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SILVER PLATING BATH

David L. Dobbs, Robert F. Gill, Jr., and Ronald B. Howes, Cincinnati, Ohio, assignors, by mesne assignments, to Lewco, Inc.

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This invention relates to silver plating solutions, particularly plating baths of the chemical displacement type for the direct plating of silver upon copper and copper alloys.

It has been common practice for many years to plate silver upon metallic surfaces by either one of two techniques, electrodeposition or chemical displacement. Electroplating, while enjoying many advantages, has its limitations in that the necessity of making electrical connection with the part to be plated renders the process economically unfeasible in many instances and inherent limitations of throwing power make it impossible to properly plate objects having very irregular surfaces including, particularly, small and deep depressions. In those applications where somewhat thinner plating is sufficient, the chemical displacement procedure is more economical and, where the objects to be plated are very small particles or have very irregular surfaces, only the displacement type of bath will give satisfactory results. A limitation on the use of this method of plating is to be found in the fact that silver may be plated from a chemical displacement solution only when the metal to be plated lies above it in the electromotive force series; that is to say, if the base metal is more reactive than silver.

Heretofore, cyanide silver baths have been most generally employed for the plating of silver by chemical displacement, ammoniacal thiosulfate solutions also being used to some extent. The use of cyanide solutions is objectionable because of the very high toxicity of the cyanide compounds. Furthermore, deposits from such solutions display an undesirable tendency to tarnish or discolor within a short time after deposition.

The principal object of the invention herein described is to provide a substantially non-toxic silver plating solution of the chemical displacement type for copper and copper alloys such as the bronzes and brasses. A co-ordinate object is to provide such a solution which is stable and non-volatile and which deposits a very satisfactory adherent, self-brightening plate which is remarkably passive and tarnish resistant. Further features of advantage are to be found in that the solution possesses good cleaning action without causticity and that used solution may be replenished for continued optimum performance.

In its essence, the plating bath contemplated by the invention comprises an acidified thiourea solution containing silver ions available for deposition upon the surfaces of copper-bearing metals, copper being taken into solution in exchange for the silver deposited, and a non-ionic wetting agent. The silver ions are provided by the dissolution of silver salts in the acidified thiourea solution. It is believed that the silver is present in the bath as a thiourea complex, each ion being at least theoretically coordinated with two molecules of this complexing agent. The reaction involved in the deposition of silver from the plating bath is actalyzed and mediated by the presence of sulfide anions in the plating solution.

Inclusion of a suitable non-ionic wetting agent in the bath insures an adherent deposit.

Although, as will be pointed out more fully below, any of a number of different acids, or mixtures thereof, may be employed, it has been found that sulfuric acid has given consistently excellent results and is, therefore, considered to be preferred for general commercial use of the invention. Similarly, silver ions may be made available from any of a number of silver salts, but since silver nitrate is most readily available and gives satisfactory results, the invention is described with reference to the use of this particular salt.

Acid solutions of thiourea readily dissolve silver sulfide and also form soluble complexes with silver and copper salts. The solubility of silver sulfide in the acid thiourea solutions is operatively important in that the sulfide catalyst is thereby held and made available in the solution, silver sulfide being highly insoluble in water. The complexing characteristic of thiourea in acid solution is important in that a substantial reservoir of silver may be made available in the bath and the copper, exchanged for the silver in the deposition reaction, is retired in the complex to minimize interference with the deposition of a high quality silver plate.

It has been found that a rather substantial excess of thiourea, over and above the stoichiometric equivalent of the silver salt, is necessary in the plating solution to provide the necessary solubilizing power for the complex and also to maintain the cleaning capacity and the ability to hold the metals in the complex. Theoretically, two moles (152.2 grams) of thiourea should fully complex one mole (169.9 grams) of silver nitrate. In spite of this relationship, it has been found that for useful results, the amount of thiourea in the plating solution should be from 10 to 50 times, by weight, the amount of silver nitrate, the preferred range being from 12 to 14 times as much thiourea as silver nitrate. In terms of the weight of thiourea to weight of silver, the useful range is about 16 to 79, and the preferred range is about 19 to 21. With reference to the thiourea-silver nitrate complex, the excess of thiourea over that theoretically engaged in the complex is from 9 to 55 times the weight of thiourea in the complex, the preferred range being from 12 to 15.

Plating results are also effected by concentration of the solution, the useful range being from 3 percent to 15 percent, based on the total weight of thiourea and silver nitrate in the solution, the optimum range being from 5 to 8 percent.

The characteristics of the silver plate deposited from a solution prepared in accordance with the invention differ with the use of different acids in the solution. As stated above, sulfuric acid has been found to give the most satisfactory results. However, any water-soluble acid capable of producing acidity of pH 2.4 or below including, for example, acetic, citric, phosphoric, tartaric, and nitric acids, produces useful results. As is inferred by the preceding statement, the acidity of the solution also has a controlling influence on the behavior of the bath and the characteristics of the plate. Solutions having a pH from 1.0 to 2.4 have been found to give useful results, the preferred range for the most satisfactory depositions being from 1.4 to 1.5.

