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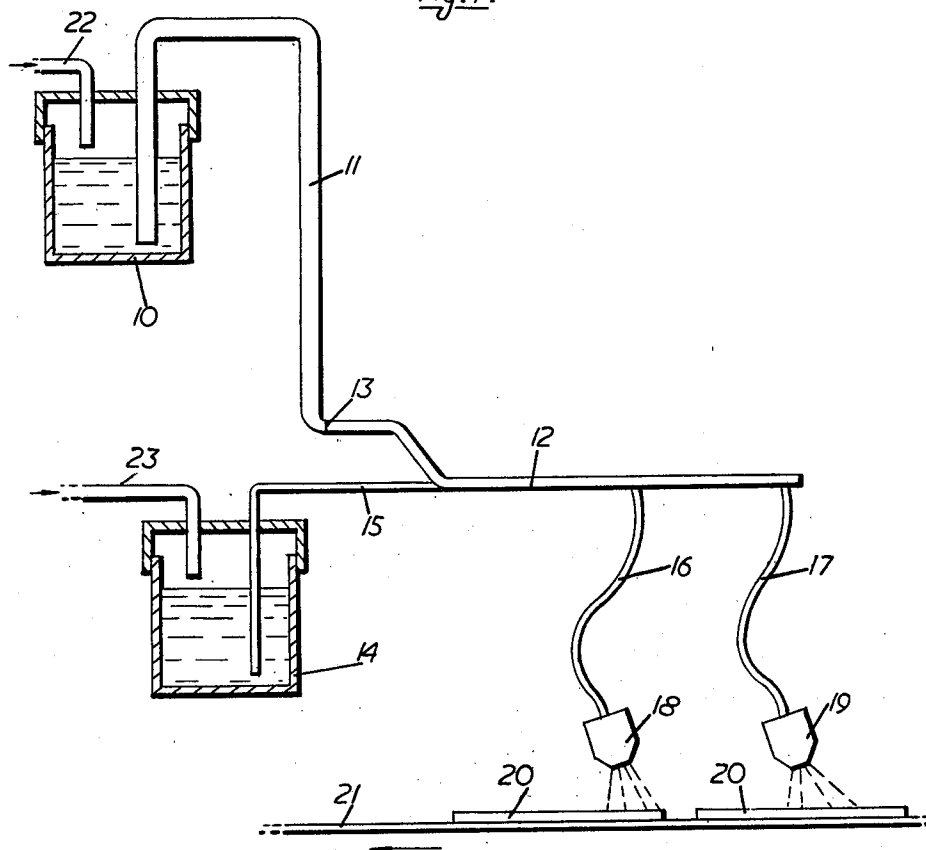
3,084,063

PROCESS AND APPARATUS FOR DEPOSITION OF COPPER

Filed Nov. 19, 1959

2 Sheets-Sheet 1

Fig. 1.



