

UNITED STATES PATENT OFFICE

2,555,375

PROCESS OF PLATING BRIGHT SILVER
ALLOY

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No Drawing. Application November 13, 1948,
Serial No. 59,963

4 Claims. (Cl. 204—43)

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This invention relates to a method of plating bright silver alloy and to an electrolyte useful in the process of producing a bright silver alloy plate. In particular, it relates to the coelectrodeposition of silver and antimony to form an adherent alloy plate having a smooth, brilliant appearance and image reflecting properties and which is scratch and tarnish resistant.

The technical and commercial advantages of bright metal plating are well known to those skilled in the art. For example, a pure silver plate is relatively dull and must be polished. A bright plate on the other hand, is a saving in metal, because there is no loss occasioned by the buffing and coloring operations that are required in making a pure silver plate bright and pleasing in appearance. This is particularly significant in the case of a costly metal like silver. The irrecoverable loss, as of silver dust in buffing and silver loss in coloring operations, although removing only a few ten-thousandths of an inch of the silver plate, amounts to many thousands of dollars per year. Obviously, then, a bright silver plate possesses great economic advantages. Heretofore, no truly bright silver plate, in the sense of possessing mirror-like reflectivity, was known.

Furthermore, the pure silver plate tarnishes readily and is rather soft and easily scratched. Additional loss of silver occurs, because the pure silver metal must be polished frequently to remove the tarnish. Due to this soft nature of the pure silver, the basis metal must be replated from time to time to restore its finish, causing the user considerable expense.

It is, therefore, an object of this invention to provide a process for coelectrodepositing silver and antimony as an alloy plate having the aforementioned improved qualities.

It is a further object of this invention to provide an electrolytic bath capable of producing an electrodeposited silver-antimony alloy plate having the aforementioned improved qualities.

It has been found that silver and antimony can be coelectrodeposited from an electrolytic bath to form an adherent alloy plate having a brilliant appearing surface which is scratch and tarnish resistant. It has been found that this bright alloy plate may be deposited on a cathode from a strongly alkaline, aqueous, silver cyanide-antimonyl tartrate bath which is operated at relatively low current densities and temperatures.

The plate, as deposited from the above electrolytic bath, is essentially a pure alloy of electro-

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deposited antimony and silver. Wherever, due to a change in the amount of bath constituents or in operating conditions, an increase in the antimony content of the alloy plate occurs, there will be a corresponding decrease in the silver content, so that there are always only two elements present, i. e., silver and antimony. Likewise, where there is a decrease in the antimony content, there will be an increase in the silver content of the plate. Very minor amounts of impurities are probably present in the electrodeposited plate of this invention, as will be obvious to those skilled in the art. However, they do not appear to materially effect the resulting bright silver-antimony alloy plate.

As little as about 0.08 per cent by weight of antimony in the electrodeposited silver alloy plate causes a brightening effect. Appreciably less than this amount of antimony does not appear to materially brighten the appearance of the plate, and the scratch and tarnish resistance characteristics of such an electrodeposited plate are approximately the same as those of the pure silver plate.

Plates containing from 2.5 to 3.0 per cent by weight of antimony are bright and have mirror-like reflectivity. By "mirror-like reflectivity" is meant the ability to reflect an image. Very bright plates have been produced containing from 11 to 12 per cent of antimony.

Since the plate becomes more brittle as the antimony content increases, a choice of bright silver-antimony plate composition is determined by the application intended. For the best ductility with good brightness, it has been found that the antimony content should not exceed about 7% by weight. Hence, the bright silver alloy plates of this and lower antimony contents can be classified as sterling in quality. Plates containing from 7 to 12% antimony still possess sufficient ductility to have many uses, but where the antimony content appreciably exceeds 12% by weight, the plate becomes brittle and is easily chipped. Thus, the commercial and industrial applications of plates having high antimony contents are limited. Furthermore, flatware having thereon an electrodeposited coating of bright silver containing over 12% antimony would be departing so much in actual silver content from the pure silver plated flatware that its sales value would be considerably reduced.

The aqueous, alkaline electrolytic bath used in this process contains silver cyanide, potassium cyanide, the double tartrate of antimony and

potassium, potassium tartrate, potassium carbonate, and potassium hydroxide.

In the bath solution, it is believed that the silver exists as the soluble silver cyanide complex while the antimony exists as the soluble antimony tartrate complex. The composition of the resulting plate can be varied by varying the proportion of the silver complex to the antimony complex in the bath. Generally, the other factors like current density and temperature etc., remaining unchanged, an increase in the ratio of the silver to antimony in the bath will result in an increase in the ratio of silver to antimony in the plated alloy. On the other hand, a decrease in the ratio of silver to antimony in the bath, will result in an increase in the amount of antimony in the bright silver alloy plate.

