*Tinning Sheet Iron. (Tin-Plate.)*—The rolled black plates as they come from the mill, cut up by the shears to proper size for the finished tin-plates, are first "pickled," to clear their surface of the black oxide with which they are covered. For this purpose they are immersed—a large number at a time—in a strong pickle of sulphuric acid contained in a wooden or lead-lined bath heated by steam. To facilitate the action of the acid, a little saw-ast is placed between each sheet, and in about twenty minutes the operation will be finished. They are then moved to washing tanks, where they are well rinsed in fresh water.

The pickled plates are next piled up in air-tight iron boxes, capable of containing a large number of them, and transferred to a reverberatory furnace, in which they are annealed by heating to redness for about 10 or 12 hours. The object of this annealing is to bring the plates to the



right condition to take the proper polish or surface in the next operation of rolling. The plates are allowed to remain in the annealing furnace until they have entirely cooled off, when they will be found to have acquired a purplish color from a film of oxide on the surface, and to have become quite soft.

The quality of the finished tin-plates will depend very largely upon the manner in which the succeeding operation of "cold-rolling" is done. This consists in passing them through several (usually three) pairs of polished steel rollers, to give them a smooth and even surface before they are tinned. They are next annealed a second time in the same manner as before described for a period of about 6 or 8 hours, to soften and toughen the sheets.

Before they are fit to accept the tin, the annealed plates must again be pickled, to remove the thin skin of oxide that has formed upon them during the last two operations of rolling and annealing. They are, therefore, immersed again for about ten minutes in a warm pickle of sulphuric acid, but considerably weaker than that used at first. This operation is called "white pickling," to distinguish it from the first, or "black pickling."

From this pickle, the sheets come out quite clean of scale; they are thereupon washed and scoured with sand, and placed in vats containing fresh water to protect them from further oxidation, until they are taken to the tin bath. We have drawn freely from various authorities in the following description of the apparatus and appliances which are necessary for tinning iron. These are termed a "set of pots," which are placed in brickwork with fire-places below the ground, the flues from which work into a large open-mouthed chimney or stack, about 45 feet high (one for each set), which serves to carry off the



smoke from the fires, the fumes from the metal, and the stife from the grease. ✓

The set of men for each set of pots consists of a tinman, a washman, a grease boy, and three girls employed for rubbing, dusting, and polishing the sheets.

From the water tanks the cleaned plates are taken to the tinning-room, where they are either dipped at once to the number of about 340 at a time into a bath of melted tin covered with three or four inches of tallow, heated to near the inflaming point of the tallow, in which they are allowed to remain for an hour and a half or longer according to their thickness, when they are removed and placed upon an iron grating to allow the superfluous tin to drain off (Bloxam, *Metals, etc.*, 146); or, they are first immersed sheet by sheet into a bath of melted palm-oil in order to remove the moisture, to heat the iron and prepare the sheets for coating; then taken from the oil with tongs, and immersed in the molten tin, where they remain for 20 minutes, "the tinman constantly, by means of his tongs, opening and re-opening the pack" to insure the contact of the metal with every part of the immersed surfaces. (Flower, *History of Tin, etc.*, 169 *et seq.*)

When the coating of tin is thought to be sufficient, they are removed and "washed," a process which is intended to impart a uniform smooth surface to the plates, and which in its most improved form is thus described: The plates are removed by the tinman and handed to the washman "who is working close to him; the washman tumbles them into a pool or pot of tin, to keep them hot till he is ready for them; then, removing them in batches of about 20 sheets at a time, he places them upon the hob (a flat iron plate); then, with a hempen brush in one hand and a tongs in the other, with the right hand he brushes over the sheets, first on one side, then

on the other, to remove the superfluous tin which has collected *between* the sheets. Then with his left hand he dips each sheet separately in the 'wash pot,' which is full of clean, bright metal (generally foreign tin) to give the sheet a parting coat, and then, without releasing the plate from the tongs, he drops it 'end on' into the 'patent pot,' which is working side by side with him, where, by means of a lever above, and a cradle below the metal, the sheet is raised to meet a pair of steel rolls revolving on the surface of the pot, and by the pressure of these rolls the wet sheet is squeezed, and at the same time extracted from the metal. The rolls are moved by small cog-wheels worked by means of a steam engine, one of which is generally attached for the separate use of each pot."

The object of this process, which is by far the most important improvement in this industry of modern times, is to spread or equalize the metal over the surface of the sheet. (Flower, *History of Tin, etc.*, 171.)

The older process in vogue for this purpose consists in using an iron pot with two compartments, both filled with melted grain tin of first quality. One of these is intended to receive the surplus metal from the plate, and the other to impart a finishing coat of pure tin. The sheets are dipped first in one bath, then brushed as above described and dipped for a moment in the second compartment. They are then placed on edge in a bath of melted tallow, where they are allowed to remain for a certain time, when the excess of tin drains down to the lower edge, and forms a rim or "list," which is removed by dipping the lower edges of the sheets, after withdrawal from the tallow and cooling on an iron grating, into the "list-pot," which contains a layer of melted tin about one-quarter of an inch deep. The rim of metal soon softens



and melts, when the plate is removed, struck a smart blow with a stick, and the superfluous metal drops off.

The process described by Flower, of which there are several modifications, has decided advantages over the older method.

After the above described operations it only remains to rub the plates with bran to remove the adhering grease, to polish them with sheepskins on an iron table covered with sheepskins, and then to sort and box them, when they are ready for the market.

Tin-plate is made to a limited extent in Germany and France, but the principal seat of the manufacture is in Wales, whence enormous quantities are annually exported to all parts of the world, the United States being by far the largest consumer—having in the years 1871 to 1883 inclusive, imported it to the value of \$172,670,121.

It is used here in large quantities in the manufacture of a great variety of kitchen utensils, platters, cups, pots, etc. ; the canning of food products, oysters, fish, meats, and fruit—industries of great magnitude in the United States—employ vast quantities yearly, while considerable quantities are consumed for roofing and analogous uses. For roofing, however, a quality known as “terne” plate (from the French, *terne*, dull, tarnished) is better adapted. These plates are coated with a mixture of *tin and lead*, the coating is heavier, and is not so readily corroded by exposure to the weather as pure tin-plate. Other alloys, in which lead enters largely, are used in coating sheet-iron, but the processes require no special description. Kitchen utensils of copper, such as sauce-pans, stew-pans, etc., should invariably be tinned, because of the poisonous qualities of copper, which is readily dissolved in small quantity in many of the acids and oils or fats used in the preparation of articles of food. The metal (copper) ac-



steps in reality. The method generally adopted consists in smoothing the interior by scouring, then cleansing of scale by heating, and introducing some stannous salt when the surface is quite bright, introducing some tin with powdered resin, heating again until the tin is raised and spreading it uniformly over the surface with a pad of tow, or allowing it to spread uniformly by turning the vessel about. Cast-iron hollow-ware is coated with tin in substantially the same manner. With such vessels, however, on account of the roughness of the interior, it is customary to remove a thin shaving in the lathe, which affords not only a smooth surface, but one also that can be better cleaned. After scouring with sand, they accept a very smooth coating of tin with the aid of fluxes and metallic tin, when heated to the melting point of the latter metal.

In order to impart greater durability to the coating of tin and render it less fusible, especially for hollow-ware, some inventors have proposed the mixture with it of other metals. Girard (*Wagner's H. V. J.*, 265) proposes an alloy of 1 part of tin to 2 of nickel. Budy and Lamarche (*Wagner's H. V. J.*, *Table*, 76) add about  $\frac{1}{4}$  of nickel to the tin, and the last-named has patented the use of an alloy of 7 parts of tin, 1 of nickel, and  $\frac{1}{2}$  of bismuth.

As an interesting fact, it may be mentioned that the steam sand jet has been introduced to some extent to cleanse cast-iron hollow-ware previous to tinning (*Journal Franklin Institute*, 3d ser. lxi, 193).

*Moirée Metallique.*—The surface of tin plate may be given the beautiful spangled appearance known by the above name, by treatment with a warm mixture of 2 parts of hydrochloric acid, 1 part of nitric acid, and 3 parts of water. Similar effects may be produced by using common

salt, or sal-ammoniac. The solution may be applied to the surfaces to be "moiréed," with the aid of a sponge or pad of tow dipped in the warm liquid, and followed by a thorough washing in water; or the tin surface may be moistened with the liquid, then heated, and suddenly cooled by immersion in cold water. Bloxam (*Metals, etc.*, 148) suggests that "the moiré may be greatly diversified by heating the plate before applying the acid, and cooling it irregularly by sprinkling water over it, or by directing the blowpipe flame over its surface before wetting with the acid." The result of this treatment is to dissolve away the smooth surface of the tin, and to expose the crystalline structure of the underlying metal. When properly done, the "spangles" thus developed are of large size, intersecting each other in the most fantastic fashion, giving to the surface of the metal a fine mother-of-pearl lustre. This process is made to serve for a variety of decorative uses. The beauty of the moiré is enhanced by covering it with transparent colored varnishes.

*Recovery of Tin from Tanners' Waste.*—The amount of tin wasted in the form of clippings, old cans, and other vessels, represents an enormous annual loss, since thus far none of the processes suggested for the recovery of the metal have proved profitable, consequently when a tinned article has served its purpose, it is consigned to the waste heap, and the tin still remaining upon it, which represents nearly all that was originally put on, is lost. The money value of the metal that is wasted annually will be practically represented by the value of the annual production, which reaches into millions of dollars. It is singular to note, that while nothing is allowed to go to waste in the electro-plating establishment, and while iron, copper, brass, etc., that have served their respective uses, find their way back into the furnaces or the melting-

pot, the valuable tin in the form of tinner's waste and worn-out tin utensils is all practically wasted. It is scarcely probable that the utilitarian spirit that is so pronounced in our industrial communities will long suffer this discreditable condition of things to exist, and a practical solution of the problem of utilizing tin waste will doubtless sooner or later be found.

Of the many processes that have been attempted for this purpose, only two seem to have given any promise of success. We refer to them briefly as a matter of record.

One plan consists in dissolving off the tin in hydrochloric acid, and throwing down the metal with the aid of granulated zinc. The tin is precipitated as a metallic powder, which, after the solution of any surplus of zinc, may be collected, washed, melted, and run into ingots. This process involves the formation of zinc chloride, for which there is but a limited demand, and much of which would therefore be wasted.

By another plan the tin scrap is roasted in a furnace with free access of air, which oxidizes the layer of tin. The scrap is then removed from the furnace and the film of oxide of tin is shaken off by a simple mechanical procedure, and smelted with other tin ore; or, treated with sulphuric acid, which takes up the oxide of iron mixed with it, and leaves the tin behind. The latter may then be regained by the usual reduction process. The iron scrap left behind by the roasting process may be utilized, and the sulphate of iron (green vitriol) resulting from the purification of the mixed oxides may be crystallized and sold as such, or disposed of to the chemical manufacturers, who may gain the sulphuric acid by distillation, while the residue in the retorts may be utilized in the manufacture of Venetian red. This procedure is the most complete that has yet been devised.



Other plans involve the treatment of the scrap with caustic alkali, and the production of stannate of sodium, which is largely used in dyeing and calico printing.

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## CHAPTER LXVI.

### GALVANIZING BY IMMERSION IN MOLTEN ZINC.

THIS is the name given to the process of coating metals, usually wrought and cast iron, with a coating of zinc, by immersion after suitable preparation, in a bath of the latter metal maintained in a state of fusion; it is therefore strictly analogous to the process of tinning previously described.

The object to be attained is likewise the same, namely, to improve the appearance of the coated metal, and to protect it from the action of corrosive agents.

The name "galvanized iron," applied to iron thus prepared, is somewhat misleading, since it would seem to imply that the coating was effected by galvanic agency. It is intended to apply, however, to the nature of the protective influence, and not to the process.

As we have noticed in the case of tinned iron, two metals in contact, in the presence of moisture, form a galvanic couple, and the result of the galvanic action set up under these conditions will be analogous to that which takes place in a galvanic battery, *i. e.*, the electro-positive element of the couple will be dissolved or corroded, while the electro-negative element remains unaffected or protected, so long as the action continues, the intensity of the chemical action being governed by the relative positions of the two metals in the electro-chemical series.

Tin and iron standing some distance apart, give rise, it was stated, to a decided galvanic action, in which the iron as the electro-positive metal is corroded more rapidly than it would be if untinned. With zinc and iron, the conditions are reversed, zinc is positive to iron, and consequently, whatever galvanic action is set up by their contact in the presence of moisture (or other excitant), must have for effect the solution or corrosion of the zinc and the protection of the iron.

Zinc and iron, however, stand so near to each other in their electrical relations, that they can only originate the feeblest galvanic action. We must look, therefore, for the explanation of the undoubtedly excellent protective influence of zinc upon iron principally to the comparative indifference of zinc to the action of air and moisture.

Unlike tinned iron, "galvanized" iron resists the action of the weather to a remarkable degree. The zinc surface, after a brief exposure, becomes coated with a thin film of oxide, but this seems to adhere tenaciously, and forming a continuous and impenetrable skin, effectually protects the underlying zinc from further oxidation.

So long, therefore, as the zinc surface remains intact, the underlying iron is effectively protected from corrosive action, but, as in the case of tinned iron, wherever the zinc coating is defective or has been removed, there the iron is oxidized. When immersed in water the zinc coating is soon completely oxidized and removed. Salt water acts more energetically; and even the sea-air, charged as it is with salty moisture, is rapidly destructive in its action upon galvanized iron wares. Under ordinary circumstances, however, where it is simply exposed to the weather, a good coating of zinc affords an excellent protection for iron, the latter remaining unaffected for several years, being in this respect, therefore, greatly su-

perior to tinned iron, and at the same time much less costly. As compared with tinning, galvanizing is a comparatively new industry, having been introduced in Europe during the early part of the present century, and brought from England to the United States less than fifty years ago. At the present time it has assumed the proportions of a great industry on both sides of the Atlantic.

Sheet iron, for architectural, domestic, and miscellaneous purposes, pipe for gas and water distribution, railings, awning-posts, chains, hoops, and bands, wire and wire cloth, park, cemetery, and garden furniture, kitchen sinks and range boilers, buckets, scuttles, hods, and numberless miscellaneous articles of cast and wrought iron, described as small hardware, comprise principally the articles that are galvanized.

As the galvanizing of sheet iron is one of the principal branches of the industry, and the one that requires the greatest care, a description of this operation as conducted in American works will answer for the rest.

*Galvanizing Sheet Iron.*—As in the case of the galvanoplastic deposits, so in “galvanizing,” the surface of the metal to be coated requires to be freed from oxide and impurities of every description before it will take a proper coating of zinc. The preliminary cleansing, however, does not require to be done with such extreme care as in the case of galvanoplastic deposits.

The first step of the process is therefore the operation of “pickling” (*i. e.*, the removal of the black scale). For this operation there is usually provided a stout, rectangular wooden tank, from five to six feet high, and nine to ten feet long, and wide enough to accommodate from 100 to 200 sheets at a time. This contains the pickling liquid, commonly commercial sulphuric acid, diluted with



from ten to twelve parts of water; and into this liquid, heated by steam, as many sheets are immersed (on edge) as the tank will accommodate. In from one to two hours the scaling of the iron is effected, a workman or two all this time industriously wedging the individual sheets apart with suitably contrived tongs to insure the penetration of the pickle to all the sheets. This done, the sheets are withdrawn from the pickle tank and transferred to large, shallow washing-vats of wood, in which they are washed in a stream of fresh water. They are next subjected to an inspection, in order that any obstinately adhering particles of scale or cinder, that the acid may have failed to take off, may be removed. For this purpose they are passed, one by one, to a bench or table, where a workman, armed with a stiff brush and a triangular-shaped steel scraper, carefully examines each sheet, and removes such patches of scale as may yet adhere in spots upon the pickled sheet. From his hands they pass into a second shallow tank filled with clean water (which should properly be renewed from time to time), and in which they are allowed to remain for 12 or 24 hours. The purpose of this washing is to remove all traces of sulphuric acid and basic sulphate of iron from the pickled sheets, the retention of which would otherwise act injuriously upon the character and the durability of the zinc coating. In order that the work may go on continuously, several of such water tanks must be provided, so that a lot of iron shall always be ready for the next operation. This is termed "clearing," and consists in immersing the sheets from the water tanks, for a few minutes, in commercial muriatic acid contained in a flat wooden tank like the water tanks above described. This treatment removes every trace of oxide from the sensitive iron skin, forms a thin layer of chloride upon it, and renders

the iron insensible to oxidizing influences during its subsequent manipulation. From the clearing tank, the sheets are arranged on edge in a rack, to keep them from touching each other (which rack is commonly mounted on a truck), and rolled, twenty-five or more at a time, into a drying chamber. In about twenty minutes or half an hour they are removed, and are then ready for dipping. The galvanizing pot for sheet-iron work is a rectangular vessel of heavy boiler plate, riveted in the most substantial manner, about four feet deep and twelve feet long and fifteen inches to two feet wide, and capable of containing from twenty to thirty tons of zinc. Its bottom rests upon solid masonry, the brickwork being carried up about it on all sides, providing a fire space all about the sides of the pot, by which the metal is kept in a molten state, and its temperature regulated to a nicety with the aid of draft spaces opened or closed by removing or inserting bricks provided for the purpose. The temperature of the zinc bath is a matter of vital importance to the quality of the work, and of great economical importance, and it is here that the skill and experience of the workman tell strongly. For sheet-iron work the heat of the bath is kept at about 1000° Fahr.

The zinc being of the right heat, a thin centre-plate of iron is put in position, its edge dipping slightly beneath the surface of the zinc, and dividing the bath longitudinally into two parts. The object of this contrivance is to insure that the sheets when dipped and passed to the other side of the bath, shall be completely immersed in the melted metal. This object is also accomplished by drawing the sheets through the bath by means of a pair of rollers submerged in the molten metal. They are passed, one by one, into the metal, guided beneath the centre-plate, and as they emerge on the other side, seized



at one end by an iron gripper and drawn through a layer of sand strewn on the surface of the metal, the object of which is to remove all the superfluous metal. The operations of dipping and drawing proceed at about the rate of one sheet per minute. In the setting of the zinc coating, which takes place almost instantly after the withdrawal of the sheet from the bath, the beautiful crystallization of the metal ensues, which is so much admired. This appearance is known to the trade as spangling, and much attention is given to the preliminary preparation of the iron, just described, upon the proper performance of which the size and beauty of the spangles are largely dependent.

From time to time, as the sheets are dipped, a handful of sal-ammoniac is strewn upon the surface of the metal bath for the purpose of clearing it of oxide, and insuring a perfect contact of the clean metals with each other. Sometimes the centre-plate and sand are dispensed with, and the sheets are "dipped bright."

From the bath the sheets pass to the rolls to be straightened; next they are bundled, then weighed and stamped, and are now ready for shipment or use. According to the size of the sheets, the task of a "gang" in charge of a pot such as here described will vary from 400 to 600 per day of ten hours.

With cast-iron and general jobbing work, the process is substantially the same. Owing to its greater impurity, however, objects of cast iron require a much longer period of immersion in the metal than sheet, which, as we have learned, takes the coating instantly. Some time, too, is required with large and heavy castings before they become heated to the temperature of the zinc bath, which is necessary before the amalgamation will ensue. Castings require on these accounts an immersion of from fifteen to thirty



minutes. Where small castings can be "tumbled," and thus deprived of much of their adhering scale and sand, it is frequently unnecessary to pickle them in the manner here described. In such cases, they are simply cleaned by a few minutes' immersion in muriatic acid, and dipped. On the other hand, common rough and unfaced castings require much time and attention to scale and prepare them for the zinc bath. Where the articles are small enough, a lot of them is placed in a perforated iron ladle with a long handle, and dipped, with occasional shaking, until they have taken a proper coating. They are then removed from the ladle singly with tongs, the surplus metal being knocked off as they are taken out. Hoop-iron and wire are passed through the zinc from a reel at a uniform speed. Wire-cloth is beaten as it comes out to remove the superfluous metal that would otherwise clog up the meshes.

A matter which seriously troubles the galvanizer, and which entails considerable pecuniary loss to him, is the formation of what is technically known as *dross*. This is an alloy of zinc and iron, which is formed in the zinc bath, partly by the solvent action of the zinc on the iron of the pot, but chiefly from the iron articles dipped, and from the dripping off of the superfluous amalgam as they come from the bath. This alloy carries from 90 to 95 per cent. of zinc and from 5 to 10 per cent. of iron and other impurities. It has a higher point of fusion, and a higher specific gravity than zinc; hence, as it is formed, it gradually forms a mushy, more or less granular, accumulation in the bath. While the work is going on, the agitation of the metal stirs up the accumulated dross, and keeps it floating through the liquid zinc, and as it greatly interferes with the smoothness of the work, it must be removed from time to time. This operation, called "drossing," is per-

formed with a large perforated iron spoon or ladle, through the openings of which the fluid zinc runs off, while the dross is retained, packed into shallow moulds so as to form slabs of about seventy-five pounds weight, and in this form is usually sold to the smelters and refiners, who gain the zinc it contains either by distillation or by special patented procedures. The formation of this "dross" is a serious item of loss, amounting in some establishments to as much as 30 per cent. of the whole amount of zinc used, though on the average it will not exceed 25 per cent.