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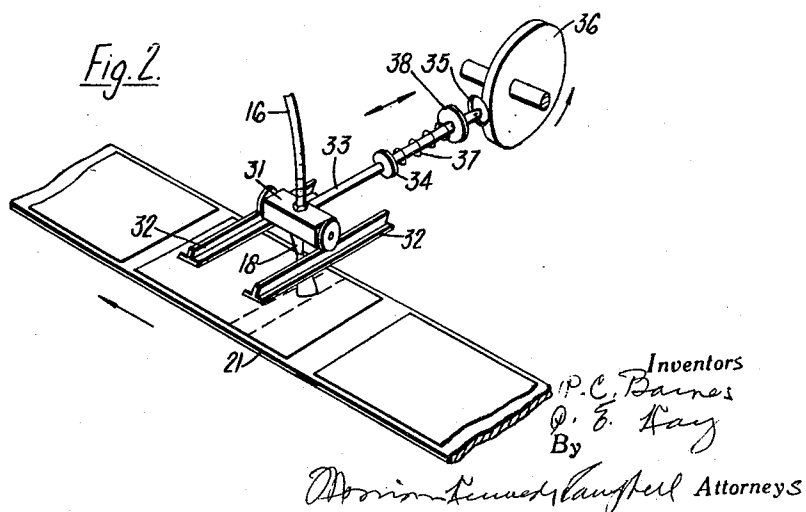
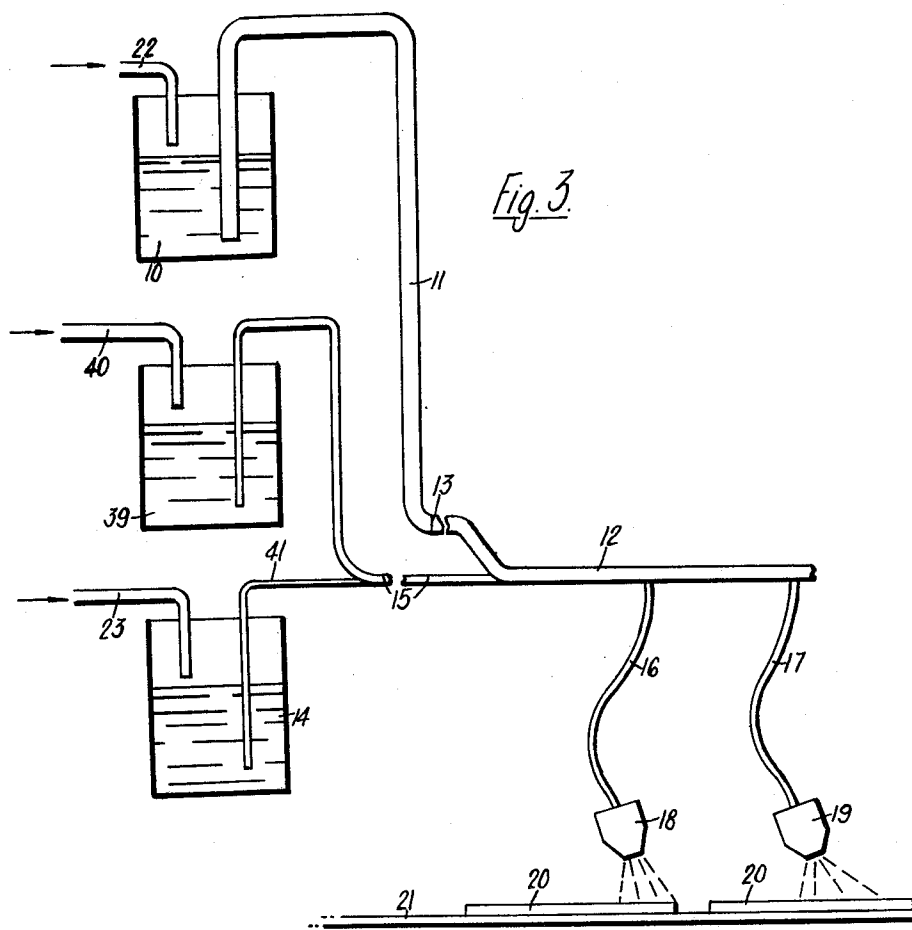
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PROCESS AND APPARATUS FOR DEPOSITION
OF COPPER

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25 Claims. (Cl. 117—35)

This invention relates to processes and apparatus for depositing a copper coating on surfaces, and especially to spray coppering processes and apparatus.

It is well known that copper can be deposited by the galvanic action of a metal higher than copper in the electrochemical series on a solution of a cupric salt. Some members of the electrochemical series of the metals, which are relevant to a process for depositing copper, are as follows, the metals being listed in order of decreasing oxidation potential and the oxidation potential of copper being given for reference.