It will be understood that since acidity is the most important functional characteristic of the acidifying agent in the solution, acid salts may be used in place of, or together with, the acid. Also, a mixture of two or more different acids may be used.

In addition to the readily available silver nitrate, other silver salts which are soluble in acid thiourea solutions may be used as a source of silver ions. For example, the sulfate, oxides, acetates, and halides may be used. Higher

concentrations of certain of these anions tend to adversely influence the nature of the silver deposit so that the selection of a particular silver salt depends somewhat upon the specification requirements of the plate.

The sulfide ion catalyst in the plating bath serves as an accelerator of the deposition reaction. While solutions to which no sulfide, as such, has been added deposit silver on copper or copper alloy surfaces, initial deposition is very slow. Plate thickness and other quality characteristics of the coating are also improved by the presence of the sulfide ion, but the greatly accelerated action of the plating baths containing the sulfide constitutes the principal advantage attendant upon its use. A sodium sulfide may be used as a source of the sulfide ion, the silver sulfide initially formed as a precipitate upon introduction of the sodium sulfide solution into the acid thiourea silver solution being readily redissolved in the bath. Other sulfides may serve as a source of the sulfide ion in the solution, as, for example, silver sulfide and sodium polysulfide. Since an excessive concentration of sulfide ions in the bath tends to cause sponginess in the silver deposit, a concentration of 10 grams of the anion per liter of bath solution is regarded as the maximum for good results.

Any of a number of commercially available non-ionic wetting agents may be used. A suitable one is that commercially available under the trade designation "Tergitol Dispersant NPX", alkyl phenyl polyethylene glycol ether (Carbide & Carbon Chemicals Corp.). The amount of wetting agent provided in the solution is not critical, and the examples given hereinafter will serve as a guide in this respect.

While it must be recognized that optimum bath formulation necessarily involves compromise as between the several factors which together determine the quality of the silver plate deposited from the bath, one formula, for example, giving a brighter plate while another results in a more rapidly deposited but somewhat less lustrous coating, the following example may be regarded as a preferred commercial formula for the bath. To prepare a twenty-gallon batch of plating solution, the following ingredients, in addition to water, are required:

Sulfuric acid, 66° Bé.	ml	286
Thiourea	lb	11
Silver nitrate, C.P.	g	375
Wetting agent (Tergitol NPX)	ml	375
Sodium sulfide hydrate	g	10

The sulfuric acid is stirred into about 15 gallons of tap water contained in a suitable crock, and the thiourea is dissolved in this mixture. The silver nitrate, dissolved in about a liter of water, is then gradually stirred in. The white, curdy precipitate, initially formed upon addition of the silver nitrate to the acid solution, will completely dissolve unless the solution is excessively cold. The wetting agent is then stirred in gently to avoid excessive foaming.

After the volume of the solution in the crock has been made up to twenty gallons, the sodium sulfide, dissolved in a small amount of water, is slowly added with continuous stirring. Care should be taken to provide good ventilation for this operation. If the pH of the solution is found to be above 1.5, sufficient sulfuric acid should be added to bring the pH within the preferred range of 1.4 to 1.5. Desirably, the batch is allowed to settle overnight before it is bottled and ready for use.

If desired, a suitable coloring agent and an odorant may be added. For special purposes, a small amount of glycerol may also be added. The presence of these addition agents, or of other acids and salts in limited quantities, do not materially affect the results obtained by use of the bath.

If preferred, the several ingredients of the invention may be prepared and packaged in the form of a dry mix for eventual solution in water by the user. For example, such a mix may be prepared by bringing together 40 parts, by weight, of silver nitrate, 400 parts of thiourea, 1 part of silver sulfide, 40 parts of a dry wetting agent, such as the sodium lauryl sulfate type of dry detergent sold under the trade designation "Duponal Me Dry," and about 400 parts of citric acid. The plating bath is prepared by dissolving about 50 grams of this dry mix in a liter of water.

Silver coatings of 0.05 mil. and thicker are obtainable with the sulfuric acid bath under favorable conditions. Under ordinary conditions, the usual range is from 0.02 to 0.03. At bath temperature of about 85° F., the practical maximum thickness of plate may be attained with immersion of from 5 to 10 minutes. The rate of deposition of silver diminishes with depletion of silver in the plating bath. Before finally discarded as exhausted, the plating bath may be replenished two or three times by the addition thereto of a concentrated replenisher which may be either in liquid or dry form. A suitable liquid replenisher intended to be added to the bath when it has become approximately one-half depleted in silver on the basis of one pint of replenisher solution to one gallon of plating bath solution may be prepared using the following ingredients:

Sulfuric acid, 96° Bé.	ml	2
Thiourea	g	30
Silver nitrate, C.P.	g	9
Wetting agent (Tergitol NPX)	ml	4

The sulfuric acid is added to about ⅔ pint of water and the thiourea dissolved in this solution. The silver nitrate, dissolved in a small amount of water, is added slowly with stirring. Finally, the wetting agent is added and the volume made up to one pint.