The simplest method for treating this alloy, by which much of the zinc it carries may be gained, consists in melting it in a separate iron pot, usually a capacious iron pot of circular form, and allowing it to cool slowly and without disturbance. The upper layers of the metal, which may be skimmed off, will be found to consist of nearly pure zinc. In this way a large quantity of metal may be regained from the dross and used again. The bottoms, rich in iron, may be disposed of to the refiners. Bloxam, (*Metals, etc.*, 167) describes a similar process in which the dross is melted in a separate pot, and allowed to cool slowly from the bottom upwards, "where an alloy of  $9\frac{1}{2}$  parts of iron, with  $90\frac{1}{2}$  of zinc, is deposited in crystals, which are removed by a perforated ladle, and the liquid zinc is left much purer. The crystallized alloy is distilled to recover the zinc."

To prevent the adhesion of the dross to the bottom of the pot, as well as to facilitate its removal therefrom, in the manner above described, it is customary to introduce a small quantity of lead into the zinc bath. This metal does not alloy with zinc or iron, and by reason of its greater density, it sinks to the bottom of the pot, forming a liquid cushion on which the dross and other heavy impurities float.

To lend additional whiteness to these galvanized wares,

some operators introduce from time to time a small quantity of tin.

The spent "pickle" (sulphuric acid) is collected in large vats, and disposed of to the manufacturers of sulphate of iron (green vitriol).

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## CHAPTER LXVII.

BRONZING—BRONZING ON MEDALS—ANOTHER FORMULA—  
BRONZING ON ZINC—GREEN OR ANTIQUE BRONZE—BLACK  
BRONZE—BRONZE POWDERS OR BRONZINES.

### *Bronzing.*

THIS operation is intended to give to new metallic objects the appearance of old ones, by imitating, as far as practicable, either by simple coatings mechanically applied, or by chemical means, the characteristic appearance imparted by age and atmospheric influence to metals, or metallic compounds, and especially to copper and its alloys. According to the composition of the metal, and also according to circumstances, this oxidization results in the production of a great variety of colors, tones, and shades, which the operator tries his best to imitate. We shall not give a complete description of the art of bronzing, since there are special treatises on the subject, which may be profitably consulted by those who desire to obtain a great variety of colors and shades; but we shall mention two or three processes which will be easily applied by galvanoplastic operators to the various articles of their manufacture, and especially to medals. The following formulæ are from Roseleur:—

### *Bronzing on Medals. (Roseleur.)*

The most simple is obtained by applying with a brush upon the cleansed object a thin paste made of water with



equal parts of plumbago and hematite (red oxide of iron). The whole is heated, and when the object is entirely cooled, it is brushed in every direction and for a long time with a moderately stiff brush, which is frequently passed over a block of yellow wax, and afterwards upon the mixture of plumbago and hematite. This process, which is very similar to that used at the Paris Mint, gives a very bright and red bronze, suitable for medals.

This bronzing may also be produced by plunging the article into a mixture of equal parts of perchloride and pernitrate of iron, heating until these salts are entirely dry, and finally producing friction with the waxed brush, as above explained.

*Another Formula. (Roseleur.)*

Cleanse the article, and wash it over with hydrosulphate of ammonium (sulphide of ammonium), which is allowed to dry entirely; then brush with the hematite and plumbago mixture, and afterwards with the waxed brush.

If the piece impregnated with hydrosulphate of ammonium be gently heated, a black bronze, called *smoky bronze*, will be obtained, which, being uncovered (lightened) at certain places, produces a good effect. This last bronzing is often used for teakettles, and is greatly improved by burnishing. Originally it was obtained (and from thence it derives its name) by heating copper articles over a lighted bundle of wet straw or hay, and it was necessary to burnish the surface in order to cause the oxide to penetrate the metal.

*Bronzing on Zinc. (Roseleur.)*

The zinc which is to be bronzed must receive a preliminary electro-deposit of brass, and it is then dipped into a weak solution of sulphate of copper, if we desire a red

tinge. When dry, it is wetted with a rag dipped into hydrosulphate of ammonium, or a solution of liver of sulphur (pentasulphide of potassium), or protochloride of copper dissolved in hydrochloric acid. After another drying, the surface is brushed over with a mixture of hematite and plumbago, or carbonate of iron and plumbago, according to the tone desired. The brush may be slightly wetted with essence of turpentine, which aids the adhesion of the powders. The parts in relief are set off (strongly rubbed), in order to uncover the brass, and make it appear as if it had been subjected to much wear. The object may afterwards receive a coating of colorless varnish.

*Green or Antique Bronze. (Roseleur.)*

Dissolve in 100 parts of acetic acid of moderate concentration, or in 200 parts of ordinary strong vinegar, 30 parts of carbonate or hydrochlorate of ammonium, and 10 parts each of common salt, cream of tartar, and acetate of copper, and add a little water. When an intimate mixture has been obtained, smear the copper object with it, and let it dry at the ordinary temperature for twenty-four or forty-eight hours. After that time, the object will be found to be entirely covered with verdigris, which presents various tints. Then brush the whole, and especially the reliefs, with the waxed brush. If necessary, the highest reliefs are set off with hematite, or chrome yellow, or other suitable colors. Light touches with ammonia give a blue shade to the green portions, and carbonate of ammonium deepens the color of the parts on which it is laid.

A variety of bronzing liquors are to be found in the trade bearing the name of acid bronzes or water bronzes. They are applied with a brush.

*Black Bronze. (Rouleur.)*

Oxidized silvering and the deep black with ammonia and blue ashes, which were described in Chapter XII., furnish a fine black bronze much in favor of late years. A *steel bronze* is more easily obtained by moistening the copper articles with a diluted solution of chloride of platinum, and slightly heating. This bronze will sometimes scale off by friction. It is also obtained by plunging the cleansed copper into a weak and warm solution of chloride of antimony (butter of antimony) in hydrochloric acid. But it happens sometimes that the coloration is violet instead of black.

*Bronze Powders or Bronzines.*

There are also found in the trade, bronze powders made of brass in an impalpable state of division, and which present the most varied shades, according to the degree of oxidation in which the brass undergoes when heated in contact with the air.

These bronze powders, or bronzines, are applied upon metals to imitate bronze, and also upon articles of plaster of Paris, and ceramic wares.

The mode of operation is entirely mechanical. After the object has been more or less cleaned, it receives a thin coating of fatty drying varnish, which is allowed to become nearly dry. The bronze powder is then laid upon it with a badger brush or otherwise, and adheres strongly. After drying, the whole is covered with a coat of transparent and colorless varnish. This process evidently fills up the details, and is suited only to large pieces which are imperfectly finished, such as cast-iron dogs for fireplaces, show-cases, common lamps, plaster statues, etc. It will not do for galvanoplastic reproductions, which are intended to respect the smallest details.



PART III.  
CHEMICAL PRODUCTS AND APPARATUS USED IN  
THE ART.

CHAPTER LXVIII.

CHEMICAL SYNONYMY.

As this book is intended especially for artists, operators, and amateurs, the majority of whom are not conversant with the chemical vocabulary, an enumeration of the principal chemicals used in galvanoplastic and electroplating operations may be of service. By consulting this table many beginners will be saved the expense of buying substances which they already possess, and which, in the book or the formula, bear different names.

*Chemical Synonymy.*

CHEMICAL NAMES.	EQUIVALENTS.
Acetate of copper . . . .	Neutral acetate of copper.
Acetate of copper (basic) . .	Verdigris.
Acetate of lead . . . .	Sugar of lead,—salt of Saturn.
Acetate of lead (basic) . .	Extract of Saturn.
Acetic acid . . . . .	Vinegar, when very diluted,—pyroligneous acid, when extracted from wood,—glacial acetic acid, when it congeals at a few degrees above 32° Fah.
Arsenious acid . . . . .	White arsenic,—arsenic, ratsbane.
Nitric acid . . . . .	Spirit of nitre,—azotic acid,—aqua fortis.

CHEMICAL NAMES.	EQUIVALENTS.
Boric acid . . . . .	Boric acid.
Cyanhydric acid . . . . .	Cyanhydric acid.—prussic acid.
Hydrochloric acid . . . . .	Chlorhydric acid.—muriatic acid.— spirit of salt.
Hypoclitric acid . . . . .	Nitrous gas, or vapor.
Nitrohydrochloric acid . . . . .	Aqua regia.—chloro-nitric acid.
Gallie acid . . . . .	
Oxalic acid . . . . .	
Phosphoric acid . . . . .	Glass of phosphorus (when in the solid state).
Hydrofluoric acid . . . . .	Fluohydric acid.—fluoric acid.
Pyrophosphoric acid . . . . .	Paraphosphoric acid.
Stic acid . . . . .	Silica.—quartz.—flint.—silica.—oxide of silicon.
Stannic acid . . . . .	Binoxide of tin.
Stearic acid . . . . .	Stearine.
Hydrosulphuric acid . . . . .	Sulphydric acid.—sulphuretted hydro- gen.
Sulphurous acid . . . . .	Sulphurous gas.—spirit of sulphur.
Sulphuric acid . . . . .	Oil of vitriol.
Tannic acid . . . . .	Tannin.
Tartaric acid . . . . .	Acid of tartar.
Alloy of . . . . .	Spirit of wine.
Alloy of silver . . . . .	Chin alloy.—silver solder.
Alloy of iron . . . . .	French alloy.—Darcet's alloy.
Alloy of copper and iron . . . . .	Iron.—bell metal.
Alloy of tin and iron . . . . .	Brass.
Alloy of tin and lead . . . . .	Plumbers' solder.—soft solder.—tin and lead solder.
Alloy of zinc and iron . . . . .	German's steel.—septant.—marie- loup's steel.
Amalgams . . . . .	Alloys of one or several metals with mercury.
Ammoniac . . . . .	Volatile alkali.—hartshorn.
Antimony . . . . .	Stibium.
Nitrate of silver . . . . .	Lunar caustic.—lap's infernalis.
Nitrate of bismuth . . . . .	
Sulphate of bismuth . . . . .	Five powder.—flowers of bismuth.

CHEMICAL NAMES.	EQUIVALENTS.
Nitrate of suboxide of mercury . . . . .	Proto- or subnitrate of mercury,—mercurous nitrate.
Nitrate of mercury . . . . .	Pernitrate of mercury,—acid nitrate of mercury,—mercuric nitrate,—quickening salt.
Nitrate of copper . . . . .	
Aurate of ammonium . . . . .	Ammoniuret of gold,—fulminating gold.
Biborate of sodium . . . . .	Borax,—borate of soda,—tincal.
Caoutchouc . . . . .	India rubber,—gum elastic.
Carbonate of potassium . . . . .	Subcarbonate of potassa,—potash,—pearlash.
Bicarbonate of potassium . . . . .	Saleratus.
Carbonate of sodium . . . . .	Subcarbonate of soda,—soda ash,—washing soda.
Bicarbonate of sodium . . . . .	Baking powder.
Carbonate of calcium . . . . .	Chalk,—marble,—limestone,—Spanish white,—precipitated chalk,—whiting,—carbonate of lime.
Sesquicarbonate of ammonium . . . . .	Subcarbonate of ammonia,—carbonate of ammonia,—sal volatile.
Carbonate of iron . . . . .	Spathic iron.
Chloride of silver . . . . .	Horn silver,—muriate of silver,—argentic chloride.
Chloride of antimony . . . . .	Butter of antimony,—terchloride of antimony.
Protochloride of tin . . . . .	Tin salt,—muriate of tin,—hydrochlorate of tin.
Subchloride of mercury . . . . .	Calomel,—sweet sublimate,—white precipitate,—mercurous chloride,—etc.
Chloride of mercury . . . . .	Corrosive-sublimate,—bichloride of mercury,—mercuric chloride.
Perchloride of gold . . . . .	Chloride of gold,—terchloride of gold,—muriate of gold,—gold salt,—auric chloride.
Perchloride of platinum . . . . .	Chloride of platinum,—muriate of platinum,—bichloride of platinum,—tetra-chloride of platinum,—platinic chloride.



CHEMICAL NAMES.	EQUIVALENTS.
Chloride of sodium . . .	Common salt,—muriate of soda,— salt,—sea salt,—salt,—etc.
Chloride of zinc . . . .	Butter of zinc,—muriate, or by chlorate of zinc,—Burnett's fluid part).
Cyanide of silver . . . .	Prussiate of silver.
Cyanide of copper . . . .	Prussiate of copper.
Cyanide of potassium . . .	White prussiate of potash.
Ferrocyanide of potassium .	Yellow prussiate of potash.
Cyanide of gold . . . . .	Prussiate of gold.
Cyanide of zinc . . . . .	Prussiate of zinc.
Gelatine . . . . .	Glue,—isinglass.
Benzine . . . . .	Benzole,—gasoline,—petroleum —etc.
Arseniuretted hydrogen . . .	Arsenide of hydrogen.
Phosphuretted hydrogen . . .	Phosphide of hydrogen.
Mercury . . . . .	Quicksilver,—hydrargyrum.
Binoxalate of potassium . . .	Salt of sorrel.
Oxide of copper . . . . .	Black oxide of copper,—copper
Binoxide of tin . . . . .	Stannic acid,—putty powder.
Potassa . . . . .	Caustic potash,—potash lye,—et
Protoxide of lead . . . . .	Litharge,—massicot,—white oxi lead, when hydrated.
Sesquioxide of lead . . . . .	Red lead,—minium,—orange mi
Binoxide of lead . . . . .	Peroxide of lead.
Oxide of sodium . . . . .	Soda,—caustic soda,—soda lye.
Plumbago . . . . .	Black-lead,—graphite.
Double sulphate of aluminium and potassium . . . . .	) Alum,—potash alum.
Double sulphate of aluminium and ammonium . . . . .	
Sulphate of calcium . . . . .	Plaster of Paris,—gypsum,—alab —selenite,—sulphate of lime.
Sulphate of copper . . . . .	Blue copperas,—blue vitriol,— sulphate.
Sulphate of iron . . . . .	Copperas,—green coppèras,— vitriol,—ferrous sulphate.
Sulphate of zinc . . . . .	White copperas,—white vitriol.
Sulphate of sodium . . . . .	Glauber's salt.
Sulphite of sodium . . . . .	Stahl's salt.

CHEMICAL NAMES.	EQUIVALENTS.
Disulphide of ammonium	Hydrosulphate of ammonium,—sulphate of ammonia.
Bisulphide of carbon . . .	Sulphuret of carbon,—spirit or liquor of Lampadius,—carbon di-sulphide.
Pentasulphide of potassium .	Polysulphide of potassium,—liver of sulphur.
Monosulphide of sodium .	Hydrosulphate of soda,—sulphuret of sodium.
Bitartrate of potassium . .	Cream of tartar,—tartar,—argols.

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## CHAPTER LXIX.

### CHEMICAL PRODUCTS ESPECIALLY EMPLOYED IN THE ART.

FROM the preceding list we select a certain number of especially important substances, for detailed description. As for those materials which are found sufficiently pure in the trade, we shall simply point out their principal characteristics, and refer the reader, desirous of more information, to the numerous and excellent works on chemistry.

*Acetate of Copper, neutral* (highly poisonous).

It is found in the market either in the form of dark-green crystals, or of a bright-green powder—*highly poisonous*—soluble in water, which becomes green; very soluble in ammonia, forming a solution of an azure-blue color; forms colorless double salts with cyanide of potassium and sulphite of sodium; powerful acids, like sulphuric acid, combine with the oxide of copper, and the acetic acid set free is recognized by its smell; is used for preparing electro-baths of copper and brass.

*Acetate of Copper, basic* (poisonous).

Verdigris.

Powder of a fine turquoise bluish-green. Imperfectly soluble in water, and difficult to combine with the sulphites and cyanides, unless previously treated with ammonia. It is often used for adulterating the salt above named.

*Acetate of Lead* (poisonous).

Sugar of lead.

This is ordinarily in the shape of crystalline masses; white; light, although having lead for its base; very soluble; savor, at first sweetish, then metallic; gives on calcination fumes of acetic acid and acetone, and the residue is oxide of lead with a certain proportion of metallic lead. Is not precipitated by carbonic acid, unless there is mixed with it some basic acetate. Obtained by dissolving litharge or massicot (protoxide of lead) in an excess of vinegar, or acetic acid. Its solution forms, with caustic potassa or soda, a white precipitate which is soluble in an excess of alkali, and then constitutes the bath for producing the *colored rings* of Nobili.

*Sub-acetate of Lead* (poisonous).

In solid masses, or syrupy. Savor, sweet but more metallic than the preceding. Heavy; white precipitated by carbonic acid; obtained by boiling a solution of acetate with an excess of litharge. Used for the same galvanoplastic processes. Renders turbid distilled water containing carbonic acid.

*Acetic Acid.*

(Vinegar. Pyroligneous acid.)

More or less concentrated and pure, according to mode of manufacture. The most concentrated crystals

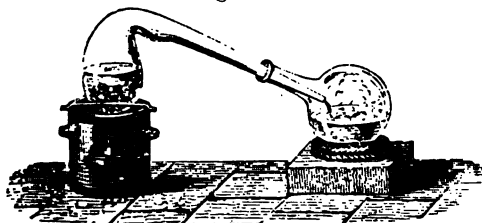


izes at 25° Fah., and often remains solid up to 50° or 54° Fah.

Wood vinegar or pyroligneous acid is employed in large quantities, and is colorless or more or less yellow. It often possesses an empyreumatic odor, and generally marks 8° of the hydrometer.

Wine vinegar is more or less colored, and may be concentrated. Its smell is sufficient to distinguish it.

Fig. 162.



Glacial or crystallized acetic acid is obtained by the distillation of perfectly dry acetate of sodium, or acetate of lead, with concentrated sulphuric acid. The vapors are condensed in a glass receiver (Fig. 162), which should be surrounded by a mixture of salt and ice.

*Arsenious Acid* (poisonous).

(White arsenic. Arsenic. Ratsbane.)

Generally in the shape of a white powder, and sometimes in vitreous-like lumps, resembling porcelain. Slightly soluble in water; savor, scarcely sensible at first, but hot and sharp afterwards, with constriction of the throat. When thrown upon incandescent charcoal it emits abundant white fumes, with a characteristic smell of garlic. Introduced into Marsh's apparatus it furnishes mirror-like arsenical rings and spots. It is employed in certain liver whitening baths, and also in the electro-baths for rashes.

*Nitrous and Hyponitric Acids* (poisonous).

(Nitrous gas. Nitrous vapors.)

We may describe these two acids together. They are gases of an orange-yellow color, more or less deep, and are always produced when nitric acid acts upon a metal.

The smell is nauseating at first, but soon becomes suffocating. They are dangerous to inhale.

They color aqua-fortis yellow, and also impart a greenish tinge to metallic solutions, those of silver for instance, which may appear as though containing copper. This coloration disappears by heating, which it will not do if copper be present. They are produced abundantly in the cleansing of copper and its alloys in aqua fortis at a low temperature, or by moderate pressure they are liquefied.

*Nitric Acid* (poisonous).

(Aqua fortis. Spirit of nitre.)

It is found in the trade of various colors and degrees of strength, but rarely chemically pure.

Liquid, and having a nauseous smell; taste, strongly acid. Destroys the skin and the majority of organic matters, dissolves most of the metals, always with a production of orange vapors; contains one equivalent of water in the monohydrated state, and then is employed for the manufacture of gun-cotton, nitro-glycerine, etc.

The acid of 40° Baumé is colorless or dark yellow; that of 50° Baumé colorless or more or less deep yellow. This coloration is generally due to the presence of nitrous and hyponitric gases and is perfectly satisfactory for cleansing copper, but it often results from the presence of hydrochloric acid, thus forming aqua-regia, or, what is worse from iodine, bromine, or chlorine, when its cleansing properties are impaired.

Pure nitric acid is absolutely necessary for the preparation of nitrate of silver. The presence of chlorine, hydrochloric acid, or sulphuric acid will transform a part of the metal into insoluble, or scarcely soluble compounds.

Pure nitric acid is obtained; 1st. By distilling in a large glass retort (see preceding figure) the commercial article, and commencing to collect the product only when it no longer produces a precipitate or turbidity in a solution of nitrate of silver. The distillate is then collected in a glass receiver, cooled with fresh water or ice. The operation is terminated when about five-sixths have been distilled.

2d. By precipitating with nitrate of silver and nitrate of barium the hydrochloric and sulphuric acids contained in commercial aqua fortis, and then distilling the whole nearly to dryness. The residuum in the retort is composed of sulphate of barium, chloride of silver, and the excess of the nitrates of these two bases.

3d. By distilling in a glass retort a mixture of 100 parts of pure nitrate of potassium (saltpetre), with 60 parts of pure concentrated sulphuric acid (oil of vitriol), and 40 parts of distilled water. The heat is gradually raised, and stopped when, after having disappeared, the yellow vapors reappear. The acid thus obtained is slightly yellow and may be bleached, by heating it almost to the boiling point. It is useless to remind the reader of the continual use of nitric acid in our art.

#### *Boracic Acid* (boric acid).

United with sodium it constitutes borax. It is found in the condensed steam of certain small, mud volcanoes of Tuscany, from which it is extracted. Boracic acid is found in the arts in the shape of scales,



with nacreous lustre, and greasy to the touch. When in vitreous masses, more or less translucent, it is anhydrous, and has been subjected to igneous fusion. Dissolved in alcohol, and ignited, it colors the flame a fine green. It is also obtained in the form of scales by decomposing, with a powerful acid, a concentrated and boiling solution of borax; the boracic acid crystallizes on cooling. It is used for making platinum adhere, by the heat of a muffle, to ceramic wares, thus causing the metallization of surfaces which are not naturally conductors of electricity. It is also employed for increasing the whiteness of silver alloys, and for the decomposition of the subsalts deposited in electro-baths containing cyanide of potassium.