The soluble silver cyanide complex is formed on the addition of silver cyanide to the bath. About 20 to 150 grams per liter of silver cyanide is sufficient. It is preferred, however, to use about 30 grams per liter of silver cyanide. This will fix the silver relative to the antimony and permit easier control of the plate composition as only one prime component has to be varied.

To aid in the formation of the soluble silver cyanide complex in the solution and in rendering the solution alkaline, about 20 to 100 grams per liter of potassium cyanide is added to the electrolyte. Excellent results have been obtained using a concentration of about 30 to 50 grams per liter which represents the preferred range.

The soluble antimony tartrate complex is obtained from the double tartrate of antimony and potassium. From about 3 to 100 grams per liter of this compound should be added to the bath. Excellent alloy plates have been obtained by adding to the bath about 5 to 36 grams per liter of potassium antimonyl tartrate so that this forms a preferred range.

Potassium tartrate, is necessary in the bath to prevent hydrolysis of the potassium antimonyl tartrate. Hydrolysis results in the loss of antimony in the bath solution (and also in a decrease of antimony in the plate) due to the precipitation of insoluble antimony compounds, probably the trioxide, and hence, a bath too low in the concentration of potassium tartrate is relatively unstable. From about 10 to 300 grams per liter of potassium tartrate is necessary in the bath to prevent hydrolysis when about 3 to 100 grams per liter of potassium antimonyl tartrate has been added to the bath. For example, when the potassium antimonyl tartrate concentration is about 5 to 36 grams per liter, the potassium tartrate concentration ranges from about 20 to 250 grams per liter. Hence, the potassium tartrate concentration required to prevent hydrolysis is somewhat proportional to the amount of the double tartrate added.

Potassium carbonate is added to the bath to provide increased alkalinity and to counteract the adverse effects of absorption of carbon dioxide from the atmosphere. It should be present in the amount of from 5 to 40 grams per liter, and it is preferred to use about 10 grams per liter.

Potassium hydroxide is added to the bath to render it strongly alkaline. From 2 to 8 grams per liter of potassium hydroxide has been found to produce the desired degree of alkalinity, and from 3 to 5 grams per liter are preferred.

The pH of the solution should range from 11

to 13.5. It is preferred, however, that the pH of the solution remain in the range of from 11.5 to 12 as this provides better control of the process and is sufficient to enable the silver and antimony to codeposit on the cathode. The pH can be controlled within these ranges, of course, by adjusting the concentrations of potassium hydroxide, potassium carbonate, and potassium cyanide.

In the electrolytic bath used in this process of electrodepositing a bright silver-antimony alloy equivalent sodium salts may be used where potassium salts are shown. Equivalent ammonium salts, i. e., salts containing the ammonium radical, NH_4^+ , may also be used without significantly altering the results obtained.

The current density in the electrolytic bath should range from 5 to 90 amperes per square foot. It is preferred to use current densities of from 20 to 70 amperes per square foot. It has been found, for example, that a current density as low as 20 amperes per square foot in a bath to which were added equal portions by weight of silver cyanide and potassium antimonyl tartrate in the bath above described produced a bright silver alloy plate having 1.89 per cent by weight of antimony therein. On the other hand, where the antimonyl tartrate compound was added to the bath slightly in excess of the silver cyanide, a current density of 70 amps per square foot produced a very bright alloy plate having from 11 to 12 per cent by weight of antimony. For producing mirror-like, bright plates containing about 3% antimony where there is also only a slight excess of the potassium antimonyl tartrate over the silver cyanide in the bath, a current density of about 30 amps per square foot was found to be sufficient.

The temperature of the bath during the plating operation has not been found to be very critical. These baths can be operated at temperatures of about 70° F. to 140° F. and produce good plates. Excellent results have been obtained when the electrolytic bath was maintained at temperatures of from about 75° F. to 100° F., so that this constitutes a preferred range.

The time during which the process is carried on relates only to the thickness of the bright silver alloy deposited on the cathode, as will be obvious to all those skilled in the art. For very thick deposits it will be necessary to plate, the other conditions being the same, for a relatively long period of time. Where only a few thousandths of an inch of bright alloy plate is desired, the process need be carried out for only a few minutes.

