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MIRROR BRIGHT SILVER PLATING

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This invention relates to an improvement in the method for producing electrodeposits of silver, and is particularly concerned with a plating bath from which mirror bright deposits of silver of any desired thickness can be obtained.

Presently accepted commercial practice of electroplating silver includes the use of a bath composed of silver cyanide, an excess of alkali cyanide over that required to dissolve the silver cyanide, alkali carbonate and water. An electric current is passed through this solution by means of silver anodes, silver depositing on the articles to be plated, i. e. which constitute the cathode. Under proper conditions of current, temperature, agitation and maintenance of proper concentration of the electrolyte, a crystalline, non-lustrous matte white deposit of silver is secured at the cathode. This deposit requires buffing or burnishing, in order to secure a bright surface, which is costly, wasteful of metal and also time consuming. It has been common practice to add to the plating bath a brightener which will give the deposit, as it is made in the bath, a slightly lustrous appearance, in order to cut down on the amount of polishing required thereafter. Also many attempts have been made to arrive at a bath which can produce an initial bright finish which would require no further polishing. Heretofore, no truly bright silver plate, in the sense of possessing "mirror brightness" was known.

It has been suggested to add protein substances, e. g. wool, casein, egg albumen, etc., to the electroplating bath in an attempt to give bright, dense, smooth, adherent and continuous deposits. Such electroplating solutions have been found to be unstable, and do not result in imparting "mirror brightness." Moreover such solutions deteriorate rapidly during use due to the formation of decomposition products of proteins. It has been common practice to add carbon disulphide to the bath. However, such an additive does not impart any appreciable luster and is usually not uniform over the entire plated surface with normal handling. Moreover, the deposit is sensitive to plating conditions in that the quantity of carbon disulphide present, the current density, temperature, agitation and solution composition must all be adjusted and maintained within closely balanced limits. At best, when using carbon disulphide, only a relatively thin plating of semi-lustrous character can be obtained, and if it is attempted to increase the thickness of the deposit, it changes to a dull white appearance.

The use of thio-carbamates has also been proposed. However, only highly lustrous deposits have been obtained, and not mirror-brightness. Also such a solution has a poor "throwing power" and is unstable, i. e. deleterious decomposition products are produced causing dull deposits. It has also been suggested to use a colloidal solution of a detergent, e. g. sodium oleate, Turkey red oil, etc. to enhance the brightness of deposit. Such a solution has also been found to be unstable in that it tends to form deleterious decomposition products. Also, when activated carbon is used to remove impurities in

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the bath, it also removes all the brightener, and thus the solution must be shut down while it is being cleaned, which is an uneconomical practice. It is usual practice to buff the article to be plated before inserting it in a bath, and when using saponifiable buffing oils as the buffing compounds, it has been found that they are carried into the solution where they are saponified by the detergent, thus causing dullness of plate and requiring the solution to be purified and/or replaced. In general it may be stated that the use of organic sulfur compounds, carbamates, hydroxy benzenes, etc. as brighteners produce an unstable solution, e. g. rapid deterioration of the solution, which after a short period of use becomes unable to produce bright deposits.

Other types of additives have been suggested, e. g. reaction products of ammonium thiosulfate with certain modifying agents, such as a commercial X-ray fixed used to dissolve silver salts from X-ray film after exposure and development. Such additives are also relatively unstable and have to be replenished frequently and continuously, the result being non-uniform plating. In all cyanide type electroplating solutions carbonates build up, and up to the present time it has been found that these carbonates deleteriously affect the electroplating operation. In the novel invention described herein, as much as 25 oz./gallon of carbonates can build up without materially affecting the operation. Also, with the electrolyte of the instant invention it has been found that practically no decomposition of the brightener takes place, either on standing or after being subjected to the passage of electrolytic current.

A still further attempt at achieving brightness has been suggested in the addition of a mixture of potassium nitrate and selenium (as selenite) to the bath. However, mirror bright deposits cannot be produced in such solutions. Furthermore, as carbonates build up in the solution as normally occurs in all cyanide baths, any beneficial effect of potassium nitrate on selenium diminishes, the deposit gradually losing its lustre, even though potassium carbonates are not included initially in the solution.