*Hydrocyanic Acid* (extremely poisonous).

(Cyanhydric, or prussic acid.)

It exists in nature only in a state of combination in certain vegetables and fruits, and especially in the kernels of the last named; as, for instance, in the peach, the berries of the cherry laurel, bitter almonds, the stones of the apricot, of plums, cherries, etc.

It may be obtained anhydrous; but in this state it is useless, and very difficult to preserve from decomposition.

Diluted hydrocyanic acid is colorless with a bitter taste, and the characteristic smell of bitter almonds.

It is prepared by introducing into a large retort attached to a receiver, which is cooled by ice (Fig. 163), 2 pounds of ferro-cyanide of potassium (yellow prussiate of potassa), 1 quart of water, and 3 pounds of concentrated sulphuric acid. The acid and water should be mixed beforehand and allowed to cool. The distillation is effected in a sand-bath, and the condensed liquid is clear and colorless. The operation is stopped when the substances in the retort be-

gin to swell up. Great caution must be exercised to avoid inhaling the vapor produced during this preparation.

Fig. 163.



Hydrocyanic acid may also be obtained by passing a stream of washed sulphuretted hydrogen through a tall glass vessel (Fig. 164), containing water and cyanide of

Fig. 164.



mercury. The latter compound is transformed into the insoluble sulphide of mercury, while the hydrocyanic acid remains in solution. After filtering, the liquid is gently heated in order to expel the remaining sulphuretted hydrogen, which is more volatile than hydrocyanic acid. This method is not so simple as the preceding one, and



for gilding is open to the inconvenience of often having the acid contaminated with undecomposed cyanide of mercury or sulphuretted hydrogen.

Hydrocyanic acid is employed for maintaining the strength of the pyrophosphate of gold in immersion baths, and for decomposing the alkaline carbonates formed in baths with cyanide of potassium.

*Hydrochloric Acid* (poisonous).

(Chlorhydric or muriatic acid. Spirit of salt.)

This acid is gaseous, and emits abundant and dense fumes in contact with the air. Water, at the temperature of 68° Fah., dissolves 460 times its own volume of this acid, that is, 1 quart of water will dissolve 460 quarts of this gas, and the primitive volume of the water will be increased about one-third.

It is this solution of the acid in water that is always employed in the arts, it is generally contaminated with sulphurous and sulphuric acids, and by perchloride of iron, which imparts to it a yellow color.

A concentrated solution of hydrochloric acid in contact with moist air emits dense fumes, which are the more apparent in the presence of ammoniacal vapors. Its smell is penetrating, and its taste strongly acid. It dissolves zinc with a copious evolution of hydrogen; and, with a silver solution, it produces an abundant, white, heavy, and curdy precipitate of chloride of silver, which becomes blue, and then black, by the action of solar light. This precipitate is insoluble in strong acids, either cold or boiling, but is soluble without coloration in cyanides, sulphites, hyposulphites, alkaline or earthy chlorides, and especially in ammonia.

Pure hydrochloric acid (in concentrated solution) is colorless, fuming, and presents the same reactions. A

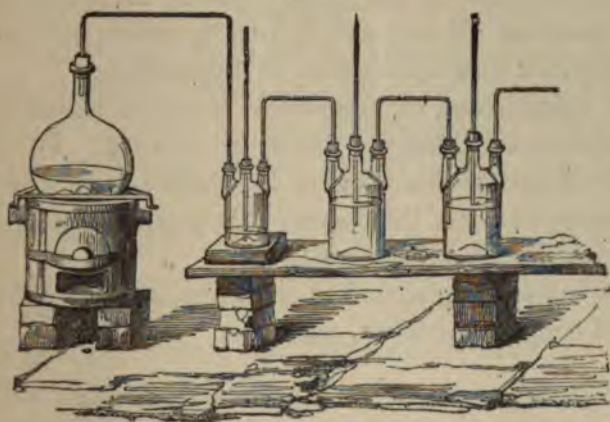


trace of organic substance is sufficient to impart to it a greenish or yellowish tinge, as if it were colored by an iron salt.

The electro-plater employs it for preparing the chlorides of certain metals, such as silver, zinc, etc.; it enters into the composition of aqua-regia; and the common salt, added to certain cleansing acids, depends for its utility on the formation of a small quantity of hydrochloric acid.

It is prepared by introducing into a glass flask (Fig. 165) common salt and an excess of commercial sulphuric

Fig. 165.



acid. A gentle heat is gradually applied, and the gas is collected and absorbed in distilled water contained in a series of tubulated flasks. These receivers should be kept constantly cooled by a stream of water, or by ice, as otherwise the elevation of temperature, caused by the combination of the water and acid, would prevent the liquid from becoming thoroughly saturated. The first bottle contains but little water, and is intended to arrest the impurities mechanically carried by the gas. The generating vessel after the operation contains acid sulphate of sodium.

*Aqua-Regia* (poisonous).

(Nitro-muriatic acid.)

When nitric and hydrochloric acids are mixed, there are formed, besides water, free chlorine and hyponitric acid. When heated this liquid disengages yellowish fumes. This mixture is called *aqua-regia* because it dissolves gold, which was formerly named the king of metals.

Chlorine alone will also dissolve gold, and as the resulting salt is the same as that obtained by its treatment with *aqua-regia*, we should infer that the dissolving action of *aqua-regia* is due to the chlorine it contains, and which it liberates in the nascent state. Moreover, *aqua-regia* dissolves all the metals, and produces salts which are chlorides, and not nitrites or hyponitrates.

The composition of *aqua-regia* is varied, according to the substances which we desire to dissolve. For gold, we mix 1 part of nitric acid of 40° Baumé, with 2 parts of hydrochloric acid of 22° Baumé; for platinum, 3 of nitric acid to 5 of hydrochloric acid.

*Aqua-regia* is employed in the preparation of the chlorides of copper, platinum, gold, etc.

*Hydrofluoric Acid* (very poisonous).

(Fluoric acid.)

This acid is gaseous when freed from its combinations, but condenses, by cooling, into a colorless liquid possessing a penetrating smell and strongly acid taste. It attacks glass and silicates, and combines with their silica to form a new acid called hydrofluosilicic or fluosilicic acid.

Hydrofluoric acid is prepared by decomposing in a retort of

Fig. 166.





lead or platinum (Fig. 166), a paste of fluoride of calcium (fluor-spar) with sulphuric acid. The various joints of the retort are carefully luted with clay or plaster of Paris, and the receiver is made of a bent tube of one of these metals, immersed in a mixture of 3 parts of broken ice and 2 of common salt, or, more simply, into ice alone. The end of the receiver is perforated with a very small hole only, in order to aid the condensation by a moderate pressure. A gentle heat is applied at the bottom of the retort.

This acid is kept in lead bottles which are but slightly acted upon, or in flasks of platinum or gutta-percha, upon which it has no action whatever.

We must carefully avoid any contact with the vapors of hydrofluoric acid, otherwise, after a few hours, even the less sensitive parts of the skin will be covered with painful blisters. The same caution applies also to inhaling its vapors.

This acid is employed for depolishing glass, and other vitreous substances, and thus to prepare a ground more easily metallized. The parts which should not be corroded are protected by a coat of wax.

When a level surface is to be operated upon, a pane of glass for instance, the easiest process consists in covering it entirely with wax, and drawing the pattern with a pointed tool, which should penetrate to the glass. The object is then placed upon a shallow dish of lead containing the mixture for the production of the acid. At ordinary temperatures, or more rapidly with the aid of feeble heat, the vapors of the acid attack the glass where it has been uncovered. On the other hand, if large surfaces are to be depolished, the acid vapors are produced in a leaden box of suitable size, and perfectly luted. The objects may also be laid in a trough of lead or gutta percha filled



with a more or less diluted solution of hydrofluoric acid. This last process is employed for the production of patterns, hollow or in relief, upon "flashed" glass, that is, glass having a surface coat of differently colored glass. Glass pearls or beads, treated in the same manner, acquire a beautiful dead lustre.

### *Stearic Acid.*

(Stearine.)

We may consider all fatty substances of animal origin, and tallow particularly, as composed of a base called *glycerine*, which is united with *oleic*, *margaric*, and *stearic* acids. The last one is the most important for us, since we take moulds with it, and render impervious certain substances which otherwise would be penetrated and injured by the sulphate of copper of the galvanoplastic baths.

This acid is white, nearly without taste and smell, and more or less greasy to the touch according as it is more or less completely deprived of margaric and oleic acids. Its fracture is rarely crystalline, but often granular. It melts at a temperature from 158° to 167° Fah. to a clear liquid, which again solidifies by cooling. It is this property which renders stearic acid valuable for taking casts. If it be too greasy it sticks to the pattern, and especially to plaster of Paris coated with plumbago; in this case, it should be mixed with a certain proportion of wax or spermaceti. When too dry, on the other hand, it contracts considerably in cooling, often breaks, and the galvanoplastic deposits have a crystalline surface. This defect is corrected by the addition of tallow or olive oil.

Heated to 535° to 575° Fah., stearic acid is partly charred, becomes brown, and gives off certain volatile pro-

ducts; it is then too dry, and much less valuable for our purposes.

The manufacturers of stearine candles extract this acid from tallow.

*Sulphuretted-Hydrogen. Sulphydric Acid* (poisonous).  
(Hydrosulphuric Acid.)

This acid is gaseous, but may be dissolved in water, which absorbs two or three times its own volume of it at the ordinary temperature, and which then acquires the same properties as the gas itself.

Sulphuretted-hydrogen is colorless; its smell is fetid, and resembles that of rotten eggs. It is slightly acid, and reddens blue litmus paper, but the primitive color reappears on heating. It precipitates many of the metals from their solutions as sulphides, of various colors—white, black, yellow, etc. Some of these sulphides appear to be good conductors of electricity.

Sulphuretted-hydrogen, which is exceedingly poisonous, may be obtained by the reaction of hydrochloric acid, or diluted sulphuric acid, upon many sulphides, such as those of antimony, iron, barium, strontium, etc. The gas is collected under receivers filled with mercury, or is dissolved in water with the aid of a Woulf's apparatus, such as that described in the manufacture of hydrochloric acid. The distilled water employed should be deprived of air by ebullition, otherwise the solution will be milky from the partial decomposition of the acid, the hydrogen of which unites with the absorbed oxygen, while the sulphur is separated.

We should carefully avoid bringing in contact with this gas, not only metallic salts, and gilt or silvered articles, but likewise pure gold and silver, which are rapidly

sulphurized by it. Sulphuretted-hydrogen is sometimes employed for the production of "oxidized" silver.

### *Sulphurous Acid.*

Is gaseous, colorless, and possesses an acid taste. Its odor is penetrating and suffocating, and is that produced by burning sulphur in the open air. One volume of water, at ordinary temperatures, dissolves about thirty-three volumes of the gas, and acquires its characteristic properties.

Sulphurous acid decolorizes and bleaches many organic substances. It reduces many metallic salts by appropriating their oxygen; it may therefore be employed, possibly, more advantageously than sulphuretted-hydrogen, for metallization by means of nitrate of silver or chloride of gold. It is employed in the preparation of the sulphites and bisulphites, which we shall study further on.

It is obtained by burning sulphur in the air, from which it takes the two equivalents of oxygen necessary for its composition; or by decomposing, in a closed vessel

Fig. 167.



(Fig. 167), concentrated sulphuric acid, by means of some substance possessing a great affinity for oxygen. Sulphur, charcoal, dry sawdust, copper, mercury, etc., may be used for the purpose, although copper is generally preferred.



This metal, finely divided (chips, filings, or turnings), is rapidly corroded, produces a pure gas, and leaves a residuum of sulphate of copper useful for galvanoplastic operators.

*Sulphuric Acid* (poisonous).

(Oil of vitriol.)

This compound, the most powerful and useful acid in the arts, may exist in the solid or anhydrous state. It is always used in a more or less hydrated form. Its name of oil of vitriol comes from its oily consistency, and from the green vitriol (sulphate of iron) from which it was formerly obtained by distillation in closed vessels. It is now produced in large quantities, by oxidizing in lead chambers moist sulphurous acid by the vapors of nitric acid.

Commercial sulphuric acid generally marks 66° of the hydrometer of Baumé. It is colorless, dense, flowing like oil, with feeble odor, and strong acid taste. It decomposes nearly all salts, and extracts water from most substances which contain its elements. It attacks and blackens organic substances, becoming itself more or less dark in color thereby. The particles of dust flying in the air and falling into it are sufficient to produce this phenomenon.

Poured into a concentrated solution of hydrochloric acid, sulphuric acid absorbs the water with production of heat, and the acid first named is driven off with effervescence. It displaces all the other acids from their combinations, and forms very stable compounds with metallic oxides.

We employ it in our art at nearly every stage: for cleansing, for dipping, in the preparation of many products, in batteries, etc.

*Tannic Acid.*

(Tannin.)

This substance, which should not be confounded with gallic acid, although it produces this last by fermentation and other chemical reactions, appears to be already formed in gall-nuts, which are supposed to be the result of the puncture of certain insects upon oak leaves. Tannic acid exists also in many vegetables, and especially in the bark of certain trees, such as the oak, hemlock, chestnut, elm, etc.

This acid is generally prepared by digesting powdered gall-nuts, at a temperature of about 85° Fah., in commercial ether, in a closed vessel. After about eight days, the settled liquid, which is quite syrupy, is decanted and spread upon many dishes, which are put into a stove. The ether is evaporated, and the nearly pure tannic acid remains in the form of uncrystallized scales, which are light, thin, yellowish, and with nacreous lustre. It is purified by solution in boiling water, which, on cooling, allows it to deposit in the shape of needle-like crystals.

Tannic acid possesses the singular property of coagulating, and rendering insoluble, certain gums, gluten, and gelatine especially, the latter being transformed into leather, which will not putrefy.

It will be remembered that in the article on *moulding with gelatine*, we indicated the employment of a small proportion of this acid for preventing the softening and solvent action of the baths. Gallic acid cannot take the place of tannic acid for this purpose.

*Alloys.*

These are combinations, or mixtures, effected by the fusion of two or more different metals in definite propor-

tions. The hydroplastic operator employs them so constantly that it is important that he be acquainted with the composition of the most usual alloys, and that he learn the preparation of several of them, which, like the fusible alloys of Darcet, will often be serviceable.

*Fusible Alloys of Darcet.*

*No. 1.*

Bismuth	.	.	.	.	.	.	.	8 parts.
Lead	.	.	.	.	.	.	.	4 "
Tin	.	.	.	.	.	.	.	4 "
								16

*No. 2.*

Bismuth	.	.	.	.	.	.	.	8 parts.
Lead	.	.	.	.	.	.	.	5 "
Tin	.	.	.	.	.	.	.	3 "
								16

*No. 3.*

Bismuth	.	.	.	.	.	.	.	5 parts.
Tin	.	.	.	.	.	.	.	3 "
Lead	.	.	.	.	.	.	.	2 "
								10

All the metals are melted together in a crucible, stirred with an iron rod, and cast. Various proportions of mercury are added to these alloys, when great fusibility is desired.

*Alloys of Copper.*

BRASS FOR ARTICLES WORKED WITH THE HAMMER.

Copper	.	.	.	.	.	.	.	70 parts.
Zinc	.	.	.	.	.	.	.	30 "
								100



**BRASS FOR TURNING.**

Copper . . . . .	66 parts.
Zinc . . . . .	32 "
Lead . . . . .	2 "
	<hr/>
	100

**SIMILOR.**

Copper . . . . .	100 parts.
Zinc . . . . .	12 "
	<hr/>
	112

**ANOTHER FORMULA.**

Copper . . . . .	100 parts.
Zinc . . . . .	8 "
	<hr/>
	108

**STATUARY BRASS.**

Copper . . . . .	91.4 parts.
Zinc . . . . .	5.5 "
Lead . . . . .	1.7 "
Tin . . . . .	1.4 "
	<hr/>
	100.0

**PINCHBECK.**

Copper . . . . .	5 parts.
Zinc . . . . .	1 part.
	<hr/>
	6

**BRONZE FOR BELLS.**

Copper . . . . .	75 parts.
Tin . . . . .	25 "
	<hr/>
	100

**BELLS FOR CLOCKS.**

Copper . . . . .	75 parts.
Tin . . . . .	25 "
	<hr/>
	100

**BRONZE FOR LARGE ORDNANCE.**

Copper . . . . .	90 parts.
Tin . . . . .	10 "
	<hr/>
	100

BRONZE FOR SMALL ORDNANCE.

Copper	. . . . .	98 parts.
Tin	. . . . .	7 "
		<hr/>
		100

BRONZE FOR MEDALS.

Copper	. . . . .	100 parts.
Tin	. . . . .	8 "
		<hr/>
		108

BRONZE FOR CYMBALS.

Copper	. . . . .	80 parts.
Tin	. . . . .	20 "
		<hr/>
		100

BRONZE FOR GONGS.

Copper	. . . . .	100 parts.
Tin	. . . . .	25 "
		<hr/>
		125

TELESCOPIC MIRRORS (REFLECTORS).

Copper	. . . . .	100 parts.
Tin	. . . . .	50 "
Arsenic	. . . . .	1 part.
		<hr/>
		151

GERMAN-SILVER.

Copper	. . . . .	50 parts.
Zinc	. . . . .	3.5 "
Nickel	. . . . .	4 "
		<hr/>
		57.5

No. 2.

Copper	. . . . .	53 parts.
Zinc	. . . . .	31.25 "
Nickel	. . . . .	15.75 "
		<hr/>
		100.00

No. 3.

Copper	. . . . .	8 parts.
Nickel	. . . . .	3 "
Zinc	. . . . .	3.5 "
		<hr/>
		14.5

*No. 4.*

Copper . . . . .	4 parts.
Nickel . . . . .	1 part.
Zinc . . . . .	1 "
	6

*No. 5.*

Copper . . . . .	55 parts.
Zinc . . . . .	17 "
Nickel . . . . .	23 "
Iron . . . . .	3 "
Tin . . . . .	2 "
	100

**ELASTIC ARGENTAN.**

Copper . . . . .	57.4 parts.
Zinc . . . . .	25 "
Nickel . . . . .	18 "
Iron . . . . .	9 "
	109.4

**POZIN.**

Copper . . . . .	11.9 parts.
Zinc . . . . .	54.6 "
Lead . . . . .	2 parts.
Tin . . . . .	1.5 parts.
	70.0

**YELLOW COPPER.**

Copper . . . . .	10 parts.
Zinc . . . . .	10 "
Nickel . . . . .	10 "
	30

**RED COPPER.**

Copper . . . . .	10 parts.
Zinc . . . . .	10 "
Nickel . . . . .	10 "
	30

**GREEN COPPER.**

Copper . . . . .	10 parts.
Zinc . . . . .	10 "
Nickel . . . . .	10 "
	30



It is evident that it will be possible to vary *ad infinitum* the mixtures and the proportions of the component metals, and thus to arrive at an unlimited number of alloys, which on account of slight differences of color, ductility, sonorousness, etc., have received a great variety of names.\*

### *Amalgams*

Are alloys of one or several metals with mercury, but the latter must absolutely be one of the component parts.

Only two amalgams are of importance in our art: that of Darcet, already described; and that of gold, which is the basis of fire-gilding.

Whatever be the proportions of gold and mercury put together, an amalgam is always formed; but there are certain proportions which are more or less favorable for obtaining a certain result. Thus, the gold amalgam for gilding by stirring should be more fluid, and therefore contain more mercury, than that prepared for dead gilding by fire, or for ormolu. The latter should be of the consistency of cold butter, a little rough to the touch, and with a crystalline texture, which causes the production of a crackling noise when the amalgam is pressed between the fingers. That for gilding by stirring should be of the consistency of honey and quite soft, since in this condition it easily spreads itself over the surface of a multitude of all articles.

An amalgam is generally prepared by heating distilled mercury to a temperature of about 400° Fah., and adding to it gold in the shape of a leaf or ribbon, which becomes readily incorporated with it. The whole is then thrown into cold water. If the proportion of mercury has been

\* For a full description of alloys and amalgams, see "*A Practical Guide for the Manufacture of Metallic Alloys*," from the French of Guettier, by A. A. Fesquet. Philadelphia: H. C. Baird, 1872.

too great, the amalgam may be heated over the fire, until by the volatilization of part of the mercury, the proper consistency is reached. On the other hand, should the amalgam be too hard, it may be softened by the addition of mercury, which soon mingles with the mass.

When such an amalgam is heated to a dull red heat, all of the mercury is volatilized, and the gold remains in the form of a spongy and crumbling mass. Gold, in the presence of mercury salts, does not form amalgams like copper; it is absolutely necessary that the two metals should be in the metallic state in order that they shall amalgamate.

Mercury is often adulterated by the addition of bismuth, lead, or tin; and it is evident that these various metals, which do not volatilize, remain with the gold and deteriorate it.

#### *Ammonia.*

(Spirit of hartshorn. Volatile alkali, etc.)

This compound, which generally bears the name of ammoniacal gas when in the gaseous form, and of ammonia when in solution, presents properties similar to those of potassa, soda, and other alkalies which are metallic oxides. On account of this analogy, therefore, it is customary to consider it as the oxide of a hypothetical metal, *ammonium*, a compound radical composed of nitrogen and hydrogen. This hypothesis, whether correct or not, has the advantage of convenience.

Gaseous ammonia dissolves in water eagerly, one volume absorbing, when cold, about 500 volumes of the gas. Notwithstanding this remarkable solubility, ammoniacal gas does not produce visible fumes even in contact with very moist air, as is the case with hydrochloric acid and other substances.