It is preferred to use soluble anodes, since they maintain the electrolytic bath in a more stable condition. Alloy anodes should be used in this process. They should contain from 1 to 12 per cent by weight of antimony and the balance silver, according to the plate composition desired. In place of alloy anodes of silver and antimony, individual anodes of pure silver and pure antimony can also be employed in the electrolytic bath. Where soluble anodes are employed in the disclosed process, they must be inspected at regular intervals and replaced before being entirely exhausted to prevent disruption of the bath stability. The only other appreciable losses during plating will be minor amounts of the bath constituents removed in the solution film clinging to the plated work. These small "dragout losses" can be controlled by pe-

riodic checks of the bath constituents which will indicate the amount of constituent needed to maintain the bath within the disclosed operating ranges.

It is also possible to utilize insoluble anodes in plating bright antimony-silver alloy. Such procedure, however, is not recommended because of the usual problems entailed in maintaining the electrolytic bath in the proper balance. In such a case where there is no anodic replenishment, the alloy deposited on the cathode would be taken directly from the bath. This will require constant inspection of the bath to maintain it in the proper balance, thus, reducing considerably the ease and economy of the plating operation.

Bright, mirror-like electrodeposited silver-anti-

in a concentration of from 0.25 to 10 grams per liter.

Within the ranges of concentration of reagents and of operating conditions as disclosed herein, bright silver-antimony alloy plates will be readily produced. Outside of these ranges only pure silver, antimony or hydrogen will be produced; or a dull plate will be deposited, or one will be deposited having such a high antimony content that it easily cracks.

In the table below, numbers 1 to 7 indicate experiments conducted on the composition of several baths and the conditions under which these baths were operated to produce bright silver-antimony alloy plates. The appearance of the resulting plates and the per cent by weight of antimony therein is also indicated in the table.

Table

Reagents and Conditions	1	2	3	4	5	6	7
Potassium cyanide, grams per liter	30.0	30.0	30.0	30.0	30.0	44.8	50.3
Silver cyanide, grams per liter	30.0	30.0	30.0	30.0	30.0	30.0	30.0
Potassium tartrate, grams per liter	20.0	20.0	50.0	50.0	50.0	250.0	250.0
Potassium hydroxide, grams per liter	3.0	3.0	5.0	5.0	5.0	5.0	5.0
Potassium antimonyl tartrate, grams per liter	30.0	30.0	5.5	5.5	5.5	36.2	36.0
Potassium carbonate, grams per liter	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Current density, amps./sq. ft.	20.0	40.0	20.0	40.0	53.0	30.0	70.0
Temperature, ° F.	80.0	80.0	100.0	100.0	80.0	76.5	84.0
Per cent by weight of Sb in plate	1.89	1.5-2.0	trace-0.08	.5-1.0	8.0-8.7	2.9-3.0	11.0-12.0
Appearance	(1)	(1)	(2)	(3)	(3)	(1)	(4)

¹ Bright and mirrorlike.

² Semi-bright.

³ Bright.

⁴ Very bright.

mony alloy plates have been successfully applied to such commonly used cathode metals of commerce as brass, copper, and nickel-silver. The usual practices of cleaning and strike plating these cathodes to provide an adherent plate are followed in preparation for receiving the bright silver alloy plate. For example, to clean and remove dirt, grease, etc., the basis metal should be treated with steam, hydrocarbon solvents, or alkaline soaps and then rinsed. Any remaining oxide, salt, or other films can be removed by immersing the basis metal for a short period of time in an etchant or other bright dip solution, i. e., a sulfuric acid-nitric acid solution containing a minor amount of hydrochloric acid, followed by rinsing. The surface of the basis metal, being now in a cleaned condition, should be strike-plated with any one of the following metals, copper, nickel or pure silver. The strike plating can be accomplished by electroplating the basis metal.

Cathodes of steel and other metals can also be bright silver-antimony alloy plated by using the customary procedures for cleaning and strike plating, such as used prior to pure silver plating in current practice.

The brightening effect obtained by the co-deposition of antimony and silver does not depend on the use in the bath of organic compositions which are difficult to determine analytically and, thus, can not be readily controlled within predetermined ranges of concentration. Certain well-known organic brighteners will improve somewhat the appearance of the antimony-silver alloy plates which contain very little antimony, i. e., below about 1%. Examples of well-known organic brightener additions that can be employed in the practice of this invention without requiring accurate concentration control are carbon disulfide, thiourea and related derivatives of thiourea, etc. These brighteners should be used

In summary, this invention teaches that silver and antimony can be codeposited to form a bright alloy plate by a process of electrodeposition from an alkaline, silver cyanide-antimonyl tartrate bath. The electrolytic bath used in this process is easily prepared, and the method disclosed herein may be readily performed to bright plate a silver-antimony alloy on a large number of basis metals. The antimony is a major component of the electrodepositing bath and is present in such concentration as to afford easy analytical determination. The control of the process is thus facilitated, because the optimum results do not depend solely upon small quantities of organic compounds which are difficult to determine analytically.