Metal	Ion	Oxidation Potential in Volts
Mg.....	Mg ⁺⁺	3.024
Al.....	Al ⁺⁺⁺	1.67
Mn.....	Mn ⁺⁺	1.1
Zn.....	Zn ⁺⁺	0.761
Fe.....	Fe ⁺⁺	0.44
Cd.....	Cd ⁺⁺	0.402
Cu.....	Cu ⁺⁺	0.340

In general copper will be precipitated from a solution of a cupric salt by the galvanic action of any metal having a higher oxidation potential than copper in this series, and in coppering processes which have been known hitherto employing this action, the precipitating metal has been sprayed on to a surface to be coppered in the form of an aqueous suspension of finely divided precipitating metal, a cupric salt solution has been separately sprayed onto the surface, so that the cupric salt solution and the metal suspension mix on the surface.

It is a main object of the present invention to provide a coppering process in which a more uniform continuous copper coating is obtained than has hitherto been possible.

According to the present invention there is provided a coppering process employing the galvanic action of a metal higher in the electro-chemical series than copper on a solution of a cupric salt to effect precipitation of a uniform coating of copper onto a surface, which comprises the steps of producing a confined turbulent stream of a solution of a cupric salt flowing under pressure, injecting a homogeneous fluid suspension of the precipitating metal in powder form at a desired predetermined rate into said stream to induce turbulent mixing in said stream so as to produce a stream of homogeneous turbulent mixture, and spraying the mixture towards a surface to be coppered in such manner that droplets of said homogeneous mixture arrive at the surface before there has been sufficient interaction within the mixture to precipitate appreciable amounts of metallic copper.

Owing to the fact that the suspension of the precipitating metal is thoroughly mixed with the cupric salt solution to form a mixture which is sprayed on to a surface to be coppered, the precipitation of copper is substantially uniform over the surface.

The cupric salt solution may be a copper sulphate solution containing, for example, from 2 to 10% by weight of CuSO₄ · 5H₂O and acidified with sulphuric acid. Alternately the fluid suspension of the precipitating metal is first injected into a stream of acidified water to form a

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homogeneous diluted suspension which is then injected into the stream of cupric salt solution to produce a stream of homogeneous turbulent mixture. Preferably the pH value of the mixture is from 0.5 to 3.

In order that the precipitating metal may be readily maintained in suspension and in order to increase the rate of reaction between the cupric salt and the precipitating metal, it is, of course, desirable that the latter should be finely divided. We have found that a suitable state of subdivision for these purposes is such that the particles of precipitating metal have an average diameter of not more than 20 microns. As they are the cheapest and most readily available of the metals listed above, it is preferred to employ iron or zinc as the precipitating metal; powdered zinc having an average particle size of about 20 microns and powdered iron having an average particle size of from 5 to 7 microns are both readily available, and it is particularly preferred to use the latter.

In order to maintain a uniform dispersion of the precipitating metal which can be supplied at a predetermined rate the homogeneous fluid suspension of the metal powder may be in the form of a suspension of the powdered metal in a viscous aqueous dispersion of an inert hydrophilic colloid.

Suitable hydrophilic colloids for incorporation in the viscous aqueous suspension are, for example, carboxymethyl cellulose, polyvinyl alcohol and soluble starches, gums and gelatin. Such a viscous aqueous dispersion of the precipitating metal may contain, for example, from 1 to 5% by weight of the metal, from 0.1 to 0.5% by weight of carboxymethyl cellulose, and from 0.1 to 0.5% by weight of formaldehyde (40% solution).

We have found that under normal circumstances deposition of copper commences approximately 20 seconds after mixing of the precipitating metal with the cupric salt solution and the mixture should, therefore, be sprayed before this period has elapsed. It should not be understood from this, however, that a period approaching 20 seconds must necessarily elapse between mixing the precipitating metal and the cupric salt solution and spraying of the mixture as certain surfaces catalyse the reaction between the precipitating metal and the cupric salt. Thus, where the surface to be coppered is the exposed silver surface of a silvered glass mirror, the time for the reaction to take place in the presence of silver is of the order of 1 second so that in such cases the mixture can be sprayed as soon as it is formed.