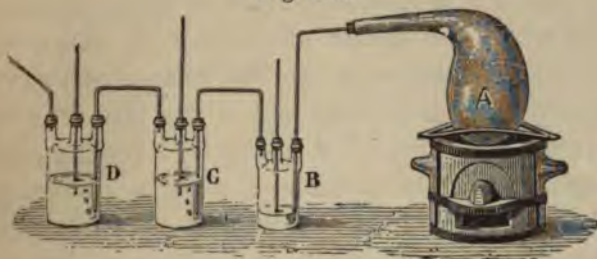


Aqua ammonia is a colorless liquid, possessing a characteristic and overpowering pungent smell.

Ammonia restores the blue color of litmus reddened by an acid, and saturates the affinities of the most powerful acids; and, on this account, is often employed for removing acid stains upon clothes. We should except, however, the stains produced by nitric acid, which become more visible instead of disappearing. All ammoniacal salts, except the carbonates, are odorless.

Ammonia is obtained, even in the cold, by treating any ammoniacal salt with a fixed alkali. Sulphate or chloride of ammonium is generally employed for this purpose, and is generally heated in a suitable retort with slaked lime. The gas produced is collected by displacement of mercury under bell glasses, or in tubes of glass, where it is wanted in the gaseous state; or is dissolved in the water contained in the flasks of a Woulf's apparatus (Fig. 168),

Fig. 168.



if we desire its solution. After the operation, there remains in the retort the sulphate or chloride of calcium according to the nature of the ammoniacal salt employed.

By far the greater proportion of the commercial aqua ammonia is, at the present time, obtained from the ammoniacal liquors of coal-gas works.

Ammonia is employed for aiding the solution of the copper salts entering into the composition of the baths



for electro-deposits of copper or brass, for ageing freshly made silver-baths, for precipitating fulminating gold from the chloride of gold, and for dissolving the film of copper deposited at the beginning of galvanoplastic operations with silver, etc.

### *Silver.*

We use silver in different forms, in plates, foil, powder, or granulated, according to the purpose for which it is intended.

We should, as far as practicable, employ it pure; but the silver found in the trade, even under the name of *virgin silver*, retains traces of copper. Coin silver contains one-tenth of copper, and stamped silverware a greater or less proportion according to the standard.

Silver is purified by several methods:—

1. The impure metal is dissolved in nitric acid, and the solution after being largely diluted with water, is treated with an excess of a filtered solution of common salt. An abundant white precipitate of chloride of silver is produced, which rapidly settles to the bottom of the vessel. All the silver salt is decomposed, when the clear supernatant liquid is not rendered turbid by a further addition of common salt. The chloride of silver is collected, and washed several times, until the wash liquors are no longer colored brown by ferro-cyanide of potassium. This is the proof that all the copper has been washed out. The washed chloride of silver is mixed with two or three times its weight of carbonate of sodium, dried, and the mixture fused in a crucible at a high temperature. After cooling, the metal is found in the shape of a button at the bottom of the crucible. To granulate it, the molten silver is poured in a thin stream from a moderate height into a large volume of water.

2. The chloride of silver is prepared as in the first method; then, after having washed out the copper salt, a considerable volume of water is added, then an excess of scraps of sheet zinc and some sulphuric or hydrochloric acid. Hydrogen gas is immediately produced in abundance, and, combining with the chlorine of the chloride of silver, reduces the metal to the form of a fine powder, which is separated when all the zinc is dissolved. As it very rarely happens that commercial zinc is free from lead or carbon, this method is seldom employed. The substitution of iron for zinc presents no advantages.

Silver is easily dissolved in pure nitric acid, but not so rapidly when the acid is contaminated by chlorine or hydrochloric acid, which forms an envelope of chloride of silver around the metal, thus hindering its solution.

Sulphuric acid also combines with silver, and the resulting salt is only slightly soluble in water. As for hydrochloric acid, the trace of silver which may be dissolved is immediately transformed into chloride, preventing the further action of the acid.

Cyanide of potassium dissolves metallic silver slowly, and forms a double salt with it. On the other hand, the sulphites dissolve only the salts of silver and have a tendency to reduce them to the metallic state.

Pure silver is employed for the preparation of the nitrate and other silver salts, and as the soluble anode in silver-baths. In the form of impalpable powder, and mixed with cream of tartar, it is used for silvering with the brush, and for the paste with which watch-works are grained before being gilded. In this case, the silver powder is prepared by reducing a very diluted solution of the nitrate of this metal by the means of strips of copper. This powder should be washed several times with ammo-



nia, which will remove all the copper which may adhere to it.

*Nitrate of Silver* (poisonous).

(Argentio nitrate. Lunar caustic. Lapis infernalis.)

This salt is found in the trade in three forms: either as crystallized nitrate of silver in thin, rhombic, and transparent plates; or in amorphous, opaque, and white plates of fused nitrate; or in small cylinders, of white, or gray, or black color, according to the nature of the mould employed, in which form it constitutes the lunar caustic for surgical uses.

The crystallized nitrate of silver still retains a small proportion of nitric acid and water between the laminae of its crystals; the white fused salt should be pure, though it is often fraudulently adulterated with nitrate of potassium or sodium. The third variety, or lunar caustic, generally has its surface coated with a film of reduced silver and of oxide of copper from the moulds into which it is run; or its color may simply be due to the inferior quality of the silver employed.

Nitrate of silver is very soluble in distilled water,\* but with ordinary water gives a precipitate which is the more or less copious according to the quantity of chlorides the water may contain. This precipitate at first is white, but soon darkens by the action of solar light, but this transformation does not take place when it contains even traces of chloride of mercury.

The solution of nitrate of silver forms yellow precipitates with the iodides, phosphates, and bromides; and white

\* However, when the nitrate of silver has been kept too long in igneous fusion, it is less soluble in distilled water, and the white turbidity of the liquid is probably due to the formation of a subnitrate of silver.



s with the soluble chlorides, sulphites, cyanides, ites, and pyrophosphates. With the exception phosphates and pyrophosphates, the other reagents, employed in greater or less excess, will redissolve tate with the formation of double salts.

precisely this property of the cyanides, sulphites, sulphites, which is the basis of the preparation tths by simple immersion, or with the battery. dissolves even the most insoluble silver salts iodides; but as this solution attacks copper, remarks that it cannot be used as a silvering ithstanding the advice of Boettger.

of silver is prepared by dissolving pure silver, or laminated, in double its weight of pure ni- 40° Baumé. This operation is conducted in sk, or in a porcelain capsule. Nitrous vapors sly disengaged, and the metal soon disappears olorless liquid (blue or green if copper be pres- er cooling, and a rest of a few hours, a mass of nitrate of silver is found, which is drained, and the excess of acid, washed with a little distilled ated with nitrate of silver. The crystals are stove, and kept away from solar light. If, in- oling the liquid after the silver has been dis- evaporation be continued, the mass will become d then fuse by a greater heat to a grayish liquid, e be run into moulds and forms the so-called tic. The mass obtained by the fusion of the nitrate of silver is whiter, and is known as r caustic. It may be either run into moulds or solidify by cooling on the sides of the capsule. ; whatever be its mode of preparation, should black or blue bottles, and free from contact ic substances, which would reduce the metal.

It is employed for preparing silvering baths, metallizing moulds, and for many other purposes.

*Nitrate of Mercury* (poisonous).

(Mercuric nitrate. Acid nitrate of mercury. "Quicking" solution.)

This salt is generally sold in the form of an oily, colorless liquid, which is the denser as it contains more free acid. It stains the skin a violet-red, and in contact with water produces a pulverulent and yellowish-white precipitate, of a subnitrate. This precipitate disappears upon the addition of a few drops of sulphuric or nitric acid, and the liquid becomes clear. Should the solution of nitrate of mercury be concentrated, sulphuric acid, instead of dissolving the precipitate, increases it, from the formation of insoluble subsulphate of mercury.

This salt is used in our art for slightly amalgamating (coating with quicksilver) the pieces which are to be silvered or gilded. This amalgam forms a kind of solder between the metallic surface operated on, and the deposited metal.

Nitrate of mercury is obtained by dissolving at a temperature of about 212° Fah. a certain quantity of mercury in double its weight of nitric acid of 40° Baumé, and continuing the heat until yellow fumes no longer appear.

If, instead of operating with the aid of heat, the reaction be effected in the cold; or, if the proportion of mercury be in excess of the necessary quantity of nitric acid, we obtain a salt of suboxide which is not so suitable for our purpose.

*Nitrate of Potassium.*

(Potassium nitrate. Saltpetre. Nitre.)

This salt is sometimes produced by the action of carbonate of potassium upon nitrate of calcium; the latter



substance being spontaneously formed on old, damp walls which contain lime, and which are exposed to the emanations from decomposing vegetable or animal matters.

A natural saltpetre with sodium for base (nitrate of sodium) is found in great quantities in Peru and Chili, and constitutes an important article of commerce.

Nitrate of potassium is colorless, odorless, and has a cooling, saline taste; it is very soluble in water, and a concentrated solution deposits, on cooling, fine prismatic crystals, which are more or less translucent. Thrown upon burning coals, it fuses, and increases the combustion by parting with a portion of its oxygen. Concentrated sulphuric acid, poured upon nitrate of potassium, disengages white fumes of nitric acid; on the other hand, these vapors are yellow when a metallic powder, such as copper, iron, zinc, etc., has been mixed with the nitrate of potassium.

Distilled in closed vessels with more or less concentrated sulphuric acid, nitrate of potassium produces nitric acid, or aqua-fortis, of various degrees of concentration.

Before using the crude nitrates of sodium or potassium for the manufacture of aqua-fortis, it is advantageous to purify them by one or two crystallizations, in order to separate the chlorides, iodides, and bromides with which they are impurified and which remain in the mother liquors.

We employ saltpetre for producing a dead lustre upon objects gilded by fire, and in the preparation of desilverizing baths.

#### *Bicarbonate of Potassium.*

Salaxatus. (Hydrogen-potassium carbonate.)

This salt is white and colorless, and crystallizes either in tabular forms, like nitrate of silver, or in cubes, like



common salt or iodide of potassium. It is soluble in tepid water, without decomposition; but at the boiling point, it loses one-fourth of its carbonic acid and becomes a sesquicarbonate. At red heat it is transformed into simple carbonate, that is to say, it loses another fourth of carbonic acid.

Bicarbonate of potassium blues red litmus paper, and possesses little taste. Its cold solution is not precipitated by one of sulphate of magnesium, but an abundant precipitate is formed on applying heat, since, then, part of the carbonic acid is disengaged, and an insoluble sesquicarbonate of magnesium is formed.

This salt, which is employed for the preparation of certain baths for gilding by simple immersion, and for the preparation of cyanide of potassium, is obtained by conducting a stream of carbonic acid gas through a concentrated solution of carbonate of potassium, until the liquid is no longer rendered turbid by the addition of sulphate of magnesium, or nitrate of calcium. It crystallizes after a brief period of rest, being much less soluble than the simple carbonate.

#### *Bicarbonate of Sodium.*

(Hydrogen-sodium carbonate. Baking powder.)

The properties, uses, and preparation of this compound correspond with those of the bicarbonate of potassium.

#### *Binoxalate of Potassium (poisonous).*

(Salt of sorrel.)

Is a white crystalline salt, which occurs already formed in the sap of certain plants, and especially in that of the sorrel (*Rumex acetosella*), from which it is extracted by the simple concentration of the liquid.

This salt is acid and decrepitates in the fire, the oxalic acid which it contains decomposing into carbonic acid and

carbonic oxide, which last is disengaged. It enters into the composition of the silver paste for cold silvering by friction.

*Bitartrate of Potassium.*

(Hydrogen-potassium tartrate. Cream of tartar. Argol.)

This salt occurs nearly pure in wine, from which it becomes separated in the shape of small white or red crystals, according to the color of the liquor. It is collected from the sides of wine casks, and purified by bone black, in which state it is known as cream of tartar. Before this purification, it is crude tartar or argol.

Bitartrate of potassium is acid, slightly soluble in water, and it decrepitates in the fire, where it blackens, disengaging a smell like that of burnt sugar. It is employed for the preparation of the whitening silver baths, for those of tin, and for the silvering paste by friction.

*Biborate of Sodium.*

(Sodium biborate. Borax. Tincal.)

This well-known compound occurs generally in the shape of colorless prismatic crystals. It occurs abundantly in natural deposits in the borax lakes of Nevada and elsewhere.

Borax is soluble in water, has an alkaline reaction, and a bitter saline taste. When heated, it fuses in its water of crystallization, which it loses, after which it swells up considerably. A further increase of heat causes it to fuse again, and it becomes transformed into a kind of transparent and colorless glass, which may be drawn out into long filaments,

Vitreous (fused) borax is a powerful solvent of most metallic oxides, which impart to it various colors. This property of dissolving metallic oxides renders borax very useful for soldering, brazing, or welding different metals.

A powerful acid, poured into a hot and concentrated solution of borax, separates the boracic acid in the form of scales. Borax ground with a little sulphuric acid and alcohol imparts to the flame of the latter a characteristic yellowish-green color.

The biborate of sodium is prepared by saturating with an excess of boracic acid a hot and concentrated solution of carbonate of sodium; or the natural mineral is simply purified by several crystallizations.

Borax is employed for restoring the shade of defective gildings, and for destroying the subsalts of silver formed in electro-silvering baths, and which injuriously affect the color of the electro-silver deposits.

#### *India-Rubber.*

(Caoutchouc. Gum-elastic.)

This substance is white when pure; but its color is generally brown or red, caused by the smoke of the fire employed in drying it.

India-rubber is extracted from the sap flowing from incisions made in the trunk of *Ficus elastica* or *cahuca*, a tree indigenous to Java. The milky sap, by settling, becomes divided into two layers, the lower one of which is liquid, and the other thicker and cream-like, and formed of a multitude of small globules. This portion is removed, washed with salt water, and spread in thin layers upon tables or over pear-shaped clay balls with a stick as a handle. The drying is done at the ordinary temperature, or with the aid of heat; and, in the latter case, the smoke colors the substance of the gum.

India-rubber is essentially elastic, and this property renders it very valuable for many purposes, as, for instance, moulding highly wrought patterns. The elasticity increases with the temperature; but at 250° to 260° Fah.



the gum melts, and furnishes a viscous liquid which seldom returns to its primitive consistency. If the temperature be raised still higher, the mass remains permanently liquid and sticky. Lastly, at a still greater heat, India-rubber will burn with a sooty flame.

The combination of sulphur with India-rubber furnishes a peculiar product equally elastic, but free from the disadvantage of becoming softened and sticky by heat. This product is called vulcanized rubber, and, by modification of the treatment, may be converted into the substance known as "hard rubber," which is used for a multitude of purposes.

Water, alcohol, and acids do not dissolve India-rubber; on the other hand, ethers, bisulphide of carbon, essential oils, and benzole dissolve and leave it behind after the volatilization of the solvent. These solutions give us the means of obtaining very delicate moulds; but, in this case, we should only apply very thin and successive coats of the solution, otherwise the exterior surface being the first to solidify, will prevent the drying of the intermediary layers.

### *Chloride of Silver.*

(Argentie chloride. Horn silver. Muriate of silver.)

This substance, when obtained by precipitation, is pure white, but soon turns blue and then black by exposure to the light; to prevent this decomposition it should be kept in blue or opaque bottles. It fuses at a high temperature, and acquires the appearance of horn, from which it derives its name of horn silver.

When chlorine water, hydrochloric acid, or any soluble chloride is introduced into a solution of a silver salt there is immediately produced a copious precipitate of chloride of silver, which is insoluble in water and in con-

concentrated acids, but soluble in ammonia, the cyanides, hyposulphites, and sulphites of the alkalis or alkaline earths. This precipitate is soluble, though to a much less degree in the bromides, iodides, chlorides and fluorides of the alkalis or alkaline earths.

Chloride of silver is employed in the preparation of the baths for electro-silvering, for the whitening baths, and for the pastes for silvering by friction.

#### *Protocloride of Tin (poisonous).*

(Stannous chloride. Murate of tin. Chloride of tin. Tin salt.)

This salt is manufactured in large quantities, and occurs in the form of small needle-like crystals. It is greasy to the touch, fuses readily, communicates to the fingers a characteristic odor, and has a taste at first saline and then acrid and astringent.

Protocloride of tin is soluble in water, but is partly precipitated in the state of a white substance, which is easily dissolved in a slight excess of acid.

Alloys composed of tin, antimony and bismuth are prepared in the same manner as solutions of this salt, but an excess of the solution will dissolve the precipitate. This solution is the best of the preparations of the same kind, and is used for the purpose of this work.

The preparation of this compound by dissolving granulated tin in excess of the hydrochloric acid, evaporating the solution to a certain consistency, and filtering it, is described.

When the tin is dissolved, that the tin is in the state of a precipitate, which can be dissolved in a small quantity of hydrochloric acid. The operation is completed when the white fumes begin to be evolved, which is a sign that the solution is complete.

volatilize. The fused chloride of tin thus obtained is preferable for tinning with alkaline baths.

### *Chloride of Gold.*

(Auric chloride. Trichloride of gold. Muriate of gold.)

This salt occurs in masses of needle-like crystals, which are yellow, red, or brownish-red, according as it has been more or less perfectly deprived of acid. That generally used by manufacturers of chemical products is a light yellow; and besides the fact that it contains less gold than ought to, it still retains an excess of acid, which is injurious to the baths.

Chloride of gold is decomposed by light into metallic gold and chlorine; hence the necessity of keeping it in aqueous bottles, with ground-glass stoppers. Cork, like other organic substances, decomposes this salt.

Chloride of gold absorbs atmospheric moisture, and becomes resolved into a liquid of a fine yellow color. It produces violet stains on the skin, and dissolves in water nearly all proportions.

It is distinguished by giving a precipitate of purple of Cassius with protochloride of tin, and by depositing spongy gold when strongly heated. A diluted solution of chloride of gold is decolorized by sulphurous acid, and, after a certain time, or more rapidly by heat, the metal is precipitated as a powder, which is green by transmission, and red by reflected light.

If a solution of this salt is added drop by drop to a diluted solution of sulphite or hyposulphite of sodium, a colorless double salt is produced. On the contrary, should we pour the solution of the sulphite or hyposulphite into that of the gold, this metal is immediately and completely precipitated.

The soluble cyanides or prussiates, precipitate the chloro-



ride of gold at first as cyanide from *concentrated* solutions; but an excess of the reagent redissolves the precipitate, and forms with it colorless double salts, which form the usual electro-gilding baths.

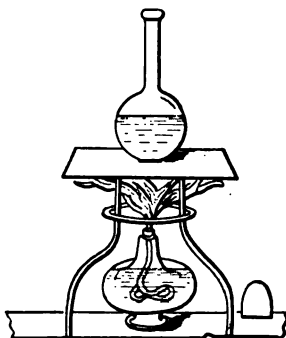
Carbonates, bicarbonates, and pyrophosphates also produce double salts, which may be crystallized, and which, in certain cases, form the simple-immersion gilding baths.

Chloride of gold may be prepared by different methods; the most simple of which consists in dissolving the finely laminated, or otherwise comminuted, metal in aqua-regia, made by the addition of two parts of pure hydrochloric acid to one of pure nitric acid. The operation is conducted in a glass flask, and with the aid of a gentle heat, until all of the gold has dissolved to form a yellow liquid, which still retains a great excess of acid. The heat is then slightly increased, and continued until the liquid is a hyacinth-red. After cooling, a crystallized mass of a fine yellow color is obtained, which is well adapted to the preparation of the immersion-gilding baths. On the other hand, for electro-gilding baths, we should continue the action of the fire until the liquid in the flask has acquired a blackish-red color, without losing its fluidity. On cooling, the crystals are brown-red. Roseleur prefers to use a glass flask for this purpose in preference to a porcelain capsule or dish, because the evaporation is too rapid in the latter, and part of the chloride of gold may be carried mechanically out of the vessel.

The flask (Fig. 169) should stand upon a perforated plate of sheet-iron. We thus avoid the reduction, by an excess of heat, of a portion of the chloride of gold. Should the heat be too great, or too protracted beyond the time necessary to expel the excess of acid, the terchloride of gold will be transformed first into an insoluble sub-

chloride, and then to the metallic state, and the operations of solution, etc., would have to be begun anew.

Fig. 169.



Some operators buy their aqua-regia already made, which is not advisable, as the acids react one upon the other, even without the presence of the metal; the useful portion becomes lost, and what remains is nearly useless. It is advisable in all cases to make the mixture just before using it. Some prepare the chloride of gold with a mixture of nitric acid and sal-ammoniac or common salt. This method is not as good as that described above, and is retained at present only by gilders on porcelain wares. Lastly, gold may be dissolved in chlorine water; but this process is expensive.

#### *Chloride of Platinum.*

(Platinic chloride. Tetra-chloride of platinum. Muriate of platinum.)

This salt is amorphous, of reddish-yellow or blackish-red color, according to the degree of evaporation of the excess of acids. It has a great analogy with the chloride of gold, both in its appearance and deliquescent properties (when strongly acid); but it is not so readily decomposed by light and organic substances.

Its aqueous solution is gold-yellow when diluted, and dark-yellow when concentrated; but never wine-red, unless it contains palladium, iridium, or rhodium. It is colored a wine-red by iodide of potassium. Potassa and its salts in concentrated solution give a yellow precipitate with chloride of platinum; sometimes it is necessary to stir the mixture with a glass rod before the precipitate takes place. Soda does not produce this result, unless in highly concentrated solutions. Ammoniacal salts also give a yellow precipitate, which, on calcination, leaves behind spongy platinum.