It is accordingly an object of the invention to provide a method of electroplating which produces plated articles having substantially a mirror bright finish through a complete range from flash to heavy deposits. It is a further object of the invention to provide an electrolyte solution which is clear, water-white and capable of imparting a substantially mirror bright finish of a silver plate wherein the deposits are hard and highly ductile. A further object is to provide a silver plating solution which is stable, produces no deleterious decomposition products, and is operable to produce uniform mirror bright silver plate requiring no further burnishing or polishing. It is a still further object to provide a silver plating electrolyte operable to produce very heavy deposits of silver which are smooth, lustrous, and free of roughness; such as is required for electroforming processes and/or producing bearings or bearing surfaces. Other objects and advantages of my novel silver plating solution will be apparent from the description hereinafter following.

The distinctive and novel feature of the electrolyte of the invention is the use of an electrolyte containing a very small amount of bismuth. The bismuth is preferably added in the form of a soluble complex of potassium, bismuth and a polyhydroxy aliphatic compound together with free or uncombined amounts of the latter. The term "bright covering power" is used hereinafter to refer to the range of current densities over which mirror bright finishes are obtained.

The bismuth of the instant invention is preferably introduced as a soluble potassium bismuth glycerol complex or by anodic dissolution from a soluble bismuth, or silver-

bismuth alloy electrode, in which latter case it would form the complex with the glycerine in the bath.

In analyzing the results obtainable with the novel electrolytes described herein, the "bent cathode" test was used. As will be understood by those skilled in the art, the technique of using bent cathodes makes it possible to obtain a picture of the effect of varying the current density over wide limits, in one operation. The bent cathodes employed in this investigation were pieces of nickel-silver about 3 inches long and about 1 inch wide, being bent at a right angle 1 inch from the bottom. The tests were run initially at a current density of 15 amps. per square foot and at room temperature. The bent portion extended towards the anode when the cathode was in position for plating. Moderate agitation of the solution was employed. For solutions within the preferred working limits, which are described hereinafter, the bent cathodes were mirror bright all over at this current density. The two tables below illustrate the use of a glycerine bath, i. e. wherein the polyhydroxy aliphatic compound of the abovementioned complex is glycerine. The operative range is considered to be a preferred working range, however, it may still be possible to exceed the limits of the operative range set forth below in the tables and still obtain "mirror bright" plating.

TABLE A.—POTASSIUM FORMULATION

Reagent	Preferred Operative Range		Optimum value	
	oz./gal.	gm./liter	oz./gal.	gm./liter
Silver Cyanide.....	3-16	22.5-120.0	6.0	45.0
Potassium Cyanide:				
Total.....			7.0	52.5
Free.....	1-6	7.5-45.0	4.0	30.0
Potassium Carbonate.....	2-20	15.0-150.0	6.0	45.0
Glycerine.....	1-20	7.5-150.0	ca. 5.0	37.5
Bismuth.....	0.0013-0.13	0.01-1.00	0.03	0.25
Potassium Hydroxide.....	1.0-4.0	7.5-30.0	3.0	22.5

TABLE B.—SODIUM FORMULATION

Reagent	Preferred Operative Range		Optimum value	
	oz./gal.	gm./liter	oz./gal.	gm./liter
Silver Cyanide.....	3-16	22.5-120.0	6.0	45.0
Sodium Cyanide:				
Total.....			7.0	52.5
Free.....	1-6	7.5-45.0	4.0	30.0
Sodium Carbonate.....	2-20	15.0-150.0	6.0	45.0
Glycerine.....	1-20	7.5-150.0	ca. 5.0	37.5
Bismuth.....	0.0013-0.13	0.01-1.00	0.03	0.25
Sodium Hydroxide.....	1.0-4.0	7.5-30.0	3.0	22.5

As further examples of solutions including polyhydroxy aliphatic compounds other than in the preferred glycerine complex, the following formulations are given:

Example 1

	Ozs./gal.
Silver cyanide.....	5
Potassium carbonate.....	6
Potassium cyanide (free).....	4
Bismuth.....	0.0013
Ethylene glycol.....	2.0
Potassium hydroxide.....	3.0

Example 2

	Ozs./gal.
Silver cyanide.....	5
Potassium carbonate.....	6
Potassium cyanide (free).....	4
Bismuth.....	0.003
Sorbitol.....	2.0
Potassium hydroxide.....	3.0

Example 3

	Ozs./gal.
Silver cyanide.....	7
Potassium carbonate.....	4
Potassium cyanide (free).....	6
Bismuth.....	0.01
Erythritol.....	2.0
Potassium hydroxide.....	3.0

In a manner similar to that shown in Table B, sodium formulations of the aliphatic polyhydroxy compounds are also useable.

