F. NIEMEYER.

PROCESS OF LITHOGRAINING METAL PLATES.

APPLICATION FILED FEB. 24, 1912.

1,045,068. Patented Nov. 19, 1912.

Fig. 1.

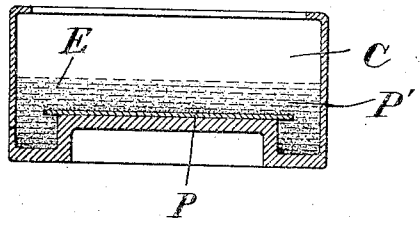



Fig. 2.

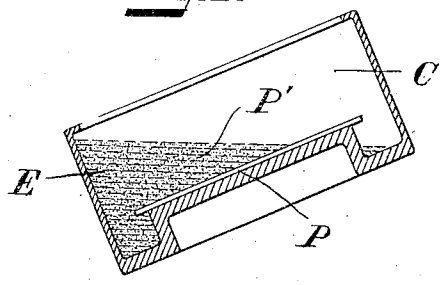



Fig. 5.

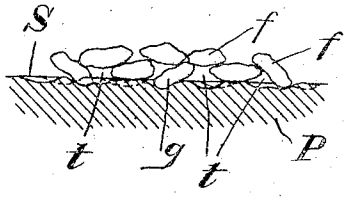



Fig. 3.

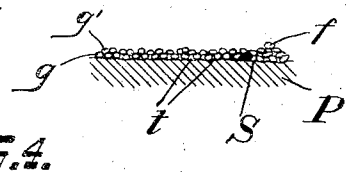
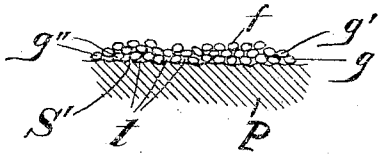



Fig. 4.

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# UNITED STATES PATENT OFFICE.

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## PROCESS OF LITHOGRAINING METAL PLATES.

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Application filed February 24, 1912. Serial No. 679,745.

*To all whom it may concern:*

Be it known that I, FREDERICK NIEMEYER, a citizen of the United States, residing in Hoboken, in the county of Hudson and State of New Jersey, have invented certain new and useful Improvements in Processes of Lithograining Metal Plates, of which the following is a specification.

This invention relates to the manufacture of surface-grained metal plates for use in the art of printing by the lithographic method.

The object of my present invention is to produce on a metal plate, especially on plates of zinc, a finely-grained surface in which the elevations or "grain" shall be or consist of the solid metal free of coating substances or adherent salts, and shall be of a character to take and properly hold the substance, while resisting the force, of the artist's pencil when the plate is being prepared for use by such method, and also to receive the figures or outlines when applied thereto by the usual transfer method; and, to furnish such a grained plate which shall have its interstices, or the spaces between such elevations, of a depth and character proper and effective for taking and holding the required amount of water, or moisture, in the areas between the treated or ink-holding areas, while the plate is in use on a lithographic printing-press.

In the accompanying drawing illustrative of my present improvements in lithographic printing plates,—Figure 1 is a sectional side view of a receptacle with a plate therein for treatment while submerged in a bath of the character hereinafter described. Fig. 2 is a similar view showing the receptacle in a changed position, it being tilted toward the left-hand, and adapted to be also reversely tilted toward the right-hand, whereby to subject the surface of the plate to a relatively forcible washing action. Fig. 3 is a fragmentary and diagrammatic view, similar to a portion of Fig. 1 but greatly enlarged, for illustrating the following description regarding the deposition of granules by flotation and gravity. Fig. 4 is a view similar to Fig. 3 but much more enlarged, for illustrating certain portions of the following description and explanations; and Fig. 5 is a view supplemental to Fig. 4.

Similar characters designate like parts in all the views.

In preparing to treat a plate by my process, I place the plate, as P, in some suitable receptacle, as C, of a depth to hold the bath E, when the receptacle is standing level, as in Fig. 1, and also when tilted, as in Fig. 2. The size and proportions of the receptacle should, of course, be suitable for the size of plate to be treated, and for using a sufficient quantity of the fluid bath of the required character. When the quantity of the fluid is larger, of course it will not need to be renewed so often; but I prefer to keep the bath effective by using only a moderate quantity and then renewing with sufficient frequency.

