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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

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in 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 fixer 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 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 mirror bright finish of a silver plate wherein the deposits are hard and highly ductile. A still 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. 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 a tartrate-free electrolyte containing a very small amount of antimony. The antimony is preferably added in the form of a soluble complex of potassium, antimony and a polyhydroxy aliphatic compound together with free or uncombined amounts of the latter. There has been described in the literature a process of plating bright silver alloy (i. e. not silver plate) which involves the use of from 2.5 to 3.0 per cent by weight of antimony to about 11 to 12 per cent antimony. This process relates to the coelectro-deposition of silver and antimony, by the use of a strongly alkaline silver cyanide-antimony tartrate bath. Such antimony tartrate baths exhibit a very poor "throwing power" i. e. a very narrow range of current densities over which a mirror bright finish is obtained. The term "bright throwing power" is used hereinafter to refer to the range of current densities over which mirror bright finishes are

obtained. As indicated above the antimony of the instant invention is preferably introduced as a soluble complex of potassium, antimony and a polyhydroxy aliphatic compound or by anodic dissolution from a soluble antimony electrode, in which latter case it would form a complex with the polyhydroxy aliphatic compound in the bath.

In comparing the results obtainable with the novel electrolytes described herein as contrasted to that used in the so-called "antimony tartrate" bath, 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 above-mentioned 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.....	3-8	22.5-60.0	6.0	45.0
Potassium Cyanide:				
Total.....			17.0	127.0
Free.....	10-15	75.0-112.5	14.0	105.0
Potassium Carbonate.....	6-20	60.0-150.0	6.0	45.0
Glycerine.....	1-20	7.5-150.0	ca. 5.0	ca. 37.5
Antimony.....	ca. 0.04-0.67	0.3-5.0	ca. 0.19	1.4

TABLE B.—SODIUM FORMULATION

Reagent	Preferred Operative range		Optimum value	
	oz./gal.	gm./liter	oz./gal.	gm./liter
Silver Cyanide.....	3-8	22.5-60.0	6.0	45.0
Sodium Cyanide:				
Total.....			11.0	82.4
Free.....	6-12	45.0-90.0	3.0	60.0
Sodium Carbonate.....	4-12	30.0-90.0	6.0	45.0
Glycerine.....	1-20	7.5-150.0	ca. 5.0	ca. 37.5
Antimony.....	ca. 0.04-0.67	0.3-5.0	ca. 0.19	1.4

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	4.0
Potassium carbonate	10.0
Potassium cyanide (free)	12.0
Antimony	0.04
Ethylene glycol	2.0

Example 2

	ozs./gal.
Silver cyanide	4.0
Potassium carbonate	10.0
Potassium cyanide (free)	12.0
Antimony	0.08
Sorbitol	2.00

Example 3

	ozs./gal.
Silver cyanide	6.0
Potassium carbonate	6.0
Potassium cyanide (free)	14.0
Antimony	0.2
Erythritol	2.0

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 antimony is added to the bath in the form of a soluble complex, e. g. potassium-antimony-erythritol complex. However, the exact stoichiometrical relationship of the elements of the complex has 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 complex are: 1 part antimony, 1-6 parts of the straight chain polyhydroxy aliphatic compound and 1-4 parts of an alkali metalhydroxide.

All of the abovementioned complexes are prepared in a similar manner. For example, to prepare a potassium-antimony-glycerol complex there is added 48 g. of glycerol, 24 g. of potassium hydroxide and 50 ml. water to 10 g. of antimony tri-oxide or 10.7 g. of antimony pentoxide. 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 0.04 g. antimony per ml. The antimony 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 antimony concentrate is required.

Also, for example, a sodium-antimony-glycerol complex for use with baths containing sodium salts may be prepared as follows: To 10 grams of antimony trioxide, or to 10.7 grams of antimony pentoxide there are added 48 g. of glycerol, 17 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 between 11.8 and 13, with the preferred value being 12.4. The temperature was varied between 20° C. and 40° C., with the optimum value being 28° C. (about room temperature). In the course of the operation of the bath, the antimony may be replenished by addition in the form of the complex or by anodic dissolution from a soluble silver-antimony or antimony anode.