A dry replenisher mix, intended to be dissolved in about 100 ml. of water and added to a liter of partially depleted plating bath may be prepared by mixing 5 grams of silver nitrate, 10 grams of thiourea, and 5 grams of citric or tartaric acid, all ingredients being powdered.

Silver coatings deposited from plating baths prepared in accordance with the invention as herein described are characterized by extraordinary passivity. They are highly resistant to attack by acids, heat oxidation, sulfide tarnishing, and many other chemical agents. In this respect the coatings are substantially more effective than electrodeposited silver of comparable thickness.

It will be recognized that it is neither practicable nor necessary to set out at length the many possible variations in composition of the plating bath herein fully described in its essential characteristics. The invention may readily be practiced on the basis of the disclosures contained, although formulations of particular baths may be varied somewhat to adapt them to the particular needs of a given application.

Invention is claimed as follows:

1. A plating bath for the deposition of silver upon a copper-containing metal surface by chemical displacement consisting essentially of an acidified solution of thiourea, a silver salt, an acidifying agent, and sulfide ions, said solution having a pH of between 1.0 and 2.4 and providing silver ions in sufficient concentration to effect a useful silver deposit upon said metal surface, said thiourea being present in an amount equal to from about 16 to about 79 times the weight of silver, and said sulfide ions being present in an effective amount but less than about 10 grams per liter of solution.

2. A plating bath in accordance with claim 1 in which the acidifying agent is sulfuric acid.

3. A plating bath for the deposition of silver upon a copper-containing metal surface by chemical displacement consisting essentially of an acidified solution of thiourea, a silver salt, an acidifying agent, and sulfide ions, said solution having a pH of between 1.4 and 1.5 and providing silver ions in sufficient concentration to effect a useful silver deposit upon said metal surface,

said thiourea being present in an amount equal to from about 16 to about 79 times the weight of silver, and said sulfide ions being present in an effective amount but less than about 10 grams per liter of solution.

4. A plating bath in accordance with claim 3 in which the acidifying agent is sulfuric acid.

5. A plating bath for the deposition of silver upon a copper-containing metal surface by chemical displacement consisting essentially of an acidified solution of thiourea, a silver salt, an acidifying agent, and sulfide ions, said solution having a pH of between 1.0 and 2.4 and providing silver ions in sufficient concentration to effect a useful silver deposit upon said metal surface, said thiourea being present in an amount equal to from about 19 to about 21 times the weight of silver, and said sulfide ions being present in an effective amount but less than about 10 grams per liter of solution.

6. A plating bath for the deposition of silver upon a copper-containing metal surface by chemical displacement consisting essentially of an acidified solution of thiourea, a silver salt, an acidifying agent, a wetting agent, and sulfide ions, said solution having a pH of between 1.0 and 2.4 and containing a complex of thiourea with a silver salt, an excess of thiourea sufficient to hold said complex in solution, and sulfide ions in an effective amount but not greater than 10 grams per liter of solution.

7. A plating bath for the deposition of silver upon a copper-containing metal surface by chemical displacement consisting essentially of a sulfuric acid solution of thiourea, a silver salt, a wetting agent, and sulfide ions, said solution having a pH of between 1.4 and 1.5 and providing a complex of thiourea with a silver salt, an excess of thiourea sufficient to hold said complex in solution, and sulfide ions in an effective amount but no greater than 10 grams per liter of solution.

8. A plating bath for the deposition of silver upon a copper-containing metal surface consisting essentially of an aqueous solution of silver nitrate, thiourea in an amount equal to from 12 to 14 times the weight of the silver nitrate, water in sufficient amount to dilute the solution to a concentration of from 5 percent to 8 percent total of thiourea and silver nitrate based on total solution by weight, sulfuric acid sufficient to acidify the solution to a pH between 1.4 and 1.5, sodium sulfide in an effective amount but no greater than 10 grams per liter of solution, and a wetting agent.

9. A plating path for the deposition of silver upon a copper-containing metal surface consisting essentially of an equeous solution of silver nitrate, thiourea in an amount equal to from 10 to 50 times the weight of the silver nitrate, water in sufficient amount to dilute the solution to a concentration of from 3% to 15% total thiourea and silver nitrate to total solution by weight, sulfuric acid in sufficient amount to acidify the solution to a pH between 1.0 and 2.4, a wetting agent, and sodium sulfide in an effective amount but no greater than 10 grams per liter of solution.

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