For the bath E, water acidulated with some suitable acid may be used, and for treating zinc I preferably employ nitric acid for that purpose, but only of a strength to act rather slowly upon the metal surface. In practice I usually employ about one part of the ordinary fluid acid of commerce to about fifty parts of water, but this may be varied in order to regulate the rapidity of reduction of the metal surface.

As a means for regulating or properly modifying the distribution and the regularity of the metal-reducing action, to form the desired inequalities of surface and so produce the grain, I add to the bath a quantity of sedimentation material in the form of granules or fine particles adapted to be readily brought to flotation and having an acid-resistant quality, and having such a specific gravity as to settle or deposit on the plate in a slow and progressive manner, so that the granules accumulate on the plate in a constantly increasing layer or depth during the action of the acid on said plate. Thus the plate is concurrently subjected to reduction by the acid and to a modifier consisting of a deposition or sedimentation of a flotation material accumulating thereon during the action of the acid. In practice, I prefer granules having a specific gravity of between one and one-half and two and one-half times that of water, depending somewhat on the fineness and shapes of the granules, and somewhat, also, on the acidity of the bath.

The flotation of the granules is indicated at P' Figs. 1 and 2, where the small granules are for the time being in suspension, or flotation; and in practice many of them so remain, practically continuously, but this

has, I find, slight if any disadvantage. On the bath E standing still for even a brief time, many of the granules *f* become deposited by gravity into a relatively evenly-spread layer upon the plate-surface S, approximately as indicated for instance at *g*, Figs. 3 and 4; and, by reason, as I suppose, of the chemical and voltaic or other qualities of the materials, and of the conditions thus established, the surface S is at once subjected to a reducing action of such a character as to tend to form a grain therein of the quality and water-retaining capacity required in the lithographic art.

When the plate is in the acidulated bath and at a suitable distance below the surface thereof, the granules continue accumulating on the plate while the acid is eating away the surface of the metal. The greater the depth of the bath over the plate, the greater will be the amount of that accumulation, or deposition during a given time and from a given initial proportion or quantity of the granules in the fluid. Therefore by suitably regulating those proportionate amounts and the depth of the fluid, the rapidity of the granule-deposition may be controlled within proper limits, which in practice are ascertainable by trial and observation of the amounts of surface reduction in given times, for the production of such a coarseness and depth of the grain as may be desired.

When the reducing action proceeds for a short time certain dissociations appear to take place, with the formation of salts which by their position on the plate-surface tend to reduce and suspend the chemical or metal-reducing action, and therefore I subject the plate at intervals to a washing or clearing operation which may be performed by flowing the bath over the surface with sufficient force for thereby dislodging such accumulations or deposits,—if any there may be produced,—and then again cover the plate by the deposition of the granules thereon by gravity, when the reduction process goes on again; these successive steps or stages are repeated to the extent required for bringing the grain up to the desired depth and formation. At each successive re-deposition of the granules, the undulations then already produced tend to modify, as I apprehend, the manner of such new deposition, so that the metal is removed by successive stages in which any particular small area, or given area,—such for instance as one of a size less than that of a granule,—is deepened little by little, while at each successive stake such obstructive salts as may have been formed on the surface, S, are cleared off by the washing operation.

The acid begins acting upon the metal over nearly the whole surface, and it appears to be probable that the metal-reducing action is in some way progressively modified as to the distribution of the points of relatively greater and lesser effect, during the progress of the deposition which accumulates upon the plate. When by the agitation of the bath, however performed, the flotation of the granules is accomplished, the acid will, of course, act about equally over the entire surface of the metal, and will, as I suppose, become variable or irregular during the immediately subsequent and gradual re-deposition by gravity of the flotation material. By repeating the flotation at frequent intervals while continuing the plate in the bath, the metal is subjected to successive treatments which in one respect are each of a similarly varying or progressive character, since during each said treatment the restriction of the metal-reducing action goes on progressively from a beginning at which this action extends over the whole, or nearly the whole, surface and is thereafter progressively reduced toward or nearly to the point of cessation.