Spraying may be effected by means of any convenient spraying apparatus, that is apparatus incorporating at least one spraying head which is adapted to form a suitable stream of droplets under the action of the pressure of the liquids alone or incorporating spray heads which each form a stream of droplets by means of compressed air.

The present invention also comprises apparatus for carrying out the method in which the viscous aqueous suspension of the precipitating metal is injected into a stream of a solution of a cupric salt, which apparatus comprises a reservoir for cupric salt solution, a first conduit leading from the solution reservoir into a mixing conduit, a reservoir for a homogeneous fluid suspension of a precipitating metal, a second conduit leading from the suspension reservoir to the mixing conduit at a point downstream from the point of entry of the first conduit, and a third conduit leading out of the mixing conduit at a point downstream from the point of entry of the second conduit, to a spray head, the bore of the mixing conduit being sufficiently small relative to the bore of the first conduit to maintain the liquid in the mixing conduit turbulent.

The present invention also includes apparatus for carry-

ing out the method in which the viscous aqueous suspension of the precipitating metal is first injected into a stream of acidified water, the homogeneous diluted suspension thus formed is injected into a stream of a solution of the cupric salt and the resultant mixture is then sprayed, which apparatus comprises a reservoir for cupric salt solution, a first conduit leading from the solution reservoir directly into a mixing conduit, a water reservoir, a second conduit leading from the water reservoir to the mixing conduit at a point downstream from the point of entry of the first conduit, a reservoir for a homogeneous fluid suspension of a precipitating metal, a third conduit leading from the suspension reservoir to the second conduit, and a fourth conduit leading out of the mixing conduit at a point downstream from the point of entry of the second conduit, to a spray head, the bore of the mixing conduit being sufficiently small relative to the bore of the first conduit to maintain the liquid in the mixing circuit turbulent.

Turbulence in a liquid flowing in a conduit occurs when the mean linear velocity of the liquid in the conduit exceeds a certain value that depends upon the characteristics of the liquid. We have found that turbulence can be achieved in the mixing conduit by making the bore of the latter approximately a quarter of that of the first conduit and at the same time it is also advantageous that the bore of the second conduit should be approximately one-eighth of that of the first conduit. Rapid and effective injection of the suspension of the precipitating metal into the cupric salt solution can be obtained by arranging the portion of the second conduit which joins the mixing conduit to be substantially co-axial with that part of the mixing conduit situated downstream of the point of entry of the second conduit into the mixing conduit.

Generally speaking, the area of the surface to be coppered, for example that of an already silvered glass mirror, will be considerably greater than that which can be covered by the spray stream emerging from a stationary spray head. The glass or other surface is, therefore, conveniently mounted on a conveyor passing underneath the spray head whilst the spray head is mounted on a frame which may be reciprocated transversely to the direction of movement of the glass or other surface so that successive transverse bands of the surface are sprayed. Where this arrangement is adopted, the conduit leading from the mixing conduit to the spray head is flexible.

In order that the invention may be more clearly understood, some preferred embodiments of apparatus in accordance therewith will now be described, by way of example, with reference to the accompanying diagrammatic drawings in which:

FIGURE 1 is a diagrammatic elevation of apparatus according to the invention for coppering a surface,

FIGURE 2 shows means for reciprocating a spray head across a conveyor for articles to be coppered, and

FIG. 3 is a view similar to FIGURE 1 of modified coppering apparatus.

In the drawings the same reference numerals indicate the same or similar parts.

Referring to the drawing, the apparatus comprises a reservoir 10 for the acidified cupric salt solution, a first conduit 11 leading from the reservoir 10 directly into a mixing conduit 12, the point of junction between the first conduit 11 and the mixing conduit 12 being indicated at 13. The apparatus also comprises a reservoir 14 for the suspension of the precipitating metal, a second conduit 15 leading from the reservoir 14 to the mixing conduit 12 at a point downstream from the junction 13. In the embodiment illustrated in the drawing, the bore of the first conduit 11 was 1 inch, the bore of the mixing conduit 12 $1\frac{1}{2}$ -inch and the bore of the second conduit 15 $1\frac{1}{4}$ -inch; it will be noted that the latter part of the second conduit 15 is arranged so as to be co-axial with that part of the mixing conduit 12 which lies downstream of the point

of entry of the second conduit 15 into the mixing conduit 12.

