UNITED STATES PATENT OFFICE.

HANNIBAL GOODWIN, OF NEWARK, NEW JERSEY.

METAL ORNAMENTATION.

SPECIFICATION forming part of Letters Patent No. 670,277, dated March 19, 1901.

Application filed January 20, 1892. Serial No. 418,700. (No specimens.)

To all whom it may concern:

Be it known that I, HANNIBAL GOODWIN, a citizen of the United States, residing at Newark, in the county of Essex and State of New Jersey, have invented certain new and useful Improvements in Methods of Preparing Plates for Decoration or Utility; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention has for its objects, stated generally, the securing upon metal by chemical and electrochemical means designs in another metal for utility or ornament, in sharper and clearer outline, and in finer definition of detail and with a greater facility and certainty than have hitherto been obtained.

The invention relates to that class of processes represented by those described in my prior patents, Nos. 444,951, 459,136, and 459,137.

The invention consists in the improved process of preparing plates for decoration or utility, all substantially as will be hereinafter set forth, and finally pointed out in the claims.

Among the defects hitherto in the formation of a metallic design in one metal facing on or upon a bed of another metal by means of stripping all portions of the metal facing except all those constituting the design one has been the great difficulty of preserving the design from the loss of a certain amount of sharpness, fineness, and definition of detail arising both from the irregular action of the stripping agent and from an inadequate fineness, sharpness, and delicate outline of the resisting design—as, for example, in the latter case the resisting designs applied in viscid organic matter, such as asphaltum, by hand and brush did not and could not possess those qualities of sharpness and detail contemplated in this invention. To avoid these defects, I employ on my plate a resisting design of such sharpness and perfection of detail as cannot be produced by the hand and brush, and I employ a chemical stripping agent which entails no raggedness or unevenness upon the completed metallic design.

Among the defects hitherto in the process of forming upon the bed metal a metallic design by electrodeposition one has been the tendency of the deposited metal to penetrate through the resisting matter designed to exclude the said deposition metal and then adhere to the bed metal. To avoid this defect, I render the said portions of the bed metal non-adherent.

The chief defect hitherto in engraving deeper those portions of the bed-plate not covered by the design when it is required to enhance the ornamental effect or to employ the plate for other utilities has been the injury done to the outline of the remaining design by the mordant employed for engraving the bed metal. To avoid this defect, I employ such metals for the design as are not affected by the mordant used in the process of engraving.

In carrying into effect that part of the invention which relates to the formation of an ornamental or otherwise useful metallic design on a bed metal by the stripping of the portions of the metal adjacent to the design I first proceed by any of the well-known methods to face a plate of metal or an article of metal ware with a facing of silver or gold or platinum, these metals being the most ornamental and also most resisting to engraving-mordants, both because of the electronegative relation to the bed-plate which they ordinarily assume when immersed in etching agents and because of more or less inherent insolubility in most of said mordants. I next proceed to apply to said facing a resisting-design in organic matter, which I preferably apply by means of some one of the well-known photographic methods, because such a method requires less labor and less artistic skill and yet secures the utmost sharpness of outline and delicacy of detail, and this method is industrially useful. The organic matter thus employed may consist of an attenuated film of gelatin photographically impressed directly on this plate and preferably covered with a coating of fatty ink and reinforced by some resisting-dust. There are other methods of forming a suitable design in resisting organic matter too well known to require specification. The design having been thus applied, I next proceed to strip away those portions of the facing not protected by

the design by a process which is one of the features of my invention and which just here I must distinguish from other processes employed for similar purposes.

Two other processes have hitherto been employed for stripping one metal from another, both of which when used for stripping such metals as silver, gold, and platinum bearing a design in organic matter applied as above described are attended with such defects as render them for the purposes of the invention industrially useless. One of these processes referred to consists in subjecting the metallically-faced plate or ware as an anode in an electrolyte consisting of cyanid of potassium; but while this process is successful in stripping the metallic facing it is fatal in that it also strips away the design in organic matter and then renders liable the stripping away of all the facing. Cyanid as an electrolyte is powerfully detergent or a destroyer of organic matter. The other and more commonly employed process of stripping one metal from another is that by strong acids. There are several serious defects in this acid process when applied for the purposes of this invention. Acids appear to produce, between the bed-plate and the facing metal, a galvanic current which seems to render the formation of an electronegative facing difficult in most cases and in some cases impossible and all the more so in proportion as the negative metals possess highly electrical conductivity. Either gold or platinum or silver is not only a facile conductor, but when immersed in an acid and in contact with most other metals becomes highly electronegative, and, as is well known, such a metal standing in such a relation is rendered extremely difficult to dissolve if not quite insoluble, though it would be quite soluble if unconnected with another metal less negative it were immersed in the same acid. For example, silver immersed by itself in a moderately-strong solution of acid is readily dissolved, but if connected with a less negative metal in the same acid it, under the influence of the voltaic current, becomes quite insoluble, or silver, if immersed alone in aqua regia, is rapidly dissolved, but if connected as above aqua regia is powerless. This generation of a voltaic current between the bed metal and the electronegative facing contributes to another very serious defect in the acid process of stripping. The increased insolubility of the facings thus caused by the current demands an increased strength of acids to strip them, and that entails damage upon the organic matter constituting the design. The acids hitherto employed for the specified metals have been aqua regia a mixture of concentrated nitric and hydrochloric acids for stripping gold and platinum, and a mixture of concentrated sulfuric and nitric acids for stripping silver. Nitric acid alone has been unavailing for stripping either gold, platinum, or silver, so also has hydrochloric, and this latter acid would dissolve silver did it not immediately form an insoluble layer of a chlorid of the metal which prevents further action of the acid, a consequence which I avail myself of when I come to etch down a bed metal bearing a design in silver by means of a chlorin-imparting mordant, such as chlorid of iron; but the foregoing acids which have proved successful in stripping away the facings are not less successful in stripping all such designs in organic matter as can be employed for the purposes of this invention, and even if such a design could prove sufficiently resisting there would in consequence of the violent action of the acids be entailed upon the remaining underlying ornamental metal design a raggedness and unevenness of line as another defect in stripping by the acid process, and a further objection not to be overlooked to the use of strong acids is the stifling fumes inimical to health as well as severely disagreeable.