In practice it will usually be sufficient to carry this progressive reduction only to a point where there is a substantial lessening of the metal-reducing action, and then clear off the accumulation on the plate of the flotation-material and also at the same time clear off such products as may have been formed by the action of the acid-bath and the metal removed thereby from the plate. This step being performed, including the re-flotation of the granular material, the re-deposition again begins and goes on as before, for subjecting the partially grained surface to a further stage of reduction; and so on, until the depth and character of grain is obtained, as may be required.

When the surface S has been reduced to a partially-formed grain, and the surface is cleared of such obstructive salts, aqueous or otherwise, as may have been formed between the metal of the plate and a metal of the granules, it is evident that on a re-deposition on the plate of the said granules, these will normally deposit or form the lower series or layer, *g*, Fig. 5, in an undulating arrangement or formation, so that the specific relations of those metal elements to the grain of the plate will naturally be modified at each successive re-deposition stage of the process. This feature will be understood by comparing Figs. 4 and 5, in view of the preceding explanations. The plate P with its partially grained surface S′ is shown with granules, *g*″, re-deposited thereon in an undulating and irregular arrangement, such as naturally would be caused by the process above set forth, when the granules fall by a slow and gentle action through a fluid upon an undulating surface. Each successive stage of the process, therefore, is not merely a repetition of the first, or of a next preced-

ing stage, but may properly be considered as differing from the next preceding stage, since each successive re-deposition is made on a more advanced formation of the grain-surface of the plate.

As a suitable flotation-material, I preferably employ some metallic salt which is not materially reduced or affected by the acid-bath, when this is of the moderate degree of strength or acidity which is sufficient for slowly eating away the metal surface; and which, at the same time has a granular form, preferably of a flake-like character, and has the granules of a size suitable for the fineness of grain desired, and of a specific gravity low enough to prevent a too rapid accumulation on the plate after any re-flotation of this material in the bath.

One kind of granule or flotation material which I employ, more especially for treating zinc plates, is a compound material compounded preferably of the salts of two metals, and preferably of two metals other than zinc; and other than the metal of the plate, when this is not of zinc. One such material is a compound formed from iron and copper which, because of its resistance to the acid of the bath and the small size and low weight of its granules, produces by flotation and gravity a deposition of good quality and effect. For this compound I prefer one of the formula $FeCy+2CuCy$. This material appears to be particularly suitable because of the qualities above mentioned, and also, as I apprehend, because of its effect on, or the part it takes in certain reactions, which it appears may take place during or incident to the metal-reducing action upon the plate while in the bath.

While I am unable and deem it unnecessary at this time to fully set forth and explain the specific phenomena which evidently or probably occur in the solution, such for instance as the ionization and the voltaic action, or such others as may take place, I apprehend that in some manner the granules of the copper and iron salts operate to modify the chemical and electrolytic actions and reactions upon the zinc and to relatively localize or accentuate the metal-reducing action upon a great number of minute areas, and thus regulate or control the reduction of the plate-surface to the desired grain-formation; and, I apprehend this may be due to some intimate connection between chemical activity and electrical conductivity, since the acid, especially nitric acid, employed as the electrolytic element, appears to have the proper, and a relatively high, electrical conductivity. One explanation as to the way these reducing actions may perhaps be regulated, I have indicated in Fig. 3, where a layer of the metal-salt granules, *g*, lie close to the surface S, while other granules, as *g'*, are more or less superposed on such first layer. As a result, there are formed great numbers of minute intervening spaces, as *t*, Figs. 4 and 5, between compounds of metals which have the relative character of electrodes, while these spaces are filled with a fluid having the character of an electrolyte, thereby producing, as I suppose, some kind and degree of voltaic relationship or condition whereby the usual and corresponding changes are effected in the several metals or elements by reactions involving the electrolytic element. Not only are the electrically different metals connected by the same electrolyte, but the resultant chemical action may produce a difference in the strength of this electrolyte in the spaces *t*, and so in some manner cause an unequal amount and distribution of such chemical action on the surface S.