The chloride of platinum resists the action of the fire better than that of gold; it is presently, however, converted first into a subchloride of platinum, and finally into pulverulent metal.

When a brass surface is rubbed with chloride of platinum it acquires the color and lustre of steel, and this coating is often quite durable.

Perfectly neutral chloride of platinum, mixed under a muller with certain fatty and essential oils, furnishes a paste which is used for applying thin coatings of metal upon stoneware, pottery, glass, and porcelain.

Chloride of platinum is freely soluble in caustic soda, and in the carbonate and phosphate of this base, and thus furnishes more or less satisfactory baths for obtaining platinum deposits.

This salt is prepared like the chloride of gold; but the aqua-regia should be made of five parts of hydrochloric acid to three of nitric acid. The product is evaporated nearly to dryness in a porcelain capsule, from which it may readily be detached after cooling. If it be desired to have it more acid, and therefore more easy to dissolve, it is poured while still fluid, and not sensibly fuming, upon



porcelain plate, from which it is easily separated after cooling.

*Chloride of Zinc* (poisonous).

(Hydrochlorate or muriate of zinc. Butter of zinc.)

This substance is more or less gray, or white in color, according as it has been prepared in iron or porcelain vessels, or has been more or less thoroughly desiccated.

It is caustic, greasy, and hot to the touch. It absorbs moisture with such energy that a few minutes of exposure to the air are sufficient to cause it to completely liquefy. It may be distilled without decomposition like mercury and other volatile substances, and then possesses the appearance of butter, whence its name of "butter of zinc."

Chloride of zinc is employed for aiding soldering, brazing, or welding operations, for which uses it should be as neutral as possible in order that the metals shall not be corroded by the free acid. It enters into the composition of the brassing or zincing baths.

It is prepared by dissolving zinc in hydrochloric acid, filtering the solution after it has been left standing for a few days in contact with an excess of zinc, and evaporating it cautiously to igneous fusion. At this moment, abundant and heavy white fumes are disengaged. The mass is then cast into thin plates by pouring it out on porcelain dishes; and these plates are broken up at once after cooling, and kept in well-stoppered glasses.

*Cyanide of Silver* (poisonous).

(Prussiate, or hydrocyanate, of silver.)

This substance is white, becomes slowly black when exposed to light, and is insoluble in water and in cold acids, which, however, will dissolve it with the aid of



yellow tinge, resulting from the precipitation of a soluble copper salt by cyanide of potassium.

Whatever be its mode of production, it is freely soluble in all the alkaline cyanides.

By solution in an excess of cyanide it forms the double cyanide of potassium and copper, constituting the bath used for electro-coppering.

*Cyanide of Ammonium* (poisonous).

(Hydrocyanate of ammonia. Prussiate of ammonia.)

We may obtain with this salt the same baths as with the cyanide of potassium. It is, however, rarely used, because it is easily decomposed, and has a disagreeable cadaveric smell. It is obtained by exactly neutralizing ammonia with hydrocyanic (prussic) acid.

*Cyanide of Calcium* (poisonous).

(Hydrocyanate, or prussiate, of lime.)

This salt is employed for decomposing the carbonates formed in baths of cyanide of potassium. It will be readily understood how, by double decomposition, an insoluble carbonate of calcium is formed, while a proportional quantity of cyanide of potassium is reconstituted. This salt, in the majority of cases, should be preferred to hydrocyanic acid.

A solution of cyanide of calcium is obtained by adding hydrocyanic (prussic) acid to freshly-slaked caustic lime in excess. By filtration, the excess of lime remains behind, and the cyanide of calcium is found in the filtrate. This salt cannot be obtained in the solid state, is decomposed by heat, and it is better to use it when recently prepared.



*Cyanide of Gold* (poisonous).

(Prussiate, or hydrocyanate, of gold.)

It is of an earthy yellow color, and behaves with reagents very much like the cyanide of silver. Cyanide of gold is prepared by precipitating a solution of chloride of gold with a solution of cyanide of potassium. An excess of alkaline cyanide must be avoided, as it will dissolve the precipitate and form a double cyanide of gold and potassium. This salt is employed for the preparation of gilding baths, and is preferred to the chloride for this purpose, as it avoids the objection of introducing chloride of potassium into the gilding solution.

*Cyanide of Potassium* (extremely poisonous).

(White prussiate of potash.)

No product is more important to the electro-plater than the cyanide of potassium, which is the basis of most of the baths employed, and the purity of which is so necessary for the success of the operation.

At the same time, nothing more closely resembles a good cyanide than a bad one; a fact that has aided many manufacturers in producing, at cheap rates, products which have nothing in common with real cyanide but the name.

It may be formed by introducing dry ferro-cyanide of potassium in an iron crucible heated to redness, and maintaining the mass in a state of fusion for about a half hour, or as long as gas continues to be given off, keeping the crucible closed as much as possible during the operation. In Liebig's plan, eight parts of dry ferro-cyanide of potassium are mixed with three parts of dry carbonate of potassium and fused as above.

Cyanide of potassium, or rather all of the alkaline

cyanides at first precipitate metallic solutions, and then redissolve the metallic cyanide to form double salts. A certain number of metals, however, should be excepted, such as platinum, bismuth, antimony, tin, etc.

Cyanide of potassium forms with the salts of peroxide of iron a precipitate of Prussian blue. This color is developed especially in the presence of an excess of hydrochloric acid, but disappears on the addition of an alkali.

*Ferrocyanide of Potassium* (poisonous).

(Yellow prussiate of potassa.)

This product is manufactured on a large scale, and has many uses in the arts. It occurs in the shape of fine yellow, and semi-translucent, crystals with mother-of-pearl lustre, which break gradually and without noise. The fracture is jagged, and filled with a multitude of small bright spots.

The dried salt is yellowish-white; at a higher temperature it decrepitates, and is decomposed into white cyanide of potassium, and cyanide of iron, the cyanogen of which in its turn is expelled as gas, while the iron is reduced to the metallic state, or to that of a carbide.

The solution of ferrocyanide of potassium is straw-yellow, and, like the simple cyanide of potassium, precipitates and redissolves afterwards nearly all metallic salts. Its solvent power, however, is much less energetic. The metallic anodes are but slightly dissolved in the baths composed of yellow prussiate, which renders the use of such baths expensive.

The ferrocyanide is somewhat poisonous, and does not emit any smell, or absorb moisture.

It is prepared by carbonizing animal matters, such as blood, horn, hair, etc., with a mixture of carbonate of

1. The first step is to identify the problem or goal that needs to be addressed.

2. Next, it is important to gather relevant information and resources to understand the problem better.

3. Once the information is gathered, the next step is to analyze the data and identify the root causes of the problem.

4. After analyzing the data, it is necessary to develop a plan or strategy to address the problem effectively.

5. The final step is to implement the plan and monitor the progress to ensure that the problem is resolved.

6. It is also important to evaluate the results of the implementation and make adjustments if necessary.

7. Finally, it is essential to document the process and results for future reference and learning.

8. The overall goal is to solve the problem efficiently and effectively, while also learning from the experience.



by adding to the gelatine, before pouring it upon the pattern, a few hundredths of tannic acid, which combines with it, and forms a kind of leather which resists the action of the liquids better. At all events, gelatine moulds should be rapidly coated with the metallic deposit, otherwise they will give very imperfect, or valueless, copies.

While it is true that hot water dissolves a great proportion of gelatine, which sets on cooling, this property disappears after too prolonged ebullition, when a syrup is left which will not coagulate.

### *Benzole.*

(Benzine. Light oil from coal tar.)

When coal tar is distilled, there remains in the retort a thick mastic called pitch, and the distillate is composed of essential oils, having different specific gravities and points of ebullition. Those which are lighter than water are collected apart, and are deprived of their coloring matter by more or less prolonged treatment with concentrated sulphuric acid, and then with soda. After the proper washings and one or several distillations, a liquid is obtained which is colorless, smelling strongly of coal gas, with a sharp and bitter taste, and which is completely insoluble in water, although it imparts its odor to the latter. This product becomes oxidized and reddens under the action of solar light, when it has not been perfectly rectified.

Benzole is an excellent solvent of all the oils, resins, gums, varnishes, fats, etc., and is therefore very useful in our art. It is much superior to the alcohol and essence of turpentine formerly employed for removing stopping-off varnishes, and may be used in the cold, which is a great advantage with inflammable substances. A small proportion of naphthaline is sufficient to give a pink, red,

or brown tinge to benzole; but this is of no consequence for our operations. The preparation of this substance involves such great danger from fire that we cannot recommend our readers to undertake it. Moreover, it is found in the trade very cheap, and pure enough for our purposes.

#### *Phosphate of Ammonium.*

This salt, which is absolutely necessary for the composition of baths for thick platinum deposits, is obtained by the *exact saturation* of phosphoric acid with ammonia.

The liquid obtained is then evaporated at a gentle heat, and a few drops of ammonia are now and then added, in order to compensate for that removed by the decomposition of small quantities of the salt. When the liquid becomes syrupy it is set aside to crystallize in a cool place.

This salt may also be prepared by decomposing, with carbonate of ammonium, the acid-phosphate of calcium, resulting from the digestion in sulphuric acid of ground and calcined bones.

#### *Phosphate of Sodium.*

(Trisodic phosphate of soda.)

This salt crystallizes in fine, transparent, and colorless prisms; its taste is slightly bitter and saline, and it effloresces, losing part of its water of crystallization. It is soluble in distilled water without producing any precipitate, but causes a deposit of white phosphate of calcium in calcareous waters. The composition of this salt will be best understood by supposing it to consist of phosphoric acid containing three atoms of hydrogen, two of which have been replaced by sodium. Hence its name of

At a temperature of about 400° Fah., phosphate of sodium diminishes in volume, and loses all of its water of crystallization, but not that combined. By still raising the temperature, it melts to a glass and loses the combined water, which it will not reacquire except by remaining a very long time in solution. Its nature and properties have been entirely changed; and it gives now a white precipitate with nitrate of silver, instead of a yellow one, as was the case previous to its transformation into *pyrophosphate* or bibasic phosphate. It is capable of combining with a metallic base, in place of the equivalent of water lost. It is this property which renders the pyrophosphate valuable for the preparation of baths for gilding by simple immersion, and of tinning baths either by the battery, or by the method of double affinity. In these cases it assimilates respectively an equivalent of oxide of gold or of oxide of tin.

Phosphate of sodium is used for hot electro-gilding baths, and is prepared by treating calcined and powdered bones with sulphuric acid, and letting the mixture rest for several days. The acid phosphate of calcium is then removed by washing the residue, and the filtered liquid is saturated with carbonate of sodium until carbonic acid is no longer disengaged. The clear liquid is then concentrated until it marks 33° Baumé, and is allowed to crystallize once or several times.

### *Pyrophosphate of Sodium.*

(Bibasic phosphate of soda.)

The commercial salt is generally in the form of a white powder, odorless, and with a hot, saline, alkaline, and then bitter taste. It is soluble in water, but not so readily as the preceding salt, and requires distilled water,



in preparing baths with it, since it produces a precipitate in ordinary calcareous waters.

The pyrophosphate of sodium gives a white precipitate with nitrate of silver, whereas that with the ordinary tribasic phosphate is yellow.

It is employed for the preparation of simple-immersion gilding baths; and is obtained by fusing the ordinary dried tribasic phosphate, which by this operation loses an equivalent of combined water, and becomes *bibasic*. The temperature required is quite high, and few crucibles will stand the heat and the action of this substance which acts as a flux.

### *Plumbago.*

(Black-lead. Graphite.)

This is nearly pure carbon, and is found in crystalline or amorphous masses in several countries, as in England, Russia, Germany, Ceylon, the United States, etc. This carbon is black, with a metallic lustre, soft to the touch, without smell or taste, and is difficult to ignite.

Plumbago, in the natural state, is generally mechanically mixed with a variable proportion of iron and earths, which may be removed more or less perfectly by washing the previously finely pulverized mineral with dilute hydrochloric acid.

Plumbago varies very much in quality. The best plumbago for galvanoplastic purposes is very black, and without much lustre. A good plumbago should firmly adhere to pencils when rubbed on paper, and should not become disintegrated when being immersed into a liquid. The best method of ascertaining its quality and purity is to rub a small quantity on a piece of paper. The more uniform and regular the coating the better it is.

It is also used for imparting electric conductivity to the

surfaces of many substances which are not naturally conductors, and also for preventing the adherence of two superposed metals. Plumbago is also used for bronzing; in which case, the preliminary purification with hydrochloric acid will be unnecessary. Plumbago of extreme purity and fineness, especially prepared for the use of galvanoplastic operators, may be obtained in the trade.

When plumbago is moistened with a solution of chloride of gold in ether, and then allowed to dry in a shallow vessel exposed to solar light, we obtain a *gilded plumbago*, which is a far better conductor of electricity than plumbago alone. We may also prepare a *silvered plumbago*, by calcining at a red heat, and in a closed crucible, plumbago which has been moistened with an aqueous or ammoniacal solution of 5 to 10 parts of nitrate of silver per 100 parts of graphite employed. By incorporating various bronze (metallic) powders with plumbago, a metallized product of more or less conductivity is obtained.

*Roseleur's Amalgamating Salt* (poisonous).

This is a triple salt of mercury, or rather a mixture of three salts of mercury, namely, the sulphate, nitrate, and chloride. It is liquid, more or less colored, very dense, and gives in water a yellow precipitate, which dissolves in an excess of acid. It produces a violet stain on the skin, and amalgamates copper and its alloys thoroughly and rapidly. It is used for amalgamating the zincs of batteries, and does away with the necessity of using metallic mercury. Though not more economical than mercury alone, it is more easily applied and prevents much trouble in electro-plating establishments. It may be substituted for the nitrate of mercury "quicking" solution, but the converse is not true, as this last when employed as an amalgamating salt, rapidly perforates the zinc.

Amalgamating salt is prepared by boiling the nitrate of mercury with an excess of a powder composed of equal parts of sulphate and chloride of mercury, *i. e.*, mercuric sulphate and mercuric chloride: the liquid remaining after cooling is used.

*Sulphate of Copper* (poisonous).

(Blue-vitriol. Blue-stone.)

This salt is manufactured in large quantities for dyeing, preserving wood, galvanoplastic operations, etc. It occurs generally in the form of large rhomboidal crystals, translucent and of a fine blue color. Its taste is acid, metallic, and astringent, like ink, but more persisting. On being heated, it first loses its water of crystallization and becomes white; and, at a higher temperature, the sulphuric acid is expelled in the form of dense white fumes, and there remains a blackish-brown oxide of copper. It is freely soluble in water, especially when the latter contains some free acid, and the solution is deep blue. Hot water dissolves much more of this salt than cold, and the excess of the salt crystallizes out on cooling.

Sulphate of copper solution is used in the galvanoplastic baths proper, which are rendered more conducting by the addition of tartaric acid or citric acid, or sulphuric acid.

Sulphate of copper solution is also employed, without the aid of electricity, to deposit certain metals, such as iron, zinc, and steel, on a surface coated with copper. Tin and lead are also deposited.

Copper metal solution or copper is frequently impure, containing small proportions of the sulphates of iron and zinc, which are objectionable when their amount is too great. Sulphate of iron is detected by passing through the solution a current of sulphuretted hydrogen gas: the sulphide of copper produced is separated by filtration.



and the clear filtrate is treated with ammonia, which produces a white precipitate of oxide of zinc, soluble in an excess of alkali. The iron remains also in the acid liquor filtered from the copper, and its presence is ascertained by the addition of a small quantity of ferrocyanide of potassium, which gives a deep blue coloration. Another process for the detection of iron consists in adding to a small quantity of the solution of sulphate of copper enough ammonia to dissolve all of the oxide of copper at first precipitated, when the brownish oxide of iron will be seen floating in the intensely blue liquid.

The best sulphate of copper is made by dissolving in sulphuric acid the copper scales produced in rolling sheets of this metal. That obtained by the spontaneous oxidation of copper pyrites is always contaminated with iron or zinc.

We should avoid, for our art, those cheap copper sulphates extracted from old acid dipping liquors, since they contain zinc and other metals, and also nitrate of copper with free nitric acid. Galvanoplastic baths prepared with them are a nuisance. Such sulphates are generally very wet and in small crystals.

#### *Sulphate (of Protoxide) of Iron.*

(Ferrous sulphate. Proto-sulphate of iron. Copperas. Green vitriol.)

This salt crystallizes in forms similar to the preceding one, and has a fine green color. Its taste is that of ink, and it is very soluble in water, which it colors a light green. It is rapidly oxidized by contact with the air, and becomes first yellow, then reddish, and is transformed finally into a sulphate of peroxide of iron, which possesses quite different properties.

On heating sulphate of iron it first loses its water of

crystallization and becomes white. At red heat it is decomposed into sulphurous and sulphuric acids, which escape, and a red and pulverulent residue which, according to its fineness, its intensity of color, etc., is variously called *colcothar*, *anhydrous sesquioxide of iron*, *rouge*, etc.

The proto-sulphate of iron is employed for precipitating gold from its acid solutions. The sesqui-sulphate does not possess this property.

It is prepared, either by evaporating and crystallizing the liquors used for cleansing iron and steel, or by the oxidization, in the air, of iron pyrites. The salt obtained by this latter process generally contains some copper, which may be precipitated by placing iron scraps in the solution.

#### *Sulphate of Zinc.*

(White vitriol. White copperas.)

The trade furnishes this salt in three forms: either in white or opaque plates, or in large transparent crystals, or in a mass formed of a quantity of needle-like crystals, resembling those of sulphate of magnesium or of tin salt.

Its taste is sour, styptic, and metallic, and it is very soluble in water, which remains colorless. It is decomposed by a strong heat, leaving a residuum of oxide of zinc. Its neutral solutions yield a white precipitate with sulphuretted hydrogen, but no precipitate is produced from acid solutions. The sulphide of zinc is the only white metallic sulphide which is known; and this is the reason why zinc paints remain white, notwithstanding the presence of sulphurous gases, which so rapidly blacken lead paints.

Sulphate of zinc is employed for zinc and brass electro-baths, in the preparation of acids for dead lustre dipping, and for a frosted lustre upon clocks and jewelry.

*Sulphite (and Bisulphite) of Sodium.*

The former salt forms white prismatic crystals, which are rapidly transformed into an amorphous powder by efflorescence.

It possesses no smell, but its taste is flat, saline, and sulphurous. It is very soluble in water, and is gradually transformed into sulphate by the absorption of oxygen from the air. Powerful acids decompose it, with abundant evolution of sulphurous acid, which is easily recognized by its smell of burning sulphur. During this reaction, the solution remains clear, and is thus distinguished from the hyposulphite, which also disengages sulphurous acid, but deposits sulphur in the solution.

Sulphite of sodium, and generally all the soluble sulphites, dissolve the salts of gold, silver, copper, etc., under certain circumstances, and transform them into colorless double salts, which possess more or less stability, and are employed in the preparation of electro-baths, for gilding, coppering, and brassing.

The sulphite of sodium may absorb an excess of sulphurous acid, and thus become a bisulphite, which is always to be preferred to the neutral salt.

The neutral sulphite of sodium is prepared by passing a stream of sulphurous acid gas through a solution of carbonate of sodium until the liquid is neutral to test-paper. If the solution be very concentrated, a quantity of small crystals of bicarbonate of sodium become precipitated in the course of the operation, and it should be stirred to prevent them from obstructing the gas delivery tube. An excess of sulphurous acid decomposes them with an abundant production of carbonic acid. The saturated liquid, if concentrated, crystallizes on cooling; if it is not, it should be evaporated to the proper point.



The bisulphite of sodium is produced by continuing the passage of the sulphurous gas, when the solution first reddens, and then bleaches blue litmus paper. This salt loses in the air its excess of sulphurous gas, then becomes neutral sulphite, and, after a long while, is converted to sulphate, by the absorption of atmospheric oxygen.

*Sulphide of Ammonium* (poisonous).

(Sulphhydrate, or hydrosulphate, of ammonia.)

This salt is liquid, and of a deeper color, according as it contains more sulphur. Its smell is exceedingly pungent (ammoniacal) and offensive, and its taste is alkaline and nauseous. The sides of the bottles in which it is kept are often covered with a pellicle of sulphur or sulphides. By rapid evaporation a residue of sulphur is left.

It rapidly forms sulphides with the metals, and produces on silver the black coating, misnamed oxidation. It is often employed for bronzing, for producing the so-called "patina" on the surface of various metals or alloys. It is prepared by saturating ammonia with sulphuretted hydrogen gas.

We generally employ it with an excess of sulphur, that is to say, after it has been digested for a few hours with an excess of flowers of sulphur, at a temperature of about 160° Fah. The liquid is then of a dark reddish-yellow.

It may be prepared by the decomposition of the sulphide of barium, calcium, or strontium, by means of carbonate of ammonia. The more usual mode, however, is by passing sulphuretted hydrogen gas through strong aqua ammonia until the latter is saturated.

The operator should avoid opening a vessel containing sulphide of ammonium in rooms where silver-plating is being done.

*Sulphides of Calcium, Potassium, and Sodium*  
(poisonous).

(*Hepar Sulphuris*. Liver of sulphur, or polysulphides of calcium, potassium, and sodium.)

These salts are obtained in solution by boiling the alkali and the flowers of sulphur in a certain quantity of water. They are produced in the dry way by projecting powdered quicklime, or potassa, or soda into melted sulphur, and then casting the mixture on a marble slab.