I now come to my process of stripping as distinguished from those heretofore employed. Having, as above described, faced the bed metal with either silver or gold or platinum and having imposed thereon a design in resisting matter, I now proceed to strip away those portions of the facing not covered by the design by subjecting the plate as an anode to an electrolyte containing in solution free iodin and free iodid of potassium, the iodin uniting with the facing to form an iodid or salt of the metal and the iodid of potassium dissolving away the salt as fast as formed. Free bromin may be employed with the iodin, but its use confers no advantage over that of iodin alone, and bromid of potassium may be employed singly or in combination with the iodid of potassium, but its use confers no advantage over that of the iodid of potassium singly. Instead of stripping the facing by subjecting it as an anode I may simply immerse it in the above-specified menstruum; but the electrolyte method is preferable because more rapid. Also I may omit from the menstruum free iodin by employing the iodid of potassium in concentrated or approximately-concentrated solution, although by this substitution the process of stripping is not only slower, but is more expensive. This process of stripping is distinguished by its results and by its mode of operation. It does not generate between the bed metal and its facing a voltaic current. It effects the stripping with facility and certainty without detaching or injuring the organic matter constituting the design. It works with a gentleness that entails no ruggedness or unevenness upon the remaining ornamental metallic design and it develops no noxious fumes.

Though in the process of dissolving a metal by acids there is formed first a chemical compound of the metal which is simultaneously dissolved by the surrounding acid to complete the solution, and though in this respect my process does not differ from the acid process,

yet there are additional features and conditions in my method which distinguishes it and by which the beneficial results are obtained. In the former process the faced plate to be stripped is immersed in acid, and acid is a condition for excitation of a galvanic current between the plate and the facing. In my process the plate is immersed not in an acid, but in a neutral liquid. In the acid process the compound of the metal formed by borrowing an element from the decomposed acid is necessarily as well as simultaneously dissolved away by the acid to which it owes its existence and by nothing else. In my process the iodid compound may be formed independently of the specific menstruum which may be chosen to dissolve it away. There are many menstruums of iodin which are not solvents of iodid compounds. An alcoholic menstruum of iodin will form on the metal facing an iodid of the metal, but it will not dissolve away that salt to complete the stripping, neither will an ammoniacal menstruum nor a menstruum that is chiefly aqueous. A cyanid of potassium menstruum of iodin will complete the stripping, but unfortunately it also strips the organic matter of the design. Hyposulfite of soda is also a menstruum of iodin capable of completing the stripping; but in the process it is liable to develop and liberate an amount of acid adequate to the excitation of a galvanic current. Iodid of potassium in solution is the menstruum of iodin capable of completing the stripping with facility and certainty and in all respects satisfactorily. It is therefore apparent that in this stripping process the iodin is no more important than is the selection of the one every way qualified menstruum of iodin out of the many that are less efficient or wholly useless. Having by this stripping process secured upon a metal plate or metal ware a remaining design in silver, gold, or platinum, I have accomplished one purpose of the invention. If, however, I desire to enhance the ornamental effect of the design or secure other useful advantages, I may next proceed to etch down the portions of the bed-plate from which the facing has been removed, and for this purpose I employ a mordant which does not attack the specific metal constituting the aforesaid remaining design.