When a granule falls or is deposited on the plate-surface, it acts in a mechanical way to displace the fluid at that point, and this normally tends, I understand, to restrict or reduce the action of the acid in the minute area so covered by the granule, which may be said to form an obstacle at such point against the free approach of the acid to that area. Thus the granules may be said to operate in several respects or capacities, especially when formed of a double salt, and still more so, when formed of a double cyanate,—first, mechanically; second, chemically, and also most probably, by catalysis, including the phenomena involved in the electro-osmotic relations of the substances in the granules, the bath and the plate.

The acid resistant granules may be composed of some suitable single substance, but I prefer in practice, to use granules composed of one of that class of compounds or salts which are sometimes designated as double-salts, and of these I preferably employ a double-salt of two different metals, and to have each of these different from the metal of the plate which is to be grained. Thus for treating zinc, I preferably employ salts of iron and copper, each different from zinc; and of these compounds or salts I preferably employ the iron-cyanogen and copper cyanogen salts, respectively, and of these I prefer to employ the cyanates, and to have the copper-salt or cyanate in excess of the iron salt or cyanate. Although zinc is classed as a divalent metal, it appears in some cases to be able in reactions involving a plurality of other metals, to replace some other divalent metals, including iron; and, perhaps, copper, which is classed as both monovalent and divalent. In such reactions so far as occurring in my process, I apprehend that some of the phenomena of catalysis may also occur. Also, it may be noted that as regards the osmotic action or

pressure or the electro-osmotic value in solutions, iron is classed as having a negative electro-motive force, whereas, in comparison, both zinc and copper are classed as having a positive electrolytic, or electro-osmotic quality or value. Thus in treating zinc plates with a flotation-material having a salt of iron and a salt of a more positive metal, (such as copper for instance), the granules are composed in part of the salt of a metal which is, as regards its electro-osmotic character, negative relatively to the zinc and also relatively to the metal of the other salt of the compound of which the granules are formed.

When the gravitating granules are composed of a compound of cyanogen salts of iron and copper, and when the iron-cyanogen salt is a cyanate, that compound will therefore comprise two metal-cyanogen salts of which one is the cyanate of a divalent metal (iron) having an electro-osmotic value relatively negative to the zinc and also to the metal (copper) of the other metal-cyanogen salt. Owing to their low specific gravity and their size and character, this kind of granules are readily flotable by agitation of the bath, and are deposited therefrom onto the plate surface in a slow and regular manner particularly favorable for the requirements of this method of making the litho-grain.

In this process, the object is to reduce the original plane surface to a grain-surface, rather than to supply such a grain as an addition to the plate. In view of this purpose, and also for convenience, I designate the process as one for litho-graining metal-plates, thus referring to the adaptability of the plates when so grained for use in the art of lithographic printing.

While a granule of the double cyanate rests on the zinc surface, the molecule of iron-cyanate may be considered as being held in place by its association with the molecule of copper-cyanate, and thus may part with some of its cyanogen directly to the zinc, which has a strong affinity therefor; and such an exchange may, I infer, be aided by the oxygen supplied by the nitric acid to the iron, as well as, in part, to the zinc; and, owing to the minuteness of the granule, that exchange or recation may therefore take place, as to each such granule only in a correspondingly minute area, with the result of forming a great number of closely arranged but distinct points of reduction on the zinc surface.

When a sufficiently dilute acid bath is used, the metal-plates, particularly zinc plates, may be subjected to a primary reduction which is initially distributed over the whole surface and is then gradually restricted both as to the distribution and the regularity of the reduction, this being accomplished by a progressive gravitational deposition of an acid-resistant flotation-material; and, next, subjected to a second reduction by repeating the said operation on the primarily-reduced plate-surface; and then subjected to a further reduction by repetitions of the said operation on the secondarily-reduced plate surface, whereby the final surface is obtained by three or more successive reductions, each of which begins with the plate-surface at a different stage of grain-formation.