These dry sulphides are generally in the shape of plates, which are greenish or whitish at the surface, and reddish-yellow inside. They are soluble in water, which is colored yellow or red, according to the degree of concentration. By spontaneous decomposition they emit the smell of rotten eggs; and, when treated by an acid, they give off sulphuretted hydrogen, yielding at the same time a deposit of sulphur. Their uses in our art are the same as those of sulphide of ammonium.

*Bisulphide of Carbon.*

(Carbon disulphide. Liquor of Lampadius.)

If we bring to a red heat a stoneware or porcelain tube (Fig. 170), filled with charcoal, and then introduce into it (immediately closing the aperture) fragments of sulphur, the liquid which results from the combination of the sulphur and carbon is condensed at the bottom of the water in the connected receiver, and furnishes, after distillation, pure bisulphide of carbon.

It is a colorless and transparent liquid, which is very dense, and exhibits the property of double refraction. Its smell is characteristic and most disgusting, and may be compared to that of rotten turnips. It is very volatile, producing upon the hand the sensation of cold. It burns

with the blue flame of sulphurous acid, and carbonic acid is produced at the same time. No residue is left.

Fig. 170.



Bisulphide of carbon dissolves many kinds of resins, fats, and gums, such as India-rubber and gutta-percha, and, most important of all for us, also sulphur and phosphorus. This last solution is employed in our art for reducing the nitrate of silver to the metallic state upon certain moulds, which thus become conducting.

Fig. 171.



The apparatus for the manufacture of the bisulphide of carbon imitates on a larger scale the disposition shown in Fig. 170. A large stoneware retort is heated in a fir-



nace, and carries a tubulure, through which passes a stoneware tube reaching to the bottom of the charcoal, and the upper end of which may be closed by a stopper. The neck of the retort projects from the furnace, and communicates by a tube, with a receiver filled with water. The connecting tube is kept cool by passing a stream of cold water through a tube which surrounds it as a water jacket. When the retort is brought to a red heat, a few fragments of sulphur are introduced through the tube, which is quickly closed. The vapor of sulphur is obliged to pass through the mass of incandescent charcoal, combines with it, and condenses in the water of the receiver.

The product thus obtained contains an excess of sulphur which is removed by distillation on the water-bath. Pure bisulphide of carbon should volatilize without leaving any residue. It is now obtained in the market at a very low price.

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## CHAPTER LXX.

### INSTRUMENTS AND APPARATUS.

#### *Stirring Rods.*

THESE are rods made of various materials, and are employed for mixing together liquids, or paste, or liquids and pastes, or solids with liquids, or various solids in the dry state. Their length and thickness should be suited to the volumes to be mixed.

Suitable stirring rods are those which have no chemical action upon the substances with which they are brought in contact; neither should they become impregnated with them. Rods of glass, stoneware, or porcelain are decidedly

the best. Wood and most metals should be avoided, because the former is absorbent, and the latter are corroded and easily oxidized.

The operator in the various branches of our art should always have near at hand a complete assortment of glass stirrers of various sizes, and with fused or rounded ends, in order not to scratch the vessels in which he operates.

#### *Anodes.*

By this name are designated the plates or wires of different metals placed at the extremity of the connecting wire leading from the positive pole of a battery.

The anodes are soluble or insoluble, that is, they become dissolved under the influence of the galvanic current to partly maintain the metallic strength of the bath, or they simply convey the current into the bath without being dissolved.

The soluble anodes are, generally, of the same metal or alloy of which the bath is composed; and the insoluble anodes are of platinum, gas carbon, or any other conducting and insoluble substance.

Soluble anodes are generally completely immersed in the solution, and connected with the conducting wire by other platinum wires. Insoluble anodes, on the contrary, are rarely completely immersed, and by dipping them more or less into the bath we increase or diminish at will the amount of current.

#### *Hydrometers.*

These are instruments usually made of glass, for ascertaining the specific gravities of liquids. There are hydrometers for acids, salts, alkalies, syrups, alcohol, ether, liquors, etc.

A great many operators think that hydrometers will

not only indicate the specific gravity, but also the composition and the quality of their baths; they imagine, for instance, that if they have once had good results with a bath marking  $9^{\circ}$ , any other bath also marking  $9^{\circ}$  must be equally good. This is a great mistake, which should be corrected.

A hydrometer, in general, is an instrument intended to indicate the specific gravity of a liquid, as compared with that of distilled water at its maximum density, that is, at  $39.2^{\circ}$  Fah. As there are liquids lighter and heavier than water, it is necessary to have two kinds of hydrometers, or rather, two different graduations of this instrument.

Baumé, an apothecary of Paris, was the first to construct a hydrometer of constant weight. It is a glass tube, the lower third of which is composed of a large bulb or cylinder, terminated by a smaller bulb, in which is placed a certain weight of lead or mercury acting as ballast for sinking the instrument more or less in the liquid. The cylindrical and narrow tube, above the large bulb, receives a small cylinder of paper upon which are marked the divisions, or degrees, of the scale. The liquid, the density of which is determined, is contained in a tall cylinder of glass, deep enough to permit the hydrometer to be immersed to its lowest point without touching bottom.

This instrument is graduated by two different methods, according as it is intended for determining the specific gravity of liquids heavier or lighter than water at  $39.2^{\circ}$  Fah.

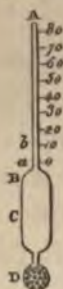
If it be intended for liquids heavier than water (for acids and saline solutions, for instance), mercury or lead is introduced into the lower bulb until the instrument has sunk nearly to the top in pure water, and the 0 of the



paper scale is made level with that of the liquid. The hydrometer is then dipped into a solution of fifteen parts of common salt (chloride of sodium) in 85 parts of distilled water, and the line where the level of the liquid touches the tube is marked  $15^{\circ}$ . The space between 0 and  $15^{\circ}$  is divided into 15 equal parts, and this graduation is continued upon the remainder of the scale.  $66^{\circ}$  is the specific gravity of concentrated sulphuric acid with Baumé's hydrometer.

For liquids lighter than water, the graduation of the preceding hydrometer is reversed (Fig. 172).

Fig. 172.



The 0 is at the lower part of the stem, and is determined by plunging the instrument into a solution of 10 parts of common salt in 90 parts of water.  $10^{\circ}$  is marked at the level line in distilled water, and the space between 0 and  $10^{\circ}$  is divided into 10 equal parts, and the same graduation continued for the remainder of the scale.

A similar method may be employed for constructing special hydrometers for special saline solutions, one of common salt, for instance. The 0 of the instrument is at the level line in distilled water;  $5^{\circ}$  in a solution of 5 parts of salt in 95 of water;  $10^{\circ}$  in a solution of 10 parts of salt in 90 of water; and so on.

But such an instrument cannot be employed for determining the *composition* of different solutions; and queer mistakes would be made if we desired to ascertain the composition of a solution of nitrate of silver with a hydrometer graduated especially for one of sulphite of soda, for instance. It is also evident that the same hydrometer will not do for determining the composition of a solution containing two different salts. Thus, a photographer may arrive at the composition of a pure solution of nitrate of

silver with a hydrometer especially constructed for the purpose ; but the same instrument will give no indication whatever as to the proportion of silver contained in an electro-silvering bath, which contains many other salts besides that of silver.

Therefore, hydrometers are useful for verifying the strength of the commercial acids used, and to indicate whether the specific gravities of the baths are too much above or below the limits between which it has been ascertained that the galvanic current will pass freely.

#### *Glass Balloons and Flasks.*

These are spheres of thin blown glass (Fig. 173) with necks of various dimensions, in length and diameter. They are employed for heating acids, dissolving metals, and a great many other uses. They should be placed upon triangular supports of iron, and at a certain distance from the fire, from the direct action of which they should be protected by the intervention of a piece of wire gauze, or its equivalent. The thinner they are, the more easily they bear sudden changes of temperature. They are preferable to porcelain evaporating dishes, for dissolving gold, because there is much less danger of losing a part of the product by spurting.

Fig. 173.



#### *Kettles and Boiling Pans.*

These are of various shapes, hemispherical, or with flat bottom, and are made of different materials (Figs. 174, 175).

Those of copper are employed for whitening with silver and cream of tartar. Cast and sheet-iron are preferable for cleansing with caustic alkalies, or for evaporating residues.

Those of stoneware heated on sand or water baths, for desilvering (stripping), or for giving a dead lustre to copper in warm acids.

Fig. 174.

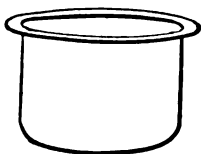
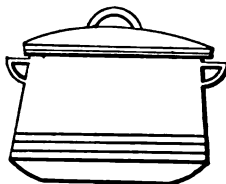


Fig. 175.



Cast-iron enamelled kettles are used for hot baths of copper, silver, gold, and platinum.

Notwithstanding their enamel, these vessels become gradually impregnated with the solutions they have held, and it is dangerous to employ them for different kinds of baths. Thus an enamelled kettle, which has been used for silvering, will not be suitable, even after the most thorough washing, for a gold bath, as the gilding will certainly be white or green, according to the quantity of silver retained by the vessel.

#### *Brushes.*

A definition of these instruments is unnecessary; and we shall simply indicate the various kinds suitable to the different operations of our art.

The fire-gilder employs, for equalizing the coating of amalgam, a long handled brush, the bristles of which are long and very stiff.

The electro-gilder uses a brush (Fig. 176), with long and flexible bristles.

For scouring with sand and pumice-stone alloys containing nickel, such as maillechort and German-silver,



which are difficult to cleanse in acids, the preceding brush with smaller and stiffer bristles is used (Fig. 178).

The gilder of watch-works has an oval brush (Fig. 177) with stiff and short bristles for graining the silver.

Fig. 176.

Fig. 177.

Fig. 178.



The galvanoplastic operator, for coating moulds with plumbago, besides a number of pencils, uses also three kinds of brushes—the watchmaker's (Fig. 178), a hat-brush, and a blacking-brush.

The bronzer uses all kinds of brushes.

Brushes are perfectly deprived of adherent grease by washing with benzole or bisulphide of carbon.

#### *Burnishing Tools.*

They have already been described in this work.

#### *Evaporating Dishes or Capsules.*

These are usually vessels of porcelain, and are intended to bear a high temperature. The best are thin and uniformly so. Like glass flasks, they should be supported

Fig. 179.

Fig. 180.



above the fire upon an iron stand and wire-gauze. As far as practicable they should be gradually heated and cooled. When taken from the fire, they should be placed upon rings made of plaited straw. They are

made with or without lips, and some have a socket for a wooden handle. Glass evaporating dishes are not durable.

### *Retorts.*

These are of glass or stoneware. They have a more or less spherical body with a tapering neck. They are sometimes supplied with a tubulure, for greater convenience in introducing materials, and, when in use, they are placed in communication with a receiving vessel of any

Fig. 181.

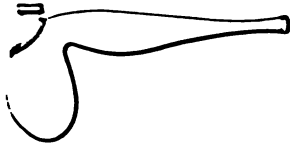


Fig. 182.

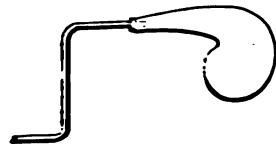


Fig. 183.



convenient form. Their uses have been briefly explained. Figs 181 and 182 represent retorts with and without a tubulure and Figure 183 shows a retort connected with a receiver.

### *Conducting Wires. Electrodes.*

These are the metallic wires, bands, spirals, or ribbons, which carry the electric current to the baths.

The conducting wires are either employed with their natural metallic surface, or are covered with some insulating, or poorly conducting, substance, such as cotton, silk, India-rubber, gutta-serena, and various varnishes. It is evident that covered electrodes should be bare and clean

their extremities, where they are connected with the battery and with the anodes, or cathodes (objects to be plated). Pure copper possesses the best conducting power; and after it come brass, silver, gold, platinum, iron, zinc, etc.

It is not meant that conducting wires should always be of copper; but if two wires, one of copper and another of iron, are connected at the same place on a battery, it is very likely that all of the electricity will preferably pass through the copper wire.

Insulated electrodes may come in contact with each other without inconvenience. Such is not the case with bare electrodes, because the electricity will pass through the shortest circuit, and will not go through the bath if the two electrodes are in metallic contact. Such contact should therefore be carefully avoided.

#### *Glass Jars.*

These are glass vessels, generally cylindrical, closed at one end, and of different capacities.

They are employed for small gilding, silvering, and cyanoplastic baths, in the cold. They are very handy and serviceable for amateurs, because their transparency permits the progress of the operation to be observed at all times.

#### *Crucibles.*

These are vessels, the shape of which is generally an inverted truncated cone (Fig. 184), the smaller end being closed, and the larger open. Sometimes the opening is triangular.

Crucibles are made of many kinds of materials: metals, refractory clay, stoneware, porcelain, plumbago or graphite, etc. They are generally provided with a cover of the same

Fig. 184.





material, and are raised above the grate bars of the furnace by means of bricks or cylinders of clay.

Metallic crucibles may be heated rapidly, but the others require to have their temperature raised gradually and carefully.

They are employed for the preparation of many salts, for the fusion of metals, etc. Non-metallic crucibles are rarely used for more than one operation.

#### *Depositing Vats. Troughs.*

These are made of different materials, and their shape may be either circular, square, or rectangular. They should be perfectly tight, impervious to the solutions, and unacted upon by them.

Stoneware, glass, or porcelain troughs are the best; but they are the most fragile and expensive. Those of wrought or cast-iron are suitable only for neutral or alkaline solutions, and they must be insulated from the anodes or the articles in the bath, so that the galvanic current may not pass through them.

Wooden vats should have their interiors covered with heavy coats of varnish or pitch, which resists the action of the baths, or with a sheathing of gutta-percha or India-rubber. They are sometimes lined with sheet lead, welded by the gas process, since any kind of tin solder would be inadmissible. Such vats are satisfactory for galvanoplastic operations, provided that the lead lining be insulated from the electric circuit.

#### *Diaphragms. Porous Cells.*

These are cylinders, plates, or partitions which from their porosity or permeability, allow liquids of different natures to be separated and at the same time in communication. Thus, if we divide a vat by a partition plate, made

of baked pipe-clay, and fill one of the chambers with diluted sulphuric acid, and the other with a solution of potassa (both liquids being at the same level), the two liquids will penetrate the porous plate or diaphragm and there react upon each other without their masses participating in the action.

We have seen, in Daniell's battery, that the porous cell separates the exciting liquid (solution of salt or sulphuric acid) from the solution of sulphate of copper. In Grove's and Bunsen's batteries they separate the acids; and also the acidulated liquor in the simple galvanoplastic apparatus.

Any porous substance, unacted upon by the solutions, will be suitable for diaphragms. Wood, sail-cloth, leather, gold beater's skin, bladder, baked porcelain and pipe-clay, etc., are employed. Nevertheless, diaphragms, or porous cells, made of unglazed porcelain, and rendered neither too much nor too little porous by a proper baking, are preferable to all others for durability and good working.

### *Filters.*

Filtering a solution, a bath, or any other liquor, consists in causing it to pass through a permeable substance, the pores or meshes of which are sufficiently closed to retain all the undissolved substances, which are thus separated from the liquid part.

Filters are of very different materials and shapes.

Cloth, muslin, etc., are coarse filters, or strainers, made in the form of pockets. Their filtering power is considerably improved by covering them with a layer of sand, wool, bone-black, etc. These latter substances themselves, properly supported, will act as filters.

Felted wool (generally rabbit's hair) is made in the shape of a conical pocket



(Fig. 185), but is suited only for neutral substances. Alkalies destroy it rapidly.

Concentrated acids are filtered through *amianthus*, or *asbestos*, compressed in the neck of a glass funnel upon broken fragments of glass.

But the most useful filtering material is unsized paper. This filter (Fig. 186), is prepared by folding diagonally a square piece of porous paper, which thus prepared forms a triangle. This is again folded in half. Then, beginning at one edge, smaller folds are made alternately to the right and to the left, but all converging towards the point, like a fan. The filter is now partially opened, trimmed on top and introduced into the funnel, with care that all the projecting edges rest against it.

Fig. 186.



If it be feared that the filter will not resist the weight of the liquid, the point is twisted to the left or to the right, and while it is still held between two fingers of the left hand, the whole filter is inverted, so that the inward folds become the outward ones. A filter with such a rounded point is better supported in the funnel and filters more rapidly.

This method is preferable for rapid filtration: but, if we desire to prevent precipitates, the filter represented by Fig. 187 is more suitable. A circular sheet of paper is twice doubled up, and is carefully covering in three thicknesses of paper on both one side, leaving one single thickness on the other side.

#### *Special Methods.*

We have already given a ~~general~~ description and use of this class



*Siphons.*

The most simple and handy siphon in many cases, is a piece of lead pipe bent so as to have two unequal branches, the smaller of which plunges into the liquid to be drawn off. A section of India-rubber tube may be employed for similar purposes.

But, as these materials may be chemically acted upon by various solutions, glass siphons are used with or without a suction tube (Figs. 188, 189).

Fig. 188.

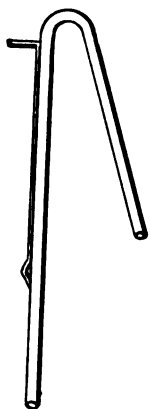


Fig. 189.



For siphoning corrosive solutions which cannot be touched with the fingers, a siphon with a suction tube is used (Fig. 188). The shorter leg is plunged into the liquid, and the longer one closed with the finger or an India-rubber pad pressed against it. Then, with the mouth, suction should be carefully applied at the lateral suction tube until the liquid fills the longer leg.

If there be danger in inhaling a poisonous vapor, the action of the mouth may be replaced by an India-rubber ball, fastened to the suction tube. The longer branch of

[www.libtool.com.cn](http://www.libtool.com.cn)

the siphon is closed as before, and the ball compressed in order to remove the air. By its elasticity the ball resumes its former volume, thus producing a suction which starts the siphon in action.

### *The Thermometer*

Is an instrument intended for ascertaining the temperature of fluids or liquids in which it is immersed. It acts by the dilatation or contraction of mercury or colored alcohol, contained in a bulb of thin glass, which is attached to a capillary tube deprived of air, and upon which the graduation is marked.

The scale employed in this work is that of Fahrenheit, which is commonly used in English speaking countries. In this, the 0 of the scale represents the temperature of a mixture of salt and ice; 32° is the point of melting ice, and 212° that of boiling water.

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## CHAPTER LXXI.

### MIXTURES.

RED ORMOLU—YELLOW ORMOLU—DEAD LUSTRE FOR JEWELRY  
—DEAD LUSTRE (HARD) FOR CLOCKS—DEAD LUSTRE (SOFT)  
FOR SMOOTH SURFACES AND FIGURES—GREEN-FOR-RED LUSTRE—GILDERS' WAX.

### *Mixtures.*

AFTER having enumerated the principal chemical products, apparatus, and instruments employed in our art, it remains for us only to give the formulæ of certain mixtures employed in gilding by fire, or by the wet processes.

Some of these have been given in the chapters on gilding, but their repetition may be serviceable.

## RED ORMOLU

Is composed of—

	Exact proportions.	In round numbers.
Potassa alum . . .	28.4 parts.	30 parts.
Saltpetre . . .	31.6 “	30 “
Sulphate of zinc . . .	8 “	8 “
Common salt . . .	3.5 “	3 “
Red ochre . . .	27.5 “	28 “
Sulphate of iron . . .	1 part.	1 part.
	<hr/> 100	<hr/> 100

We may add to it a small proportion of annotto, madder, cochineal, or other coloring matter, ground in water, or in weak vinegar.

## YELLOW ORMOLU.

	Exact proportions.	In round numbers.
Red ochre . . .	16.5 parts.	17 parts.
Potassa alum . . .	50.9 “	50 “
Sulphate of zinc . . .	10.5 “	10 “
Common salt . . .	2.1 “	3 “
Saltpetre . . .	20 “	20 “
	<hr/> 100	<hr/> 100

## DEAD LUSTRE FOR JEWELRY.

Sulphate of iron,	} equal parts of each.
Sulphate of zinc,	
Potassa alum,	
Saltpetre,	

The salts are fused together in their water of crystallization; and if the gilding be strong and durable, a small proportion of common salt may be added.



DEAD LUSTRE (HARD) FOR CLOCKS.

	Exact proportions.	In round numbers.
Water . . . . .	5 parts.	5 parts.
Saltpetre . . . . .	36.62 "	37 "
Potassa alum . . . . .	42.05 "	42 "
Common salt . . . . .	12.33 "	12 "
Pulverized glass and sul- phate of calcium . . . . .	4 "	4 "
	100	100

The whole is thoroughly ground and mixed.

DEAD LUSTRE (SOFT) FOR SMOOTH SURFACES AND FIGURES.

	Exact proportions.	In round numbers.
Water . . . . .	5 parts.	5 parts.
Nitrate of potassa . . . . .	46.32 "	46 "
Potassa alum . . . . .	45.82 "	46 "
Common salt . . . . .	2.86 "	3 "
	100	100

Treat the same as the preceding mixture.

GREEN-FOR-RED LUSTRE.

	Exact proportions.	In round numbers.
Nitrate of potassium . . . . .	65.7 parts.	65 parts.
Common salt . . . . .	25 "	25 "
Acetate of copper . . . . .	9.3 "	10 "
	100	100

The whole is ground together.

SHEDS' WAX.

Oil . . . . .	. . . . .	. 25 parts.
Yellow wax . . . . .	. . . . .	. 25 "
Acetate of copper . . . . .	. . . . .	. 13 "
Red ochre . . . . .	. . . . .	. 37 "
		100.

The whole is melted and stirred until cold.