It is thus seen that aliphatic polyhydroxy compounds other than glycerine, i. e. ethylene glycol, the hexahydric alcohols, e. g. sorbitol, mannitol, and butanetetrol (erythritol) etc. also give good results. However, I have found that the straight chain polyhydroxy aliphatic compounds preferably are those wherein the hydroxy groups are attached to consecutive carbon atoms. Also, the preferable compounds are those wherein there are as many hydroxy groups as there are C atoms and also those having from two to six C atoms.

It has been above stated that the bismuth is added to the bath in the form of a soluble complex, as for example a potassium-bismuth-erythritol complex. However, the exact stoichiometrical relationship of the elements of the complex have not been determined, nor have I determined whether mixtures of complexes of these elements are present. Nevertheless, the presence of the several elements in a soluble complex form is all that is required for the electrolyte to perform its desired function. The relative proportions by weight of the elements of the complex are: 1 part bismuth, from 1 to 6 parts of the straight chain polyhydroxy aliphatic compound and from 1 to 4 parts of an alkali metal hydroxide.

All of the abovementioned complexes are prepared in a similar manner. For example, to prepare a potassium-bismuth-glycerol complex there is added 10 g. of glycerol, 10 g. of potassium hydroxide and 50 ml. of water to 2.5 g. of freshly precipitated bismuth hydroxide. The mixture is then heated to boiling until complete solution takes place, after which the volume is brought to 200 ml. Such a solution will contain 0.01 bismuth per ml. The bismuth content may be adjusted to almost any concentration, but it has been found convenient to make it up to the above value since for every ampere hour used in the electroplating process 1 ml. of the bismuth concentrate is required.

Also, for example, a sodium-bismuth-glycerol complex for use with baths containing sodium salts may be prepared as follows: To 2.5 grams of freshly precipitated bismuth hydroxide there are added 10 g. of glycerol, 15 g. of sodium hydroxide and 50 ml. of water. The mixture is boiled until complete solution takes place and is then diluted to 200 ml. with water.

Silver plating baths are preferably made up by using potassium cyanide or sodium cyanide, but my novel brightening agent is likewise effective in baths made with the cyanide of the other alkali metals cesium, rubidium and lithium.

In determining the above listed values the current density was varied between 5 to 40 amps./square foot, the optimum value being about 20 amps./sq. ft. Also, in plating with the above described solutions, it is advisable to maintain the pH value above 13. The temperature was varied between 20° C. and 40° C. with the optimum value being 28° C. (about room temperature).

In using a solution according to my novel invention, the bath has almost water white clarity so that one can watch the work in process of being plated.

It is possible when electroplating with the above described solutions to purify by filtration through activated carbon while maintaining operation with no appreciable loss of brightener. Also, the solution should be agitated or the work to be plated should be moved.

As has been pointed out, the solution of my invention enables the electroplating of silver on an object with sub-

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stantially a mirror bright finish, which is acceptable to the trade as silver plate. If it is desired to obtain a silver alloy plate, anodes containing various percentages of bismuth may be used.

This application is a continuation-in-part of my co-pending application Serial No. 419,930 filed March 30, 1954, now abandoned.

The above description of the composition of the solution of my invention is not intended as a restriction of the invention, and it is intended to cover the invention broadly within the scope and spirit of the appended claims.

I claim:

1. The method of electrodepositing bright silver which comprises electrolyzing a solution containing silver cyanide, an alkali metal cyanide, an alkali metal carbonate, and a sufficient amount of a soluble complex of an alkali metal, bismuth, and a straight chain polyhydroxy aliphatic compound to impart brightness to the silver electrodeposit, said complex being formed by heating to boiling an aqueous mixture of 1 part bismuth compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts alkali metal hydroxide until complete solution is obtained.

2. The method of electrodepositing bright silver which comprises electrolyzing a solution containing silver cyanide, an alkali metal cyanide, an alkali metal carbonate, and a sufficient amount of a soluble complex of an alkali metal, bismuth, and a straight chain polyhydroxy aliphatic compound to impart brightness to the silver electrodeposit, said complex being formed by heating to boiling an aqueous mixture of 1 part bismuth compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts alkali metal hydroxide until complete solution is obtained, the bismuth content being at least about 0.01 gram per liter.

3. The method of electrodepositing bright silver which comprises electrolyzing a solution containing silver cyanide, an alkali metal cyanide, an alkali metal carbonate, and a sufficient amount of a soluble complex of an alkali metal, bismuth, and a straight chain polyhydroxy aliphatic compound to impart brightness to the silver electrodeposit, said complex being formed by heating to boiling an aqueous mixture of 1 part bismuth compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts alkali metal hydroxide until complete solution is obtained, the bismuth content being about 0.01 to about 1.0 gram per liter.