When it is proposed to secure a reversal of above effects prior to the last stage of engraving, whether by stripping away just that portion of the facing lying under the applied design as the first and only result sought for or by proceeding further to deposit in the place of said last-stripped portions a different metal which in its turn may serve as a resist or serve for ornamental effect as a second result, I proceed as follows: I flow the plate with a solution of matter as lac or benzoin which is not soluble in the solvent of the applied design, and then by well-known means dissolve out the applied organic design, thus leaving on the adjacent portions the lac as an organic resist and the under metallic film of the design bare. Now this bared metallic film corresponding exactly to the organic part of the design removed, being a metal with which the plate was faced, sustains to its bed-plate the electrical and other relations before named. It is either electronegative or by nature insoluble in selected mordants or is by such mordants rendered insoluble and is now to be dissolved or stripped away as the first result proposed, and to effect this I employ the stripping process which I have above described as my invention. If it is proposed to proceed to the second stage of this reversal process and deposit in place of the duplex design just removed, as last described, another metallic design of different metal, which in its turn may serve either for ornamental effect or as a resist in securing the purposes of this invention, I do before taking the first step in this reversal process—that is, before flowing the plate with the lac solution—proceed to render those parts of the plate not occupied by the design incapable of holding adhesively that electrodeposition of metal by which the proposed design is to be effected, and for this reason the deposition metal will not only go and adhere to the bared parts, but will penetrate through the lac and to the parts of the plate covered by the lac and adhere there unless those parts are beforehand prepared to resist such adherence. Accordingly before flowing with the lac and the removal of the design I either flow over the surface a slight film of greasy or waxy matter dissolved in acetone or alcohol, either singly or combined, or I iodize those said parts either by fuming with iodin or immersing the plate in a solution of that element, or before flowing the solution of lac I mix with it a sufficiency of oily or waxy matter; or for the deposition of an ornamental or useful metallic design upon the bed-plate I omit facing said bed metal in the first place with an ornamental or useful metal and first apply the design in organic matter directly upon the bed-plate, and then, by methods described above, render the bare portions of the bed metal incapable of holding adhesively an electrodeposited metal, then flow the solution of lac or benzoin, and then dissolve out the organic design by means of a solvent which is not a solvent of the lac.

I am aware that in the electrotyping process a metallic surface has been brushed with plumbago to render it incapable of holding adherently the metal deposited directly on the surface for which it was intended; but I am not aware that ever before a metallic surface which was not designed to receive a deposit and on which a film of organic matter was first applied for the express purpose of preventing such a deposit has ever been prepared to prevent the adhesion thereto of

such a portion of the electrodeposit as forces its way through the overlying organic film, notwithstanding its express purpose was to prevent such a passage. The surfaces designated being thus prepared, the solution of lac flowed and settled, the design dissolved away, and the parts of the plate thereby laid bare being properly cleansed. I next suspend the plate as a cathode in an electrolytical solution in order to secure the desired metallic deposit.

Having thus described the invention, what I claim as new is—

1. The process which consists in imposing upon a metallic surface a design in organic matter, then flowing the plate with a greasy or equivalent matter to prevent on the parts not covered by the design an adhesion thereto of a deposited metal which penetrates through the resinous, gummy or equivalent matter next to be applied to the parts not covered, then flowing the said resinous solution, then applying a solvent of the design and removing the same together with the overlying grease, and then depositing on the bared design a metal for ornamentation or utility, the grease on the adjacent portions, serving to confine adhesively said deposit to just the parts from which the design was removed, substantially as set forth.

2. The process which consists in imposing upon a metal bed, a design in organic matter, then flowing the plate with a greasy or equivalent matter to prevent on the parts not covered by the design an adhesion thereto of a deposited metal which penetrates through the resinous, gummy or equivalent matter next to be applied to the parts not covered, then flowing the said resinous solution, then applying a solvent of the design and removing the same together with the overlying grease, then depositing on the bared design a metal capable of being converted into an insoluble chlorid of the metal, the grease on the adjacent portions serving to confine adherently said deposit to just the parts from which the design was removed and then applying a chlorin-evolving solution or sulfur element to render insoluble the deposited metal by converting into a compound of the chlorid or sulfid of the metal, substantially as set forth.

3. The process which consists in imposing upon a metal bed a design in organic matter, then flowing the plate with a greasy or equivalent matter to prevent on the parts not covered by the design an adhesion thereto of a deposited metal which penetrates through the resinous or gummy matter next to be applied to the parts not covered, then flowing the said resinous or gummy solution, then applying a solvent of the design and removing the same together with the overlying grease, then depositing on the bared design a layer of silver and then with chlorid of iron or equivalent chlorinating agent, etching down the bed metal, and converting the exposed portions of the deposited silver design into an insoluble chlorid of silver, the said insoluble chlorid serving as a resist to the bed-etching fluid, substantially as set forth.

4. The process which consists in imposing upon a metal bed a design in organic matter, then flowing the plate with a greasy or equivalent matter to prevent on the parts not covered by the design an adhesion thereto of deposited metal which penetrates through the resinous or gummy matter next to be applied to the parts not covered, then flowing the said resinous or gummy solution, then applying a solvent of the design and removing the same together with the overlying grease, then depositing on the parts from which the design has been removed an electrodeposition of a metal electronegative to that of the bed-plate, the grease on the adjacent portions serving to confine adhesively said deposit to just the parts from which the design was removed, leaving the bed-plate to be etched down, the electronegative deposited metal serving as a resist against the bed-etching agent, substantially as set forth.

In testimony that I claim the foregoing I have hereunto set my hand this 16th day of December, 1891.

HANNIBAL GOODWIN.

Witnesses:
CHARLES H. PELL,
OSCAR A. MICHEL.