## CHAPTER LXXII.

## USEFUL NOTES AND COMMENTS.

## ANTIDOTES AND HYGIENE OF THE WORKSHOP.

WE have seen that the majority of the chemical products employed in our art are very poisonous, or at least unwholesome. It is therefore well, after having pointed out the dangerous properties of these substances, to furnish, in case the necessity therefor should occur, the means of neutralizing their effects, either entirely, or at least sufficiently to retard their poisonous action until professional aid can be summoned.

*Poisoning by Acids.*

All the powerful acids, with the exception of hydrocyanic (prussic) acid, operate nearly in the same manner. They are corrosive poisons, and the more concentrated they are, the more energetic is their action.

It should not be forgotten that, when very diluted, these substances lose their poisonous properties; WATER, therefore, in the greatest abundance will be the first thing to administer. Tepid water and distilled water will act as emetics, and should be preferred if they are at hand. Milk and the white of eggs, which coagulate with the acids and partly neutralize them, may be successfully employed; but no antidote excels CALCINED MAGNESIA, or the carbonate of this base, which may be introduced into the stomach without danger, and will completely neutralize the acids, forming with them purgative salts. In the

absence of magnesia, chalk or Spanish-white, made into a paste with water, or even soap-water may be used. It should be well understood that in this, as in all other cases, a physician should be immediately summoned.

*Poisoning by Hydrocyanic (Prussic) Acid, Cyanogen, or Cyanides.*

If hydrocyanic acid, or the cyanides, be concentrated or have been absorbed in considerable quantity, their action is almost instantly fatal, and there is little hope of saving the victim, although everything should be tried.

But, if these substances have been taken in very dilute condition, they may not prove immediately fatal, and there is some hope that remedial measures may be successfully applied.

In poisoning with these substances, *water as cold as possible* should be run upon the head and the spine of the patient, and he should be made to inhale, *carefully and moderately*, the vapor of chlorine water, bleaching powder, or Javelle water (hypochlorite of soda).

Should these poisons be introduced into the stomach, we should administer as soon as possible the hydrate of sesquioxide of iron, or, what is better, diluted solutions of the acetate, citrate, or tartrate of iron. With proper precautions, a very diluted solution of sulphate of zinc may be given.

*Poisoning by Alkalies.*

Use weak acids, such as vinegar, lemon juice, etc., and, in their absence, sulphuric, hydrochloric, or nitric acid diluted to the strength of lemonade. After the pain in the stomach has diminished, it will be well to administer a few spoonfuls of olive oil.



*Poisoning by most Metallic Salts.*

Administer an abundance of water, and if possible cause the patient to vomit. Milk and the white of eggs are very good, but far inferior to *flowers of sulphur* or natural sulphuretted waters. The sulphur, alkaline sulphides, and sulphuretted hydrogen contained in these waters transform most of the metallic salts into insoluble sulphides, which are temporarily inert. They should be administered as long as there is a suspicion that any of the poison is still retained in the system.

*Poisoning by Mercury Salts.*

Mercury salts, and particularly the chloride (corrosive sublimate), form, with the white of eggs (albumen), a compound very insoluble and inert. The remedy is therefore indicated. Sulphur and sulphuretted water are also serviceable for the purpose.

*Poisoning by Lead Salts.*

Besides sulphur and sulphuretted waters, we may also employ a lemonade of sulphuric acid, or an alkaline solution containing carbonic acid, such as Vichy water. Bicarbonate of sodium (baking-soda) is very serviceable.

*Poisoning by Hydrosulphuric Acid (Sulphuretted Hydrogen).*

The patient should be made to inhale the vapor of chlorine, from chlorine water, Javelle water or bleaching powder. Energetic friction, especially at the extremities of the limbs, should be employed. Large quantities of warm and emollient drinks should be given, and abundance of fresh air.

*Poisoning by Chlorine, Sulphurous Acid, Nitrous and Hyponitric Gases.*

Admit immediately an abundance of fresh AIR, and administer LIGHT inspirations of ammonia. Give plenty of hot drinks, and excite friction, in order to conserve the warmth and transpiration of the skin. Employ hot foot-baths, to remove the blood from the lungs. Afterwards maintain in the mouth of the patient some substance which, melting slowly, will keep the throat moist, such as jujube and marshmallow paste, molasses candy, and liquorice paste. Milk is excellent.

We have simply stated, in the foregoing, the expedients and remedies to be employed in urgent cases. A physician should invariably be summoned immediately.

## APPENDIX.

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*Patina for Bronzes.*—An imitation of patina suitable for applying to all articles of bronze, may be made (*Bay. Indust. u. Gewerbeblatt*, ix. 128) by making a mixture of carbonate of copper with a light-colored spirit varnish, and applying the same to the metallic surface with a brush. The hollows of the article, by this operation, receive a greenish coloration which is very decided and quite permanent on drying. The carbonate of copper imparts a bluish patina, verdigris a bright green, and the intermediate tints are obtained by the mixture of these colors.

*Bronzing Copper.*—Spon (*Workshop Receipts*, 21) directs to dissolve in vinegar 2 parts verdigris and 1 part sal-ammoniac. Boil, skim, and dilute with water until no more white precipitate separates. Meanwhile place the articles to be bronzed, properly freed from grease, in a pan, and pour the boiling solution over them, letting it boil briskly. The resulting coloration is a bright reddish-brown, but the articles should be frequently inspected and removed as quickly as the desired shade is obtained. They should then be repeatedly washed and dried. The solution must not be too strong, as in that case the bronze will come off by friction, or turn green on exposure to the air.

*Green Bronze for Brass.*—We give the following formula on the authority of Spon (*Workshop Receipts*, 19). Dissolve 2 oz. of nitrate of iron, and 2 oz. of hyposulphite of sodium in 1 pint of water. Immerse the articles therein until they have acquired the proper tint, as almost any shade from brown to red can be obtained; then wash well with water, dry and brush.

One part of perchloride of iron, and two parts of water, will give a pale or deep olive-green to articles of brass immersed in them, according to the time of immersion. If nitric acid is saturated with copper, and the brass is dipped in the liquid, and



then heated, it assumes a dark green. If well brushed, it may be lacquered with pale gold lacquer, or else polished with oil.

*A Black Coloration on Brass Instruments* may be obtained, according to the same authority, by the following procedure: Take about a thimbleful of lampblack, place it on a flat stone, add four or five spots of gold size, and well mix the whole with a palette knife. It should be about as thick as putty. Add as little gold size as possible, as if too much is added the effect will be a bright instead of a dead black. Now add turpentine, about double the volume to the whole, mix with a camel-hair brush, and apply to the brass-work.

Another formula for a *Black on Brass*, from the same, is as follows:—

Dip the article bright in aqua fortis; rinse the acid off in clean water, and place it in the following mixture until it turns black: Hydrochloric acid, 12 parts; sulphate of iron, 1 part; white arsenic, 1 part. Then remove, rinse in clean water, dry in sawdust, polish with black-lead, and lacquer with green lacquer.

*To Bronze Electrotypes.*—(Spon, 20) *Green.*—Steep the medal in a strong solution of common salt, or sugar, or sal-ammoniac, for a few days; wash in water, and allow to dry slowly, or suspend over a vessel containing a small quantity of bleaching powder, and cover over. The length of time it is allowed to remain will determine the depth of the color.

*Brown.*—Add four or five drops of nitric acid to a wine glassful of water, apply to the article and allow to dry. Then heat the article gradually and uniformly. The surface of the article will be darkened in proportion to the heat applied.

*Black.*—Wash the metallic surface with a little dilute sulphide of ammonium, and dry at a great heat. Then polish with a hard brush.

*Collodion Varnish to Prevent the Tarnishing of Silver and Silver-plated Wares.*—Many efforts have been made to devise a method of preventing the tarnishing of silver and silver-plated wares upon exposure to the atmosphere. The blackening which such articles speedily suffer is principally due, as has been explained, to the formation of a superficial film of silver sulphide by the action of the sulphurous vapors in the atmosphere, espe-

cially in cities where the large consumption of coal and of coal-gas charges the atmosphere with sulphur compounds.

Of all the suggestions that have been made to accomplish this object none appear to have given such satisfactory results as a varnish of collodion (soluble gun-cotton, photographer's cotton), a solution of gun-cotton in a mixture of ether and alcohol. All other varnishes appear to impart a yellowish tint to the silver or silvered wares; but collodion varnish is quite colorless. The articles should be carefully brushed over with the varnish, with an elastic brush, making sure that the entire surface is covered. The film of collodion will protect the underlying metal for a long time.

*Lustrous Gold or Green on Brass.*—Puscher recommends the following procedures for producing a golden coloration upon brass (*Kunst u. Gewerbe*, 1883, 59). Dissolve 4 parts each of caustic soda and milk sugar in 100 parts of water. Heat the solution to boiling for a quarter of an hour; remove the vessel containing the dark yellow solution from the fire, and add with stirring 4 parts of a cold saturated solution of sulphate of copper. When the fluid has cooled off to about 165° Fah., and after the separated suboxide of copper has settled, the clean, polished articles of brass are introduced into it, in a vessel of wood with perforated bottom. In about two minutes the golden coloration will probably be dark enough, and the articles are removed, washed and dried in sawdust. If the articles are permitted to remain for a longer time in the liquid, the yellowish color at first developed will change to a lustrous bluish-green, and finally to iridescent colors. In order to obtain uniform colorations, the temperature must be maintained between 140° and 165° Fah.

The copper bath may be used repeatedly, and for this purpose should be kept in a well-stoppered flask. When it has become spent, it may be revived by the addition of one part of caustic soda, of the quantity of water evaporated, heating to boiling, and the addition of 2½ parts of sulphate of copper. If, instead of milk-sugar, glycerine or a bitartrate is used, the colors obtained are not so uniform.

*Colorations on Surfaces.*—Puscher (*Neueste Erfind.*, etc.) proposes the following procedure for obtaining a permanent dark or



light green coating, resembling enamel on articles of zinc, especially those of sheet zinc. Fifty parts of hyposulphite of sodium are dissolved in 500 parts of boiling water, and the solution poured at once, in a fine stream, into 25 parts of strong sulphuric acid. [We should prefer to reverse the operation, namely, to pour the acid into the salt solution.—W.] The milk of sulphur that separates will soon ball together in lumps, and settle. The hot liquid containing sulphate of sodium and sulphurous acid is decanted, and the cleansed zinc placed in it. In a short time it will acquire a very brilliant light green coating, which only needs to be washed and dried.

By exposing it, and for a longer time, to this hot bath, the coating grows thicker, and the color darker and more brilliant. The temperature should not be allowed to fall below 145° Fah., to insure a fine, brilliant deposit.

By dipping the articles thus treated in diluted hydrochloric acid (1 acid to 3 water) sulphuretted hydrogen is evolved, and this enamel-like coating loses its lustre and becomes lighter in color. Aqueous solutions of aniline colors have little effect upon this dull surface, and none whatever on the brilliant coating.

The effect of "marbling" can be obtained by moistening the gray zinc and applying hydrochloric acid in spots with a sponge, then rinsing off, and, while still wet, flowing over it an acidified solution of sulphate of copper, which produces the appearance of black marble. As this has a dull surface it should be varnished.

By adding 15 parts of chrome alum and 15 more of the hyposulphite to the above solution, the article treated will take on a brownish color. The above treatment may be applied, according to Puscher, to articles of sheet and cast zinc [and also to galvanized wares.—W.].

*Colored Coatings for Metals.*—The following method of procedure for obtaining decorative effects on metal surfaces, although it has never yielded entirely satisfactory results in our hands, is so highly spoken of by some other writers (notably by Urquhart) that we are induced to attribute our want of success to our having failed in giving it proper care. It is as follows:—

In a quart of pure water dissolve one ounce of hyposulphite of



**sodium.** Stir into this another solution, made by dissolving an ounce of acetate of lead in a pint of water.

For use, heat the solution in a glass or earthenware pan to about 195° Fah., and immerse the metal required to be colored. The coating is one of lead sulphide, and its depth of color will depend upon the time the metal is immersed. In a few minutes brass articles of small size may be coated with any color, varying from golden yellow to the tint of clean copper or red gold, to carmine, down to dark red, from light aniline blue to bluish-white, then to reddish-white or brown.

Urquhart remarks of this process, that it is not a good plan to plunge the articles into the solution without previous preparation; it is by far best to chemically clean them as for plating, and, before dipping in the coloring liquid, to keep them for a few minutes in hot water, unless the coating is to be very slight indeed. Steel and iron articles may also be treated, and given a fine blue color, without the aid of such great heat as is necessary in "bluing" or oxidizing. Copper articles do not, of course, show the lighter tints. If the cleaning is well done, the adhesion will be perfect, so perfect indeed, that the burnisher may be used with impunity; but it is not prudent to use the scratch-brush. Instead of burnishing, however, the surface may be finished by a soft and smooth buff, which will impart a lasting polish.

The solution will not keep long in the heated state, as it deposits its sulphide upon the bottom of the vessel if no metals are present.

It is stated that an exceedingly beautiful red and green coloring can be given to brass articles by omitting the lead, and using in its stead an equal weight of sulphuric acid (see *Colorations on Zinc Surfaces*, page 618). If the immersion continues, the red changes to a fine, brilliant green, and then to green and brown, with a splendid iris glitter. The coating is very durable, unlike the others, which are but lacquered over with pale lacquer (Urquhart).

The same authority affirms that clean brass and copper may be covered with a firmly adherent pure black coating by placing them very near to the flames of burning straw. It will not rub off, and may be polished with a soft cloth.

## REFINING AND EXTRACTION OF METALS BY ELECTROLYSIS (on the Commercial Scale).

Although this subject does not fall properly within the province of this work, it may be of use to some of our readers to notice that great progress has been made during the past few years in the application of the electrolytic process to the extraction of metals from their ores—and the refining of impure metals (copper, argentiferous lead) on the commercial scale. In these operations, it need scarcely be explained, steam-driven dynamo-machines are used. Such electro-metallurgical processes are carried on, on a scale of greater or less magnitude, in Germany, England (Wales), and the United States.

For special information on this subject, the reader is referred to the files of the technical Journals, particularly to *Dingler's polytech. Journal*, and the *Engineering and Mining Journal*, in which the progress of this branch of the metallurgical industry is very fully recorded.

*Depositing Copper on Steel Wire.*—An interesting operation showing the perfection to which the electrolytic deposition of copper has been brought, is the manufacture of what is known as "Compound Wire," which is carried out on a large scale at Ansonia, Connecticut, by the Postal Telegraph Company.

This compound wire consists of a steel wire core, weighing 200 pounds to the mile, and having a tensile strength of 1650 pounds, on which copper is deposited continuously by the galvanic process, and of any desired thickness. On the present scale of these works, the electric currents for depositing the copper are generated by twenty-five large steam-driven dynamo-machines, with the aid of which 10,000 pounds of copper are deposited per day, representing 20 miles of "compound wire" carrying 500 pounds of copper to the mile. At the time of this writing, the company has announced its intention to shortly double the capacity of its works. The "compound wire" is used for telegraphic purposes, for which on account of its high conductivity and strength it is claimed to possess many advantages over the galvanized iron wire at present generally used for that purpose.

LISTS OF AMERICAN AND BRITISH PATENTS BEARING ON THE  
SUBJECT OF THE ELECTRO-DEPOSITION OF METALS.

AMERICAN PATENTS.

1850. December 10. No. 7,821. G. Mathiot. Electrotyping.  
1855. September 4. No. 13,516. J. A. Adams. Electrotyping machine.  
1856. December 2. No. 16,141. W. Filmer and E. Bookhout. Mode  
of backing electrotype plates.  
1857. July 7. No. 17,741. A. H. Jocelyn. Method of backing electro-  
type plates.  
1858. May 25. No. 20,353. S. P. Knight. Production of electrotype  
plates.  
“ September 14. No. 21,509. H. Lovejoy and R. Wheeler. Machine  
for coating electrotype moulds.  
1859. May 3. No. 23,836. W. H. Elliot. Mode of forming curved elec-  
trotype plates.  
“ November 1. No. 25,953. T. Crossley. Electrotype printing  
block.  
1860. November 20. No. 30,663. A. Berthoud. Electro-plating with  
alloys of gold.  
1861. November 12. No. 33,721. J. von Liebig. Electro-plating with  
copper, etc., the surfaces of mirrors, etc.  
1862. February 18. No. 34,470. J. E. Walcott. Process of electro-plat-  
ing iron and other metals with copper.  
“ March 11. No. 34,640. M. Miller, Jr. Mode of electro-plating  
steel wires for piano-strings, etc.  
“ October 21. No. 36,750. C. Beslay. Process of electro-plating iron,  
steel, etc.  
1865. December 26. No. 51,714. J. D. Grüneberg. Manufacture of plated  
metal.  
1867. February 19. No. 62,251. S. A. Chapman. Plated-ware burnish-  
ing machine.  
“ April 2. No. 63,512. S. Hallock. Surface conductor for electro-  
typing.  
“ May 28. No. 65,084. E. Hunter. Compound for silver plating.  
1868. March 10. No. 75,258. M. L. Forbes. Frame for plating spoons,  
etc., heavier at certain parts than at others.



1868. June 2. No. 78,497. W. H. Watrous. Electro-plating frame.  
“ June 30. No. 79,427. H. W. Wright. Electro-plating and plated ware.  
“ July 28. No. 80,402. W. Gates. Electro-plating apparatus.  
“ October 6. No. 82,877. W. H. Remington. Process of electro-plating with nickel.  
“ November 17. No. 84,243. J. P. Woodworth. Electro-plating.  
“ December 29. No. 85,411. S. D. Tucker. Machine for coating surface of electrotype moulds with plumbago.
1869. April 27. No. 89,522. H. Tucker. Plating metals.  
“ May 2. No. 87,442. G. J. Sturdy and S. W. Young. Cleaning metallic articles for plating and gilding.  
“ May 25. No. 90,332. I. Adams, Jr. Mode of electro-plating with nickel.  
“ June 1. No. 90,893. H. Tucker. Electro-gilding iron.  
“ June 1. No. 90,894. H. Tucker. Electro-plating and gilding cast iron.  
“ August 3. No. 93,157. I. Adams, Jr. Electro-deposition of nickel.  
“ December 21. No. 98,110. S. Rust, Jr. Electro-plating with brass and other alloys.
1870. January 25. No. 99,192. P. S. Hoe. Electrotyping battery.  
“ February 22. No. 100,098. J. S. Howard. Electro-plating with antimony.  
“ March 22. No. 100,961. I. Adams, Jr. Electro-deposition of metals.  
“ March 22. No. 101,075. H. W. Wright. Electro-plating apparatus.  
“ April 19. No. 102,077. J. A. Adams. Electrotyping.  
“ May 10. No. 102,748. I. Adams, Jr. Electro-deposition of nickel.  
“ May 17. No. 103,201. W. J. Kuhns. Nickel-plating.  
“ November 1. No. 108,940. J. Rogers. Finishing the surface of plated goods.  
“ November 29. No. 109,633. A. Law. Electro-plating iron and steel with silver.
1871. February 7. No. 111,688. D. Strymgeour. Electrotype die or mould for moulding plastic materials.  
“ February 21. No. 111,945. M. J. A. Keane. Plating and polishing compound.  
“ March 28. No. 113,090. J. J. Pratt. Electro-plating letters and numbers on metallic plates for signs, etc.  
“ May 30. No. 115,490. W. A. Leggo. Process of obtaining moulds for electrotyping purposes.  
“ April 4. No. 113,612. I. Adams, Jr. Electro-plating with nickel.  
“ April 25. No. 114,191. D. D. Parmelee. Electro-plating the interior of pipes and tubes with silver, nickel, etc.  
“ May 2. No. 114,447. S. P. Knight. Electrotype mould.

1871. June 13. No. 115,926. J. E. Bingham. Electro-plating with tin.  
“ July 4. No. 116,579. M. G. Farmer. Nickel-plating.  
“ July 4. No. 116,658. I. Adams, Jr. Nickel-plating.  
“ October 3. No. 119,622. W. A. Leggo. Electrotyping.  
“ November 28. No. 121,383. N. S. Keith. Nickel-plating.
1872. April 16. No. 125,868. J. A. Whitman and T. M. Neal. Nickel-plated articles.  
“ July 16. No. 129,124. A. L. Freeman. Apparatus for electro-plating iron with copper, etc.  
“ July 30. No. 129,881. G. W. Beardslee. Electro-plating with nickel and other metals.  
“ August 6. No. 130,140. A. Judson. Forming curved electrotypes.  
“ August 13. No. 130,362. E. E. De Lobstein. Plating and coating metals.  
“ September 10. No. 131,169. S. P. Knight. Coating electrotype moulds.
1873. March 11. No. 136,634. I. Adams, Jr. Nickel-plating.  
“ July 22. No. 140,995. A. and H. T. Dawson. Method of etching plates for electrotyping.
1874. March 10. No. 148,459. W. C. Homan. Electro-plating apparatus for weighing metal deposited.  
“ April 21. No. 149,974. G. W. Beardslee. Electro-plating with cobalt.  
“ June 9. No. 151,832. H. T. Brownell. Nickel-plating.  
“ June 9. No. 151,892. H. and H. W. Lovejoy, J. H. Ferguson, and M. J. Creagan. Electro-plating apparatus.  
“ August 4. No. 153,726. W. A. Shaw. Electro-plating tin pipes or tubes with copper, brass, etc.  
“ August 25. No. 154,435. I. Adams, Jr. Nickel-plating.  
“ October 6. No. 155,700. E. Boy. Electro-plating bath.  
“ October 13. No. 155,884. P. A. Normandeu. Nickel-plating.  
“ December 22. No. 157,965. S. P. Knight. Electrotype mould.
1875. January 19. No. 158,972. R. E. Osborn. Electro-plating rack.  
“ April 27. No. 162,627. H. G. Coyle. Electro-plating solution.  
“ April 27. No. 162,630. H. P. Dechert. Electro-plating with nickel.  
“ August 3. No. 166,367. A. Hermann and W. H. Taylor. Anodes for electro-plating with nickel.  
“ August 3. No. 166,433. E. Weston. Manufacture of anodes for nickel-plating.  
“ August 10. No. 166,606. E. Hansen. Electro-plating glass, china, etc.  
“ December 21. No. 171,464. W. E. Worthen and R. S. Gillespie. Electro-plating statuettes, etc.
1876. February 1. No. 172,862. I. Adams, Jr. Cobalt electro-plating.  
“ March 14. No. 174,691. C. Maggio and G. Maffiola. Nickel-plating.