Savings from the use of this bright silver-antimony alloy plate may be easily shown. For example, in the silver industry for silver flatware, complete mirror-like reflectivity would not be desired on the end product of sale, which has a more subdued luster. To change the appearance of pure silver it is buffed and colored, and the amount of silver lost in buffing and coloring operations varies, depending on the skill of the operator. For silver flatware, this loss will range from 5 to 25 per cent of the electrodeposited pure silver on the items being buffed. Yet, by applying the bright silver alloy electrodeposit as disclosed by this invention and coloring as required, the loss of silver plate is estimated at only two per cent.

In addition to the practical advantages of this bright silver alloy plate in the conservation of pure silver as shown above, the product has improved resistance to scratching and to tarnish in actual service. The better scratch resistance of the harder sterling silver relative to the pure silver electrodeposit is well known. The disadvantages of electrodeposited pure silver are now

largely avoided by the product of this invention.

What is claimed is:

1. A method of electrodepositing a bright silver-antimony plate upon a metal article, which comprises immersing the article to be plated in an aqueous electrolyte consisting essentially of from 20 to 150 grams per liter of silver cyanide, from 20 to 100 grams per liter of a cyanide selected from the group consisting of potassium, sodium, and ammonium cyanides, from 10 to 300 grams per liter of a tartrate selected from the group consisting of potassium, sodium, and ammonium hydroxides, from 5 to 40 grams per liter of a carbonate selected from the group consisting of potassium, sodium, and ammonium carbonates, and from 3 to 100 grams per liter of an antimonyl tartrate selected from the group consisting of potassium, sodium, and ammonium antimonyl tartrates, passing an electric current through the electrolyte in such a manner that the article becomes a cathode, regulating the electric current to provide a current density of from 5 to 90 amperes per square foot, maintaining the pH in the electrolyte of 11.0 to 13.5 by proper adjustment of said ingredients added to the bath, and heating the electrolyte to a temperature between 70° F. and 140° F.

2. In the method of coelectrodepositing silver and antimony as a bright alloy coating on a basis metal and containing from 0.08 to 12 per cent by weight of antimony and the balance silver, the steps consisting of immersing the basis metal to be bright alloy coated in an electrolytic bath consisting essentially of an aqueous solution of about 30 grams per liter of silver cyanide, from 30 to 50 grams per liter of potassium cyanide, from 20 to 250 grams per liter of potassium tartrate, from 3 to 5 grams per liter of potassium hydroxide, from 5 to 36 grams per liter of potassium antimonyl tartrate, and about 10 grams per liter of potassium carbonate, passing an electric current through the bath in such a manner that the basis metal becomes a cathode, regulating the electric current to provide a current density of from 20 to 70 amperes per square foot, maintaining the pH in the bath of 11.5 to 12 by proper adjustment of said ingredients of the bath, and heating the bath to a temperature between 75° F. and 100° F.

3. An electrolyte for electrodepositing a bright

silver-antimony alloy plate, comprising, in aqueous media at a pH of from 11.0 to 13.5, from 20 to 150 grams per liter of silver cyanide, from 20 to 100 grams per liter of a cyanide selected from the group consisting of potassium, sodium, and ammonium cyanides, from 10 to 300 grams per liter of a tartrate selected from the group consisting of potassium, sodium, and ammonium tartrates, from 2 to 8 grams per liter of a hydroxide selected from the group consisting of potassium, sodium, and ammonium hydroxides, from 5 to 40 grams per liter of a carbonate selected from the group consisting of potassium, sodium, and ammonium carbonates, and from 3 to 100 grams per liter of an antimonyl tartrate selected from the group consisting of potassium, sodium, and ammonium antimonyl tartrates.

4. An electrolytic bath for codepositing silver and antimony as a bright alloy coating containing 0.08 to 12.0 per cent by weight of antimony and the balance silver, consisting essentially, in aqueous media at a pH of from 11.5 to 12 of about 30 grams per liter of silver cyanide, from 30 to 50 grams per liter of potassium cyanide, from 20 to 250 grams per liter of potassium tartrate, from 3 to 5 grams per liter of potassium hydroxide, from 5 to 36 grams per liter of potassium antimonyl tartrate, and about 10 grams per liter of potassium carbonate.

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