Leading out of the mixing conduit 12 at points downstream from the point of entry of the second conduit 15, are flexible conduits 16 and 17 which respectively lead to spray heads 18 and 19 which are arranged to spray the articles to be coppered 20. The latter are placed on a conveyor 21 which is adapted to move the articles 20 under the spray heads 18 and 19 in the direction indicated by the arrow. The spray heads 18 and 19 are mounted on a frame which is itself mounted for reciprocating movement transverse to the direction of movement of the conveyor 21. The mounting of one of the spray heads is illustrated in FIGURE 2, which shows the spray head 18 mounted on a frame 31 which forms part of a carriage which is supported on rails 32 situated above the conveyor 21 and at right angles to it. The carriage is reciprocated at constant velocity along the rails 32 by a cam mechanism which includes a rod 33 supported in a collar 34, one end of the rod 33 being fixed to the frame 31 and the other end of the rod carrying a cam follower 35 which engages the surface of a cam 36. A spring 37 extends between the collar 34 and a flange 38 on the rod 33 to maintain the cam follower 35 in contact with the cam surface.

As the cam 36 rotates the spray head 18 is reciprocated at right angles to the direction of movement of the conveyor 21. The supply of cupric salt solution from the reservoir 10 and the supply of the precipitating metal suspension from the reservoir 14 is effected under pressure by means of compressed air introduced through the pipes 22 and 23 respectively, the reservoirs 10 and 14 being pressure resistant. As an additional precaution against settling of the precipitating metal in the reservoir 14, the latter may, if desired, be provided with a stirrer (not shown).

The lengths of the mixing conduit 12 and the flexible conduits 16 and 17 are such that, taking into consideration the rates of flow of the cupric salt solution and the suspension of precipitating metal, the diluted suspension takes considerably less than 25 seconds to traverse the distance between the point of entry of the second conduit 15 into the mixing conduit 12 and the spray heads 18 and 19 respectively.

Alternatively, as illustrated in FIGURE 3, the fluid suspension of precipitating metal is first injected into a stream of acidified water to form a homogeneous diluted suspension which is then injected into the stream of cupric salt solution in the mixing conduit. To effect this water reservoir 39 supplied with compressed air through a pipe 40 is connected to the mixing conduit by the second conduit 15.

The suspension reservoir 14 is connected to the second conduit by a third conduit 41, and the pressure in the reservoir 14 injects the metal suspension into the acidified water in the second conduit 15, so that a homogeneous diluted suspension is injected into the mixing conduit 12.

In operation, the rates of flow of precipitating metal suspension and cupric salt solution are adjusted to each other and to the width and rate of movement of the conveyor 21. For example in the case of a 6 foot wide conveyor which is moved at the rate of 3 feet per minute, we have found that suitable rates of flow of the metal suspension and cupric salt solution are respectively 200 cc. and 1500 cc. per minute.

By reason of the homogeneity of the precipitating metal suspension and the turbulence of the mixture which is sprayed on to the surface to be coppered, the distribution and relative proportions of powdered precipitating metal and cupric ions in the layer of liquid formed on the surface by coalescence of the droplets can be readily maintained substantially uniform throughout the course of the process so that formation and precipitation of metallic

copper over the surface proceeds substantially uniformly. The present invention, therefore, provides an economic coppering process utilising the galvanic action of the precipitating metal on a cupric salt solution which may be carried out in a uniform and controlled manner, thereby enabling a uniform and controlled continuous coating of copper to be produced on the surface to be coated.