1877. March 21. No. 175,134. C. S. Minchew. Electro-plating. \*
1877. November 6. No. 196,846. E. Weston and E. E. Quimby. Compound switch in dynamo-electric machine employed in electro-plating.
- “ November 20. No. 197,408. J. W. Rogers. Electro-plating frame.
1878. December 17. No. 211,071. E. Weston. Nickel-plating.
1880. January 6. No. 223,265. J. Wharton. Electro-plating with nickel.
- “ January 27. No. 223,860. J. H. Potts. Electro-deposition of nickel.
- “ February 3. No. 224,263. J. Yates. Electro-deposition of nickel.
- “ February 10. No. 224,478. J. W. Rogers. Electro-plating frame.
- “ June 1. No. 228,224. E. B. Sheldon. Electrottype mould.
- “ June 1. No. 228,389. J. Powell. Solution for electro-deposition of nickel.
- “ June 29. No. 229,274. J. Powell. Electro-plating with nickel.
- “ August 10. No. 230,857. M. Briggs. Apparatus for coating small articles, tacks, etc., with tin, lead, or zinc.
- “ August 10. No. 230,872. H. L. Haas. Solution for nickel-plating.
- “ September 28. No. 232,615. C. G. Pendleton. Solution for nickel-plating.
- “ September 28. No. 232,755. J. H. Potts. Solution for the electro-deposition of nickel.
- “ November 23. No. 234,775. R. B. Herskell. Holder for electro-plating.
- “ November 30. No. 235,034. C. N. Smith. Uniting electrottype and stereottype plates.
1881. May 17. No. 241,721. H. Roberts. Coating metals with zinc.
- “ May 31. No. 242,263. G. Brucker. Nickel-plating fluid.
- “ June 7. No. 242,624. W. Frishmuth. Coating metals with lead, zinc, or tin.
- “ July 12. No. 244,146. H. Roberts. Coating metals with zinc.
- “ July 12. No. 244,234. P. Higgs. Reduction of metals from their ores by electrolysis.
- “ August 2. No. 245,164. C. H. Hanson. Machine for metallizing electrottype moulds.
- “ August 2. No. 245,206. H. J. Müller. Electro-plating circuit.
- “ October 18. No. 248,554. M. H. Campbell. Electro-plating with an alloy of platinum and silver.
1882. January 31. No. 253,159. M. H. Campbell. Electro-plating with platinum and silver.
- “ March 28. No. 255,421. P. A. Dodé. Gilding metals.
- “ May 3. No. 257,065. A. O'Neill. Electro-plated yellow metal.
- “ May 23. No. 258,214. A. Brinckman. Apparatus for electro-plating.
- “ August 1. No. 262,124. H. Roberts. Coating metals with zinc.



- 1882.** October 3. No. 265,340. S. M. Puffer. Attachment to dynamo-electro-plating machines.
- “ November 28. No. 268,127. H. Roberts. Apparatus for coating metals with metal.
- 1883.** March 6. No. 273,324. J. M. Thomas. Composition for brass electro-plating.
- “ March 6. No. 273,467. A. Classen. Electro-plating with copper, iron, zinc, nickel, etc.
- “ June 5. No. 278,784. L. F. Dunn. Electro-plating with nickel.
- “ July 3. No. 280,466. J. A. Graham. Coating iron with lead.
- “ July 10. No. 280,864. C. F. Rebstock. Composition for coating metallic substances.
- “ August 14. No. 10,367. R. Reusch (re-issue). Plating iron and steel with other metals.

## BRITISH PATENTS.

- 1836.** June 24. N. 7134. G. R. Elkington. Gilding copper, brass, and other metals.
- 1837.** February 17. No. 7304. H. Elkington. Coating metals.
- “ December 4. No. 7496. H. Elkington. Gilding and silvering certain metals and apparatus for the same.
- 1838.** July 24. No. 7742. G. R. Elkington and O. W. Barratt. Coating metals.
- 1840.** March 3. No. 8407. J. Shore. Electro-coating metals with copper and nickel.
- “ March 25. No. 8447. G. R. and H. Elkington. Electro-deposition of silver, gold, and copper.
- “ August 15. No. 8604. P. A. Fontainemoreau. Improvements in coating metals with gold, silver, and platinum.
- 1841.** March 29. No. 8905. A. Parkes. Production of works of art by electro-deposition.
- “ September 8. No. 9077. O. W. Barratt. Electro-depositing zinc on other metals. Electro-coppering iron, etc.
- “ December 9. No. 9167. W. H. F. Talbot. Ornamenting and coloring metallic surfaces.
- 1842.** June 1. No. 9374. H. B. Leeson. Manufacturing platinum and other metals from their ores.
- “ June 4. No. 9379. E. Tuck. Plating metals and alloys with silver.
- “ August 1. No. 9431. J. S. Woolrich. Magneto-electric machine for electro-plating.
- “ November 25. No. 9528. W. H. F. Talbot. Preparing surfaces for gilding and silvering.

1843. February 21. No. 9641. B. B. Blackwell and W. Morris. Electro-deposition of copper and iron.
- “ April 11. No. 9693. J. Napier. Electro-coating fabrics.
- “ May 4. No. 9720. E. Morewood and G. Rogers. Coating metals.
- “ May 25. No. 9741. M. Poole. Thermo-electric battery for depositing metals.
- “ June 15. No. 9786. O. W. Barratt. Improvements in batteries.
- “ December 8. No. 9982. J. Schottlaender. Electro-coating fabrics, glass, earthenware, etc.
1844. July 31. No. 10,282. P. A. Fontainemoreau. Electro-depositing brass.
- “ October 29. No. 10,366. A. Parkes. Depositing metals by electric currents from their fused salts.
1845. October 9. No. 10,860. A. Parkes. Ornamenting the surfaces of metals.
1846. December 12. No. 11,448. L. H. Piaget and P. H. DuBois. Improvements in gilding solutions and batteries.
1847. August 3. No. 11,828. T. Fletcher. Manufacture of speculums.
- “ September 30. No. 11,878. C. De la Salzede. Improvements in electro-brassing and bronzing.
- “ November 4. No. 11,943. C. M. T. Du Motay. Producing incrustated or damaskene surfaces.
1849. March 14. No. 12,523. P. A. Fontainemoreau. Improvements in solutions for gilding, platinizing, brassing, etc.
- “ March 19. No. 12,526. T. H. Russell and J. S. Woolrich. Electro-depositing cadmium and its alloys.
- “ March 26. No. 12,534. A. Parkes. Electro-depositing copper, silver, tin, bismuth, etc., in successive layers.
- “ June 7. No. 12,654. S. B. Smith. Improvements in bright silvering.
1850. March 23. No. 13,020. A. G. Roseleur. Electro-tinning bath.
- “ August 9. No. 13,216. J. Steele. Coating metallic surfaces to give them the appearance of tin or bronze. Electro-gilding and silvering.
1851. February 17. No. 13,513. C. Cowper. Improvements in elastic moulds.
1852. April 20. No. 14,080. J. Ridgway. Preparing china, glass, earthenware, etc., to receive electro-deposits.
- “ October 9. No. 323. J. J. Rousseau. Producing ornamental plates by electrotyping.
- “ December 8. No. 996. J. Symonds and G. Mouchet. Cleaning or sealing metallic surfaces.
- “ December 11. No. 1032. T. Morris and W. Johnson. Electro-deposition of alloys.

- 1852.** December 28. No. 1183. C. J. E. Junot. Electro-deposition of silicium, titanium, molybdenum, etc.
- “ December 29. No. 1196. J. Power. Improvements in electro-silvering metals and glass.
- 1853.** July 2. No. 1593. R. A. Brooman. Electro-deposition of metal on yarns, threads, and fabrics.
- “ July 29. No. 1777. W. E. Newton. Electro-deposition of alloys; obtaining thick electro-deposits.
- “ August 5. No. 1836. W. Newton. Coating cast iron with copper or brass.
- “ October 7. No. 2292. W. Ellis. Electro-deposits on porcelain, pottery, etc.
- “ November 7. No. 2579. H. Pershouse and T. Morris. Electro-depositing metallic alloys.
- 1854.** March 20. No. 661. J. Perkins. Improvements in electrotyping.
- “ April 3. No. 763. G. Devincenzi. Moulds for galvanoplastic impression.
- “ April 27. No. 951. C. C. Person. Electro-zincing.
- “ May 5. No. 1006. E. Haseler. Ornamenting metals, papier mâché, horn, and shell.
- “ July 4. No. 1471. J. H. Johnson. Coating iron with copper.
- “ December 21. No. 2699. J. H. Johnson. Galvanoplastic processes.
- “ December 26. No. 2724. F. S. Thomas and W. E. Tilley. Plating lead, iron, and other metals with tin, nickel, aluminium, etc.
- 1855.** January 3. No. 18. J. H. Johnson. Coating iron with copper.
- “ February 3. No. 253. F. S. Thomas and W. E. Tilley. Electro-depositing alloys of silver, tin, copper, and nickel.
- “ February 13. No. 332. R. P. Cornfield. Electro-plating iron and other metals with zinc.
- “ March 17. No. 598. T. Petitjean and L. Pêtre. Giving a perfectly smooth, polished surface to electro-plated copper.
- “ June 5. No. 1276. F. Puls. Electro-coating iron and zinc.
- “ July 10. No. 1543. C. J. C. Elkington. Electro-depositing alloys.
- “ September 4. No. 1997. J. G. Taylor. Electro-plating with aluminium.
- “ October 4. No. 2215. H. Cornforth. Electro-coating hooks and eyes, with copper, brass, and silver.
- “ October 12. No. 2280. F. Puls. Electro-coating metals or alloys of metals.
- “ December 3. No. 2721. A. Watt. Electro-zincing iron and steel.
- “ December 6. No. 2756. F. S. Thomas and W. E. Tilley. Electro-plating metals with aluminium and its alloys.
- 1856.** January 12. No. 91. C. F. L. Oudry. Preserving metals.



1856. February 14. No. 385. E. Morewood and G. Rogers. Improvements in coating iron and copper.
- “ March 10. No. 580. L. Chablin and A. Hennique. Ornamenting porcelain, glass, etc.
- “ April 15. No. 899. E. R. Southby. Coating iron with copper.
- “ June 4. No. 1335. R. A. Brooman. Improvements in plating glass.
- “ October 25. No. 2597. G. Ernst and W. Lorberg. Electro-etching.
- “ December 17. No. 2992. C. Cowper. Improvements in electro-plating.
1857. January 1. No. 5. E. T. Noualhier and J. B. Prévost. Electro-depositing metals on hard or vitrified surfaces.
- “ January 9. No. 79. J. H. Johnson. Improvements in galvanoplastic processes.
- “ January 27. No. 240. G. T. Bousfield. Coating metals with tin.
- “ March 25. No. 826. C. F. L. Oudry. Electro-depositing copper.
- “ March 31. No. 887. S. J. Goode. Electro-depositing metallic alloys.
- “ April 25. No. 1175. J. Burrow. Improvements in coating wrought-iron.
- “ April 27. No. 1180. C. Cowper. Solutions for electro-depositing gold and silver.
- “ June 1. No. 1540. W. A. Walein. Using alkaline tartrates in electro-depositing solutions.
- “ June 24. No. 1766. A. Parkes. Improvements in coating metals.
- “ July 1. No. 1835. W. E. Newton. Producing printing surfaces.
- “ July 30. No. 2074. S. Coulson. Electro-deposition of aluminium.
- “ December 19. No. 3115. T. Newey, J. Corbett, and W. H. Parkes. Electro-tinning pens and pen-holders.
1858. February 23. No. 353. E. C. Shepard. Giving iron, zinc, and other metals the appearance of bronze, brass, copper, etc.
- “ March 12. No. 597. L. F. Corbelli. Production of aluminium by electrolysis.
- “ March 22. No. 594. G. Davies. Metallization of objects for electro-plating.
- “ March 29. No. 667. E. A. Jacquin. Coating electrotypes with iron.
- “ September 27. No. 2161. W. Lander. Ornamenting china and earthenware.
- “ October 28. No. 2409. W. Munro. Manufacturing capsules by electric deposition.
- “ December 16. No. 2890. R. A. Brooman. Improvements in electro-plating forks, spoons, etc.
1859. January 12. No. 103. C. Beslay. Electro-coating iron or steel with tin, zinc, or lead.

1859. April 30. No. 1083. J. Toussaint. New process in modelling and moulding for galvanoplastic.
- “ December 6. No. 2764. F. Potts. Electro-coating brass, iron, and other boiler tubes with copper.
1860. January 26. No. 204. W. E. Newton. Manufacture of gold by electrolysis.
- “ March 10. No. 653. T. Morris. Improvements in vats and depositing metals.
- “ March 22. No. 748. G. T. Peppe. Coating sheet lead with tin.
- “ June 6. No. 1385. E. T. Hughes. Coating or plating the faces of printing type and stereotype plates with brass and other alloys.
- “ June 22. No. 1523. N. Grattan. Improvement in gilding steel and other metals.
1861. January 7. No. 44. W. Bagley and W. Wincher. Coating metals and alloys of metals.
- “ January 19. No. 145. B. Piffard. Rendering non-conductive surfaces conductive.
- “ March 13. No. 619. J. Cimeg. Silvering glass and other surfaces.
- “ May 13. No. 1214. T. Bell. Electro-deposition of aluminium.
- “ August 14. No. 2023. R. A. Brooman. Coating wire with copper, silver, gold, or other metal or alloy.
- “ November 5. No. 2784. G. T. Bousfield. Electro-depositing copper from solutions in igneous fusion.
- “ November 23. No. 2944. J. Weens. Improvements in the manufacture of metallic tubes, and in coating and plating metals.
1862. May 21. No. 1538. W. E. Newton. Manufacture of mineralized fabrics.
- “ June 28. No. 1896. C. Beslay. Coating metals by electro-chemical agency, and apparatus therefor.
- “ August 30. No. 2410. J. H. Johnson. Electro-coating cast or wrought iron, zinc, etc., with copper.
- “ October 3. No. 2675. A. Dalrymple. Depositing metals by galvanic action, and ornamenting metallic surfaces thereby.
- “ December 8. No. 3288. C. Sanderson. Electro-brassing steel driving bands.
1863. August 22. No. 2088. S. Moore. Improvements in apparatus for electro-plating.
1864. February 29. No. 497. F. Weil. Improvements in electro-plating solutions.
- “ August 15. No. 2029. S. Moore. Improvements in electro-gilding.
- “ December 14. No. 3095. S. B. Thompson. Improvements in coating iron or steel with silver, gold, platinum, etc.
1865. June 5. No. 1541. W. E. Newton. Photo-electrotyping process.
- “ October 2. No. 2521. T. Allan. Preparation of iron and steel and other metals for electro-plating.

1865. October 7. No. 2592. J. B. Thompson. Improvements in coating iron and steel with gold, silver, platinum, and copper.
- “ October 26. No. 2762. H. Wilde. Electro-magnetic induction machine.
1866. February 14. No. 469. M. Henry. Printing surfaces by electro-metallurgy.
- “ August 15. No. 2095. J. Webster. Improvements in coating and recovering metals from chloride and other metallic solutions
- “ November 20. No. 3047. C. E. Brooman. Coating or covering iron and steel with copper or copper alloys.
1868. May 29. No. 1777. G. T. Bousfield. Improvements in plating spoons.
- “ August 14. No. 2545. J. B. Thompson. Coating iron and steel with gold, silver, and copper, and apparatus for the same.
- “ October 10. No. 3117. W. R. Lake. Improvements in electro-plating with nickel.
- “ October 15. No. 3153. H. A. Bonneville. Elastic moulds for electrotyping.
- “ December 19. No. 3871. J. Jones. Removing vapor from electro-depositing baths.
- “ December 24. No. 3930. W. H. Walenn. Electro-deposition of copper and brass.
1869. July 26. No. 2268. W. E. Tilley. Electro-plating various metals with tin.
- “ August 17. No. 2456. M. H. Jacobi. Galvanoplastic deposition of iron.
- “ October 6. No. 2901. B. Hunt. Producing reliefs by galvanic deposition.
- “ October 28. No. 3125. W. Brookes. Electro-deposition of nickel (Adams's process).
- “ October 30. No. 3159. A. Minton. Electro-coating iron and other metals.
- “ November 23. No. 3377. H. A. Bonneville. Improvements in electro-plating.
1870. February 2. No. 363. I. Adams, Jr. Electro-deposition of nickel.
- “ April 12. No. 1068. I. Adams, Jr. Electro deposition of nickel.
- “ August 27. No. 2359. W. R. Lake. Improvements in the manufacture of tacks and nails.
- “ September 15. No. 2491. H. E. Towle. Electro-plating the interior of lead and other metallic tubes or pipes.
- “ September 28. No. 2580. J. E. Bingham. Electro-deposition of tin.
- “ November 16. No. 3005. G. Haseltine. Electro-plating iron and steel with gold or silver.
- “ December 30. No. 3396. E. D. Nagel. Electro-deposition of nickel or cobalt.



1871. June 8. No. 1511. H. Wilde. Improvements in the manufacture of boiler tubes and apparatus therefor.
- “ June 21. No. 1626. J. Unwin. Coating metals with nickel.
- “ August 29. No. 2266. T. Fearn. Depositing alloys by electricity.
- “ September 16. No. 2450. W. H. Maitland. Coating metals with copper.
- “ October 4. No. 2623. E. E. de Lobstein. Coating and ornamenting metals.
- “ December 21. No. 3459. J. Unwin. Coating metals with nickel.
1872. May 6. No. 1376. Fitzgerald and Molloy. Decomposing compound substances by electricity.
- “ July 24. No. 2208. W. T. Allen and D. T. Fitzgerald. Electro-deposition of metals.
- “ December 5. No. 3680. T. Petitjean. Producing metallic surfaces and articles by electro-deposition.
- “ December 18. No. 3839. J. Noad. Manufacture of electrotypes.
- “ December 31. No. 3970. J. H. Johnson. Depositing copper and its alloys on iron.
1873. April 7. No. 1277. T. Fearn. Electro-deposition of tin.
- “ July 2. No. 2302. W. R. Lake. Electro-plating with nickel.
- “ October 14. No. 3322. S. Delalot. Silvering and gilding iron.
1874. April 29. No. 1492. H. J. Brook, E. G. Draper, and J. Unwin. Preparation of articles to be electro-coated with nickel and other metals.
- “ April 29. No. 1493. W. Baker and J. Unwin. Electro-deposition of nickel.
- “ September 4. No. 3033. J. B. Thompson. Improvements in coating steel and iron with gold, silver, and other metals.
- “ September 15. No. 3148. W. Morgan Brown. Deposition on metals on glass and earthenware.
- “ October 19. No. 3587. J. W. Perkins. Anodes for nickel-plating.
1875. December 11. No. 4302. R. J. Blewitt. Electro-coating iron and other metals with tin.
1876. June 20. No. 2554. R. M. Prior. Electro-plating with nickel.
1877. March 14. No. 1023. E. T. Hughes. Electro-plating wire.
- “ April 20. No. 1548. J. Unwin. Electro-depositing solutions of nickel.
- “ September 15. No. 3476. W. R. Lake. Electro-coating metals with tin.
1878. January 29. No. 380. A. Van Winkle. Coating baser metals with gold, silver, or platinum.
- “ August 27. No. 3392. F. Maxwell-Lyte. Coating iron and steel with copper or nickel, and producing iridescent films.
- “ November 11. No. 4573. G. Zanni. Electro-deposition of metals.

1878. December 2. No. 4921. W. R. Lake. Electro-deposition of nickel and other metals.
- " December 14. No. 5127. F. C. Glaser. Plating metals with nickel and cobalt.
1879. February 11. No. 529. T. H. Blake. Electro-plating brass. German-silver, nickel, copper, iron, and steel.
- " March 26. No. 1203. E. A. Clowes and J. Batey. Moulds for electrotyping.
- " April 8. No. 1397. H. Krupp. Improvements in silver-plating.
- " September 30. No. 3927. W. E. Gedge. Improved galvanoplastic process.
- " October 11. No. 4119. W. H. and G. Wilkinson. Ornamenting electro-plated wares.
1880. April 16. No. 1556. H. A. V. Wirth. Electro-plating and gilding wood.
- " July 24. No. 3043. F. C. Glaser. Plating iron and steel, copper and alloys, with nickel, cobalt, etc.
1881. March 3. No. 922. J. Elmore. Galvanizing iron by electricity.
- " April 23. No. 1764. A. Gutensohn. Coating lead and other metals with tin.
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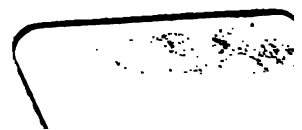
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