4. The method of electrodepositing bright silver which comprises electrolyzing a solution containing silver cyanide, an alkali metal cyanide, an alkali metal carbonate, and a sufficient amount of a soluble complex of an alkali metal, bismuth, and a straight chain polyhydroxy aliphatic compound to impart brightness to the silver electrodeposit, said complex being formed by heating to boiling an aqueous mixture of 1 part bismuth compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts alkali metal hydroxide until complete solution is obtained, and in which aliphatic compound there are as many hydroxy groups as there are carbon atoms.

5. The method of electrodepositing bright silver which comprises electrolyzing a solution containing silver cyanide, an alkali metal cyanide, an alkali metal carbonate and a sufficient amount of a soluble complex of an alkali metal, bismuth, and a straight chain polyhydroxy aliphatic compound to impart brightness to the silver electrodeposit, said complex being formed by heating to boiling an aqueous mixture of 1 part bismuth compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts alkali metal hydroxide until complete solution is obtained, said straight chain polyhydroxy aliphatic compound containing from 2 to 6 carbon atoms.

6. The method of electrodepositing bright silver which comprises electrolyzing a solution containing silver cyanide, potassium cyanide, potassium carbonate and a sufficient amount of a soluble complex of an alkali metal, bismuth, and a straight chain polyhydroxy aliphatic compound to impart brightness to the silver electrodeposit,

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said complex being formed by heating to boiling an aqueous mixture of 1 part bismuth compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts alkali metal hydroxide until complete solution is obtained, said alkali metal being potassium.

7. The method of electrodepositing bright silver which comprises electrolyzing a solution containing silver cyanide, sodium cyanide, sodium carbonate, and a sufficient amount of a soluble complex of an alkali metal, bismuth, and a straight chain polyhydroxy aliphatic compound to impart brightness to the silver electrodeposit, said complex being formed by heating to boiling an aqueous mixture of 1 part bismuth compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts alkali metal hydroxide until complete solution is obtained, said alkali metal being sodium.

8. The method of electrodepositing bright silver which comprises electrolyzing a solution containing 3 to 16 ounces per gallon of silver cyanide, 1 to 6 ounces per gallon of free potassium cyanide, 2 to 20 ounces per gallon of potassium carbonate, 1 to 20 ounces per gallon of a straight chain polyhydroxy aliphatic compound, and about 0.0013 to about 0.13 ounce per gallon of bismuth, the latter being present in a sufficient amount of a soluble complex of potassium, bismuth and a straight chain polyhydroxy aliphatic compound to impart brightness to the silver electrodeposit, said complex being formed by heating to boiling an aqueous mixture of 1 part bismuth compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts potassium hydroxide until complete solution is obtained.

9. The method of electrodepositing bright silver which comprises electrolyzing a solution containing 3 to 16 ounces per gallon of silver cyanide, 1 to 6 ounces per gallon of free sodium cyanide, 2 to 20 ounces per gallon of sodium carbonate, 1 to 20 ounces per gallon of a straight chain polyhydroxy aliphatic compound, and about 0.0013 to about 0.13 ounce per gallon of bismuth, the latter being present in a sufficient amount of a soluble complex of sodium, bismuth, and a straight chain polyhydroxy aliphatic compound to impart brightness to the silver electrodeposit, said complex being formed by heating to boiling an aqueous mixture of 1 part bismuth compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts sodium hydroxide until complete solution is obtained.

10. An electrolyte for depositing mirror-bright silver coatings consisting of an aqueous solution containing silver cyanide, an alkali metal cyanide, an alkali metal carbonate and a sufficient amount of a soluble complex of an alkali metal, bismuth, and a straight chain polyhydroxy aliphatic compound to impart brightness to the silver electrodeposit, said complex being formed by heating to boiling an aqueous mixture of 1 part bismuth compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts alkali metal hydroxide until complete solution is obtained.

11. An electrolyte for depositing mirror-bright silver coatings consisting of an aqueous solution containing silver cyanide, an alkali metal cyanide, an alkali metal carbonate, and a sufficient amount of a soluble complex of an alkali metal, bismuth, and a straight chain polyhydroxy aliphatic compound to impart brightness to the silver electrodeposit, said complex being formed by heating to boiling an aqueous mixture of 1 part bismuth compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts alkali metal hydroxide until complete solution is obtained, the bismuth content being at least about 0.01 gram per liter.