I have determined that, contrary to the teachings of the prior art, the use of tartrates is deleterious since they decrease the bright throwing power. Thus, in the instant invention it is of utmost importance that no tartrate be

present in the solution and the expression "tartrate-free electrolyte" is used hereinafter to define such an electrolyte solution and to distinguish from the suggestions of the prior art.

I have found that when eliminating the tartrates, the antimony content can be decreased to as low as 0.01 gram per liter (0.0015 ounce per gallon) while still obtaining mirror bright results. The use of high Sb content tends to embrittle the plate, especially if thicker plates are made. However, with higher silver content the Sb content can be increased and I have successfully used as much as 5 grams per liter of Sb. I have also found that theoretically there is no upper limit to the antimony content if one is willing to increase the silver content beyond commercially practical values. Preferably, however, it is here recommended that the Sb content be kept within the range of about 0.2 g./liter to about 5.0 g./liter. Also, 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.

The term "mirror brightness" is used herein and the following considerations are set forth in order to define this term as clearly as possible. It is well known that if a surface is perfectly plane, mirror-like reflection is obtained. According to the wave theory of light, a surface reflects like a plane surface as long as there are no elevations or depressions in it which have dimensions exceeding a small fraction of the wave length of light. For a given degree of roughness, it also follows that the regularity of the reflection depends not only on the wave length of the light but also on the angle of incidence. The smoothness of the surface is therefore best tested with light falling on it at nearly grazing incidence. This may be seen by examining a plate which is just on the border line of being fully bright. When looked at in the usual way, it seems bright, but if it is held so that it can be viewed by light falling on it at nearly grazing incidence, it shows a faint haziness or cloud. Perfectly bright plates, though, do not show this cloud. "Mirror brightness" is generally measured by the per cent of diffuse reflection. Results obtained with the above described solutions showed mirror brightness without cloudiness at every angle, with no measurable diffuse reflectivity.

As has been pointed out, the solution of my invention enables the electroplating of silver on an object with 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 antimony may be used.

Even when the underlying metal has a surface which is dull but has a smooth finish to begin with, by the use of solutions as described above, the surface becomes more and more bright as the plating proceeds and the final appearance is greatly improved if sufficient thickness of deposit is applied, whereas the usual result gives a rougher and more matte finish.

This application is a continuation-in-part of my co-pending application Serial No. 415,710 filed March 11, 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.

What I claim is:

1. The method of electrodepositing bright silver, which comprises electrolyzing a tartrate-free solution containing silver cyanide, an alkali metal cyanide, an alkali metal carbonate, and a sufficient amount of a soluble complex of an alkali metal, antimony 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 antimony 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 tartrate-free solution containing silver cyanide, an alkali metal cyanide, an alkali metal carbonate, and a sufficient amount of a soluble complex of an alkali metal, antimony 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 antimony compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts alkali metal hydroxide until complete solution is obtained, the antimony content being at least about 0.01 gram per liter.

3. The method of electrodepositing bright silver, which comprises electrolyzing a tartrate-free solution containing silver cyanide, an alkali metal cyanide, an alkali metal carbonate, and a sufficient amount of a soluble complex of an alkali metal, antimony 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 antimony compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts alkali metal hydroxide until complete solution is obtained, the antimony content being about 0.01 to about 5.0 grams per liter.

4. The method of electrodepositing bright silver which comprises electrolyzing a tartrate-free solution containing silver cyanide, an alkali metal cyanide, an alkali metal carbonate, and a sufficient amount of a soluble complex of an alkali metal, antimony 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 antimony 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 being one in which there are as many hydroxy groups as there are carbon atoms.