In litho-graining metal-plates in the foregoing manner, the grain is developed or produced in a clean and effective condition, being formed or composed of the solid metal and free of adherent films, deposits or coatings, and without the formation of substantial salts or the like to impair the quality of the surface-grain for use in lithographic printing. On zinc plates, the process may be properly carried out in from three to eight minutes, depending on the strength of the acid, the depth of the bath over the plate, the quantity of the flotation-material in the bath, and the frequency of the re-flotation and re-deposition of the granules of that material. In practice I prefer to so regulate those periods and quantities as to provide for from three to six of the said re-depositions during the complete operation.

In applying my present process to the graining of plates of metals other than zinc, such an aluminum or copper, either pure or alloyed, other dilute acids, instead of the nitric acid, may be used, preferably selecting such a kind and degree of dilution of the acid as will act slowly on the metal-surface, and thus give time for the desired number of re-depositions of the flotation material during the process. In some instances such other acids may be used in graining the zinc plates, especially when the compounds or salts, whether cyanates or not, of which the granules are composed, shall be of a character to work in harmony with the particular kind of acid employed and not be rapidly consumed or neutralized in the bath.

Having thus described my invention, I claim:

1. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath under an accumulating deposition by gravity of granules which are floatable by agitation of the bath and are resistant to the acid.

2. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath under an accumulating deposition from flotation of granules and continuing such reduction to the point of forming a partial grain, next clearing off the plate-surface and refloating the granules,

and then subjecting the plate-surface to further reduction under an accumulating redeposition of the granules.

3. That improvement in the art of litho-graining metal-plates, which consists in subjecting the plate-surface in an acid bath to a primary reduction initially distributed over the whole surface and then gradually restricting that distribution and the regularity of that reduction by the gravitational deposition of an acid-resistant flotation-material, and next subjecting the surface to an additional reduction by repeating the said operations on the plate surface after such primary reduction.

4. That improvement in the art of litho-graining metal-plates, which consists in subjecting the plate-surface in an acid bath to a primary reduction initially distributed over the whole surface and then gradually restricting that distribution and the regularity of that reduction by the gravitational deposition of an acid-resistant granular flotation-material, and next subjecting the surface to successive additional reductions after such primary reduction, by subjecting the plate-surface to repeated gravitational depositions of the flotation granules while continuing the acid treatment.

5. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules of a double salt of two different metals, and continuing the acid treatment while accumulating a gravitational deposition of such flotation material upon the plate-surface.

6. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules of a double salt of two different metals, and continuing the acid treatment during successive gravitational re-depositions of such flotation material.

7. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules of a double salt of two different metals other than the metal of the plate, and continuing the acid treatment while accumulating a gravitational deposition of such flotation material upon the plate-surface.

8. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules of a double salt of two different metals other than the metal of the plate, and continuing the acid treatment during successive gravitational re-depositions of such flotation material.

9. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules of a double salt of two different metals other than the metal of the plate and one of which is iron, and continuing the acid treatment while accumulating a gravitational deposition of such flotation material upon the plate-surface.

10. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules of a double salt of two different metals other than the metal of the plate and one of which is iron, and containing the acid treatment during successive gravitational re-depositions of such flotation material.

11. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules of a double salt of iron and copper, and continuing the acid treatment while accumulating a gravitational deposition of such flotation material upon the plate-surface.

12. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules of a double salt of iron and coper, and containing the acid treatment during successive gravitational re-depositions of such flotation material.

13. The process of litho-graining metal-plates, which consist in reducing the plate-surface in an acid bath containing in flotation gravitating granules of a double salt of iron and copper and having the copper-salt in excess of the iron-salt, and continuing the acid treatment while accumulating a gravitational deposition of such flotation material upon the plate-surface.

14. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules of a double salt of iron and copper and having the copper-salt in excess of the iron-salt, and continuing the acid treatment during successive gravitational re-depositions of such flotation material.

15. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of the cyanates of two different metals, and continuing the acid treatment while accumulating a gravitational deposition of such flotation material upon the plate-surface.

16. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of the cyanates of two different metals, and continuing the acid treatment during successive gravitational re-depositions of such flotation material.

17. The process of litho-graining metal-

plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of the cyanates of two different metals other than the metal of the plate, and continuing the acid treatment while accumulating a gravitational deposition of such flotation material upon the plate-surface.

18. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of the cyanates of two different metals other than the metal of the plate, and continuing the acid treatment during successive gravitational re-depositions of such flotation material.

19. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of a compound metallic salt comprising an iron cyanogen salt, and continuing the acid treatment during a gravitational deposition of such flotation material upon the plate-surface.

20. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation granules composed of a compound metallic salt comprising an iron-cyanogen salt, and continuing the acid treatment during successive re-depositions by gravity of such flotation material.

21. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of the cyanates of two different metals other than the metal of the plate and one of which is iron, and continuing the acid treatment while accumulating a gravitational deposition of such flotation material upon the plate-surface.

22. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of the cyanates of two different metals other than the metal of the plate and one of which is iron, and continuing the acid treatment during successive gravitational re-depositions of such flotation material.

23. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of the cyanates of iron and copper, and continuing the acid treatment while accumulating a gravitational deposition of such flotation material upon the plate-surface.

24. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of the cyanates of iron and copper, and continuing the acid treatment during successive gravitational re-depositions of such flotation material.

25. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of the cyanates of iron and copper and having the copper-cyanate in excess of the iron-cyanate, and continuing the acid treatment while accumulating a gravitational deposition of such flotation material upon the plate-surface.

26. The process of litho-graining metal-plates, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of the cyanates of iron and copper and having the copper-cyanate in excess of the iron-cyanate, and continuing the acid treatment during successive gravitational re-depositions of such flotation material.

27. The process of litho-graining metal-plates of zinc, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of salts of two metals other than the metal of the plate and one of which is iron, and continuing the acid treatment while accumulating a gravitational deposition of such flotation material upon the plate-surface.

28. The process of litho-graining metal-plates of zinc, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of salts of two metals other than the metal of the plate and one of which is iron, and continuing the acid treatment during successive re-depositions of such flotation material.

29. The process of litho-graining metal-plates of zinc, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of cyanates of two metals other than the metal of the plate and one of which is iron, and continuing the acid treatment while accumulating a gravitational deposition of such flotation material upon the plate-surface.

30. The herein described process of litho-graining metal-plates of zinc, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of cyanate of two metals other than the metal of the plate and one of which is iron, and containing the acid treatment during successive gravitational re-depositions of such flotation material.

31. The process of litho-graining metal-plates of zinc, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed

of salts of iron and copper, and continuing the acid treatment while accumulating a gravitational deposition of such flotation material upon the plate-surface.

32. The process of litho-graining metal-plates of zinc, which consists in reducing the plate-surface in a dilute nitric acid bath containing in flotation gravitating granules composed of salts of iron and copper, and continuing the acid treatment during successive gravitational re-depositions of such flotation material.

33. The process of litho-graining metal-plates of zinc, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of a compound salt which comprises an iron-cyanogen salt, and continuing the acid treatment while accumulating a gravitational deposition of such flotation material upon the plate-surface.

34. The process of litho-graining metal-plates of zinc, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of a compound salt which comprises an iron-cyanogen salt and a copper-cyanogen salt, and continuing the acid treatment during successive re-depositions of such flotation material.

35. The process of litho-graining metal-plates of zinc, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of a plurality of salts which comprise at least one cyanate of a metal, and continuing the acid treatment during a gravitational deposition of such flotation material upon the plate-surface.

36. The herein described process of litho-graining metal-plates of zinc, which consists in reducing the plate-surface in an acid bath containing in flotation granules composed of a plurality of salts which comprises at least one cyanate of a metal, and continuing the acid treatment during successive re-depositions of such flotation material.

37. The process of litho-graining metal-plates of zinc, which consists in initially reducing the plate-surface in a dilute nitric acid bath containing in flotation gravitating granules composed of a compound metallic salt which comprises an iron-cyanogen salt and a copper-cyanogen salt and having one of these salts a cyanate, and then further forming the grain by continuing the acid treatment during successive re-depositions of such flotation material.