We claim:

1. A coppering process employing the galvanic action of a metal higher in the electro-chemical series than copper on a solution of a cupric salt to effect precipitation of a uniform coating of copper onto a surface, which comprises the steps of producing a confined turbulent stream of a solution of a cupric salt flowing under pressure injecting a homogeneous fluid suspension of the precipitating metal in powder form at a desired predetermined rate into said stream to induce turbulent mixing in said stream so as to produce a stream of homogeneous turbulent mixture, and spraying the mixture towards a surface to be coppered in such manner that droplets of homogeneous mixture arrive at the surface before there has been sufficient interaction within the mixture to precipitate appreciable amounts of metallic copper.

2. A coppering process according to claim 1, in which the cupric salt solution is a copper sulphate solution acidified with sulphuric acid.

3. A coppering process according to claim 2, in which the pH value of the mixture is from 0.5 to 3.

4. A coppering process according to claim 1, in which the fluid suspension of the precipitating metal is first injected into a stream of acidified water to form a homogeneous diluted suspension which is then injected into the stream of cupric salt solution to produce the stream of homogeneous turbulent mixture.

5. A coppering process according to claim 4, in which the pH value of the mixture is from 0.5 to 3.

6. A coppering process according to claim 1, in which the precipitating metal is zinc.

7. A coppering process according to claim 6, in which the zinc is in the form of a suspension of powdered zinc in a viscous aqueous dispersion of an inert hydrophilic colloid, the viscosity of the dispersion being such that a uniform concentration of the powdered zinc is maintained in suspension.

8. A coppering process according to claim 7, in which the hydrophilic colloid is selected from the group comprising carboxymethyl cellulose, polyvinyl alcohols and soluble starches, gums and gelatins.

9. A coppering process according to claim 8, in which the viscous aqueous suspension contains from 1% to 5% by weight of powdered zinc, from 0.1 to 0.5% by weight of carboxymethyl cellulose, and from 0.1 to 0.5% by weight of 40 aqueous formaldehyde.

10. A coppering process according to claim 1, in which the precipitating metal is powdered iron having an average particle size of from 5 to 7 microns.

11. A coppering process according to claim 10, in which the powdered iron is in suspension in a viscous aqueous dispersion of an inert hydrophilic colloid, the viscosity of the dispersion being such that a uniform concentration of the powdered iron is maintained in suspension.

12. A coppering process according to claim 11, in which the hydrophilic colloid is selected from the group comprising carboxymethyl cellulose, polyvinyl alcohols and soluble starches, gums and gelatins.

13. A coppering process according to claim 12, in which the viscous aqueous suspension contains from 1 to 5% by weight of powdered iron, from 0.1 to 0.5% by weight of carboxymethyl cellulose, and from 0.1 to 0.5% by weight of 40 aqueous formaldehyde.

14. A coppering process according to claim 13, in which the surface to be coppered is the exposed silver surface of a silvered glass mirror.

15. A coppering process employing the galvanic action of a metal higher in the electro-chemical series than copper on a solution of a cupric salt to effect precipitation of a uniform coating of copper on to a surface, which comprises the steps of producing a confined turbulent stream of copper sulphate solution acidified with sulphuric acid, which stream flows under pressure, injecting a homogeneous fluid suspension of powdered zinc at a desired pre-determined rate into said stream to induce turbulent mixing in said stream so as to produce a stream of homogeneous turbulent mixture, and spraying the mixture towards the surface to be coppered in such manner that droplets of said homogeneous mixture of cupric salt solution and powdered zinc suspension arrive at the surface before there has been sufficient interaction within the mixture to precipitate appreciable amounts of metallic copper.

16. A coppering process employing the galvanic action of a metal higher in the electro-chemical series than copper on a solution of a cupric salt to effect precipitation of a uniform coating of copper on to a surface, which comprises the steps of producing a confined turbulent stream of copper sulphate solution acidified with sulphuric acid, which stream flows under pressure, injecting into said stream at a desired predetermined rate to induce turbulent mixing in said stream so as to produce a stream of homogeneous turbulent mixture, a homogeneous fluid suspension of powdered iron having an average particle size of from 5 to 7 microns in a viscous aqueous dispersion of an inert hydrophilic colloid, the viscosity of the dispersion being such that a uniform concentration of the powdered metal is maintained in suspension, and spraying the homogeneous mixture towards a surface to be coppered in such manner that droplets of said homogeneous mixture of copper sulphate solution and powdered iron arrive at the surface before there has been sufficient interaction within the mixture to precipitate appreciable amounts of metallic copper.