5. The method of electrodepositing bright silver which comprises electrolyzing a tartrate-free solution containing silver cyanide, an alkali metal cyanide, an alkali metal carbonate, and a sufficient amount of a soluble complex of an alkali metal, antimony 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 antimony 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 tartrate-free solution containing silver cyanide, potassium cyanide, potassium carbonate, and a sufficient amount of a soluble complex of an alkali metal, antimony 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 antimony 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 tartrate-free solution containing silver cyanide, sodium cyanide, sodium carbonate, and a sufficient amount of a soluble complex of an alkali metal, antimony 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 antimony com-

pound, 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 tartrate-free solution containing 3 to 8 ounces per gallon of silver cyanide, 10 to 15 ounces per gallon of free potassium cyanide, 6 to 20 ounces per gallon of potassium carbonate, 1 to 15 ounces per gallon of a straight chain polyhydroxy aliphatic compound, and about 0.0015 to 0.7 ounce per gallon of antimony, said antimony being present in a sufficient amount of a soluble complex of potassium, antimony 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 antimony 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 tartrate-free solution containing 3 to 8 ounces per gallon of silver cyanide, 6 to 12 ounces per gallon of free sodium cyanide, 4 to 12 ounces per gallon of sodium carbonate, 1 to 15 ounces per gallon of a straight chain polyhydroxy aliphatic compound, and about 0.0015 to about 0.7 ounce per gallon of antimony, said antimony being present in a sufficient amount of a soluble complex of sodium, antimony 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 antimony compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts sodium hydroxide until complete solution is obtained.

10. A tartrate-free 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, antimony 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 antimony compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts alkali metal hydroxide until complete solution is obtained.

11. A tartrate-free 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, antimony 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 antimony compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts alkali metal hydroxide until complete solution is obtained, and the antimony content being at least about 0.01 gram per liter.

12. A tartrate-free 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, antimony 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 antimony compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts alkali metal hydroxide until complete solution is obtained, the antimony content being about 0.01 to about 5.0 grams per liter.

13. A tartrate-free electrolyte for depositing mirror-bright silver coatings consisting of an aqueous solution containing from 3 to 8 ounces per gallon of silver cyanide, 10 to 15 ounces per gallon of free potassium cyanide, 6 to 20 ounces per gallon of potassium carbonate, 1 to 15 ounces per gallon of a straight chain polyhydroxy aliphatic compound and about 0.0015 to about 0.7 ounce per gallon of antimony, said antimony being present in the form of a sufficient amount of a soluble complex of potassium, antimony 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 antimony compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts potassium hydroxide until complete solution is obtained.

14. A tartrate-free electrolyte for depositing mirror-bright silver coatings consisting of an aqueous solution containing from 3 to 8 ounces per gallon of silver cyanide, 6 to 12 ounces per gallon of free sodium cyanide, 4 to 12 ounces per gallon of carbonate, 1 to 15 ounces per gallon of a straight chain polyhydroxy aliphatic compound, and about 0.0015 to about 0.7 ounce per gallon of antimony, said antimony being present in the form of a sufficient amount of a soluble complex of sodium, antimony 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 antimony 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. A tartrate-free electrolyte for depositing mirror-bright silver coatings consisting of a water solution containing 6 ounces per gallon of silver cyanide, 17 ounces per gallon of potassium cyanide, 6 ounces per gallon of potassium carbonate, about 5 ounces per gallon of glycerine, and about 0.19 ounce of antimony.

20. A tartrate-free electrolyte for depositing mirror-bright silver coatings consisting of a water solution containing 6 ounces per gallon of silver cyanide, 11 ounces per gallon of sodium cyanide, 6 ounces per gallon of sodium carbonate, about 5 ounces per gallon of glycerine, and about 0.19 ounce per gallon of antimony.

21. A brightener to be used for the preparation of a 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, antimony 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 antimony compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts alkali metal hydroxide until complete solution is obtained.

References Cited in the file of this patent

UNITED STATES PATENTS

2,555,375 Ruemmler June 5, 1951

FOREIGN PATENTS

450,979 Great Britain July 27, 1936