38. The process of litho-graining plates of divalent metal having a positive electro-osmotic value, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of salts of two different metals of which one is a divalent metal having in the acid bath a relatively negative electro-osmotic value, and containing the acid treatment while progressively accumulating a gravitational deposition of such flotation material upon the plate-surface.

39. The process of litho-graining plates of divalent metal having a positive electro-osmotic value, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of salts of two different metals of which one is a divalent metal having in the acid bath a relatively negative electro-osmotic value, and continuing the acid treatment during successive gravitational re-depositions of such flotation material upon the plate-surface.

40. The process of litho-graining metal-plates of zinc, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of a compound of metallic salts which comprises two metal-cyanogen salts of which one is the cyanate of a divalent metal having an electro-osmotic value relatively negative in the bath to the zinc and also the metal of the other metal-cyanogen salt, and continuing the acid treatment while progressively accumulating a gravitational deposition of such flotation material upon the plate-surface.

41. The process of litho-graining zinc metal-plates of zinc, which consists in reducing the plate surface in an acid bath containing in flotation gravitating granules composed of a compound of metallic salts which comprises two metal-cyanogen salts of which one is the cyanate of a divalent metal having an electro-osmotic value relatively negative in the bath to the zinc and also to the metal of the other metal-cyanogen salt, and continuing the acid treatment during successive gravitational re-depositions of such flotation material.

42. The process of litho-graining metal-plates of zinc, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of a substance which comprises the cyanate of a metal having an electro-osmotic value which is negative relatively to the zinc, and continuing the acid treatment while accumulating a deposition of such flotation material upon the plate-surface.

43. The process of litho-graining metal-plates of zinc, which consists in reducing the plate-surface in an acid bath containing in flotation gravitating granules composed of a substance which comprises the cyanate of a metal having an electro-osmotic value which is negative relatively to the zinc, and continuing the acid treatment during successive re-depositions of such flotation material upon the plate-surface.

44. The herein described process of litho-graining metal-plates of zinc, which consists in reducing the plate-surface in an acid bath containing in flotation granules composed of a compound of metallic salts, which comprises the cyanates of two metals other than zinc and having, respectively, relatively negative and positive electro-osmotic values, and one of these having its said value negative relatively to that of the zinc, and continuing the acid treatment while accumulating a gravitational deposition of such flotation material upon the plate-surface.

45. The process of litho-grai ing metal-plates of zinc, which consists in reducing the plate-surface in an acid bath containing in flotation granules composed of a compound of metallic salts, which comprises the cyanates of two metals other than zinc and having, respectively, relatively negative and positive electro-osmotic values, and one of these having its said value negative relatively to that of the zinc, and continuing the acid treatment during successive redepositions of such flotation material upon the plate-surface.

46. That improvement in the art of litho-graining metal-plates of zinc, which consists in subjecting the plate-surface in an acid bath to a primary reduction initially distributed over the whole surface and then gradually restricting that distribution and the regularity of that reduction by a progressive gravitational deposition of an acid-resistant flotation-material; next subjecting the surface to a second reduction by repeating the said operation on the primarily-reduced plate-surface; and then subjecting the surface to a third reduction by again repeating the said operation on the secondarily-reduced plate-surface, whereby the final surface is obtained by three successive reductions, each of which begins with the plate-surface at a different stage of grain-formation.

47. That improvement in the art of litho-graining metal-plates of zinc, which consists in subjecting the plate surface in an acid bath to a primary reduction initially distributed over the whole surface and then gradually restricting that distribution and the regularity of that reduction by a progressive gravitational deposition of an acid-resistant flotation-material; next subjecting the surface to a second reduction by repeating the said operation on the primarily-reduced plate-surface; and then subjecting the surface to a plurality of further reductions by successively repeating the said operation on the partially-reduced plate surface, whereby the final surface is obtained by at least four successive reductions, each of which begins with the plate-surface at a different stage of grain-formation.

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Witnesses:
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