17. A coppering process according to claim 16, in which the fluid suspension of powdered iron is first injected into a stream of acidified water to form a homogeneous diluted suspension which is then injected into the confined stream of copper sulphate solution.

18. A coppering process employing the galvanic action of a metal higher in the electrochemical source than copper on a solution of a cupric salt to effect precipitation of a uniform coating of copper on to the exposed silver surface of a silvered glass mirror, which comprises the steps of producing a confined turbulent stream of a solution of a cupric salt flowing under pressure, injecting a homogeneous fluid suspension of the precipitating metal in powder form at a desired predetermined rate into said stream to induce turbulent mixing in said stream so as to produce a stream of homogeneous turbulent mixture, and spraying the mixture towards the exposed silver surface in such manner that the droplets of said homogeneous mixture arrive at the surface before there has been sufficient interaction within the mixture to precipitate appreciable amounts of metallic copper.

19. Apparatus for coppering a surface comprising a reservoir for cupric salt solution, a first conduit leading from the solution reservoir, a mixing conduit, connected to the first conduit and having a smaller bore than the first conduit, a reservoir for a homogeneous fluid suspension of a precipitating metal, a second conduit leading from the suspension reservoir to the mixing conduit at a point downstream from the point of entry of the first conduit, means connected to the reservoirs to maintain pressure therein so that the suspension is injected through the second conduit into the solution in the mixing conduit, and a third conduit leading out of the mixing conduit at a point downstream from the point of entry of the second conduit, to a spray head, the ratio of the bore of the mixing conduit to the bore of the first conduit being

such that turbulence is maintained throughout the mixed liquid in the mixing conduit.

20. Apparatus according to claim 19, in which the bore of the mixing conduit is approximately one-quarter of that of the first conduit.

21. Apparatus according to claim 20, in which the bore of the second conduit is approximately one-eighth of that of the first conduit.

22. Apparatus according to claim 21, in which the portion of the second conduit which joins the mixing conduit is substantially co-axial with that part of the mixing conduit situated downstream of the point of entry of the second conduit into the mixing conduit.

23. Apparatus according to claim 22, in which the conduit leading from the mixing conduit to the spray head is flexible and the spray head is arranged to reciprocate transversely to the direction of movement of a surface to be coppered.

24. Apparatus for coppering a surface comprising a reservoir for cupric salt solution, a first conduit leading from the solution reservoir, a mixing conduit connected to the first conduit and having a smaller bore than the first conduit, a water reservoir, a second conduit leading from the water reservoir to the mixing conduit at a point downstream from the point of entry of the first conduit, a reservoir for a homogeneous fluid suspension of a precipitating metal, a third conduit leading from the suspension reservoir to the second conduit, means connected to the reservoirs to maintain pressure therein so that the suspension is diluted in the second conduit and is injected therefrom into the solution in the mixing

conduit, and a fourth conduit leading out of the mixing conduit at a point downstream from the point of entry of the second conduit, to a spray head, the ratio of the bore of the mixing conduit to the bore of the first conduit being such that turbulence is maintained throughout the mixed liquid in the mixing conduit.

25. Apparatus according to claim 24, in which the bore of the mixing conduit is approximately one-quarter of that of the first conduit, the bore of the second conduit is approximately one-eighth of that of the first conduit, the portion of the second conduit which joins the mixing conduit is substantially co-axial with that part of the mixing conduit situated downstream of the point of entry of the second conduit into the mixing conduit, the fourth conduit is flexible, and the spray head is arranged to reciprocate transversely to the direction of movement of the surface to be coppered.

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