12. An electrolyte for depositing mirror-bright silver coatings consisting of an aqueous solution containing silver cyanide, an alkali metal cyanide, an alkali metal carbonate and a sufficient amount of a soluble complex of an alkali metal, bismuth, and a straight chain polyhydroxy aliphatic compound to impart brightness to the silver electrodeposit, said complex being formed by heat-

ing to boiling an aqueous mixture of 1 part bismuth compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts alkali metal hydroxide until complete solution is obtained, the bismuth content being about 0.01 to about 1.0 gram per liter.

13. An electrolyte for depositing mirror-bright silver coatings consisting of an aqueous solution containing from 3 to 16 ounces per gallon of silver cyanide, 1 to 6 ounces per gallon of free potassium cyanide, 2 to 20 ounces per gallon of potassium carbonate, 1 to 20 ounces per gallon of a straight chain polyhydroxy aliphatic compound, and about 0.0013 to about 0.13 ounce per gallon of bismuth, the latter being present in the form of a sufficient amount of a soluble complex of potassium, bismuth, and a straight chain polyhydroxy aliphatic compound to impart brightness to the silver electrodeposit, said complex being formed by heating to boiling an aqueous mixture of 1 part bismuth compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts potassium hydroxide until complete solution is obtained.

14. An electrolyte for depositing mirror-bright silver coatings consisting of an aqueous solution containing from 3 to 16 ounces per gallon of silver cyanide, 1 to 6 ounces per gallon of free sodium cyanide, 2 to 20 ounces per gallon of sodium carbonate, 1 to 20 ounces per gallon of a straight chain polyhydroxy aliphatic compound, and about 0.0013 to about 0.13 ounce per gallon of bismuth, the latter being present in the form of a sufficient amount of a soluble complex of sodium, bismuth, and a straight chain polyhydroxy aliphatic compound to impart brightness to the silver electrodeposit, said complex being formed by heating to boiling an aqueous mixture of 1 part bismuth compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts sodium hydroxide until complete solution is obtained.

15. The electrolyte of claim 13, wherein said compound is glycerine.

16. The electrolyte of claim 13, wherein said compound is erythritol.

17. The electrolyte of claim 14, wherein said compound is glycerine.

18. The electrolyte of claim 14, wherein said compound is erythritol.

19. An electrolyte for depositing mirror-bright silver coatings consisting of a water solution containing 3 to 16

ounces per gallon of silver cyanide, 1 to 6 ounces per gallon of free potassium cyanide, 2 to 20 ounces per gallon of potassium carbonate, 1 to 20 ounces per gallon of glycerine, 0.0013 to 0.13 ounce per gallon of bismuth, and 1 to 4 ounces per gallon of potassium hydroxide.

20. An electrolyte for depositing mirror-bright silver coatings consisting of a water solution containing 3 to 16 ounces per gallon of silver cyanide, 1 to 6 ounces per gallon of free sodium cyanide, 2 to 20 ounces per gallon of sodium carbonate, 1 to 20 ounces per gallon of glycerine, 0.0013 to 0.13 ounce per gallon of bismuth, and 1 to 4 ounces per gallon of sodium hydroxide.

21. An electrolyte for depositing mirror-bright silver coatings consisting of a water solution containing 6 ounces per gallon of silver cyanide, 7 ounces per gallon of potassium cyanide, 6 ounces per gallon of potassium carbonate, about 5 ounces per gallon of glycerine, and 0.03 ounce per gallon of bismuth, and 3 ounces per gallon of potassium hydroxide.

22. An electrolyte for depositing mirror-bright silver coatings consisting of a water solution containing 6 ounces per gallon of silver cyanide, 7 ounces per gallon of sodium cyanide, 6 ounces per gallon of sodium carbonate, about 5 ounces per gallon of glycerine, about 0.03 ounce per gallon of bismuth, and 3 ounces per gallon of sodium hydroxide.

23. A brightener to be used for the preparation of a bright silver plating bath together with silver cyanide, an alkali metal cyanide, and an alkali metal carbonate, said brightener comprising a sufficient amount of a soluble complex of an alkali metal, bismuth and a straight chain polyhydroxy aliphatic compound to impart brightness to the silver electrodeposit, said complex being formed by heating to boiling an aqueous mixture of 1 part bismuth compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts alkali metal hydroxide until complete solution is obtained.

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