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PLATING TARNISH-INHIBITED BRIGHT SILVER ALLOY

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ABSTRACT OF THE DISCLOSURE

A plating bath, process and alloy comprising tin, silver and nickel for tarnish-inhibited bright silver applications. An alkaline cyanide water bath is employed. The alloy composition is 20 to 45% by weight of tin, 45 to 70% by weight of silver, balance nickel and impurities.

DISCLOSURE OF INVENTION

The present invention relates to electrolytes, electroplating processes and alloys for tarnish-inhibited bright silver applications.

A purpose of the invention is to deposit a tarnish-inhibited bright silver alloy which resembles the noble metals especially platinum or white gold, but is much more economical.

A further purpose is to plate a tarnish-inhibited bright silver alloy which is resistant to oxidation, from an alkaline cyanide water bath containing tin ion, silver ion and nickel ion.

A further purpose is to employ an alkaline cyanide water bath containing 3.0 to 30.0 grams per liter of tin ion, preferably 5.3 grams per liter of tin ion, 0.3 to 3.0 grams per liter of silver ion, preferably 0.65 gram per liter of silver ion, and 0.13 to 1.35 grams per liter of nickel ion, preferably 0.13 gram per liter of nickel ion.

A further purpose is to deposit an alloy of tin, silver and nickel in an attractive tarnish-inhibitive bright silver like deposit which is effective in coverage and continuity, firmly adherent and resistant to the forces of deterioration, commonly encountered by silverware such as flatware, tableware, for a reasonable time.

A further purpose is to produce an alloy having by weight 20 to 45% of tin, preferably 25 to 45% of tin and most desirably 25 to 30% of tin by weight, 45 to 70% by weight of silver, preferably 50 to 70% by weight of silver, and most desirably 65 to 70% of silver, and the balance nickel and impurities.

A further purpose is to produce an alloy having by weight 29% of tin, 70% of silver and the balance nickel and impurities.

A further purpose is to produce an alloy having by weight 30% of tin, 69% of silver and the balance nickel and impurities.

A further purpose is to produce an alloy having by weight 20% of tin, 70% of silver and the balance nickel and impurities.

A further purpose is to produce an alloy having by weight 45% of tin, 45% of silver and the balance nickel and impurities.

A further purpose is to plate at a temperature range of from 120 to 155° F.

A further purpose is to employ a current density of 5 to 60 amperes per square foot and preferably 15 to 30 amperes per square foot.

A further purpose is to employ in the cyanide plating bath an adequate quantity of an alkali such as sodium or potassium hydroxide, to maintain a pH of between 11.5 to 12.5. The quantity of added alkali may be from 7 to 21 grams per liter.

A further purpose is to electroplate on a base of any of the common metals suitable for silverware (flatware and vessels), jewelry and the like, for example, steel, copper, brass, bronze and Monel, applying the electroplating of the invention directly or if desired with intermediate layers, such as copper plating or nickel plating.

Further purposes appear in the specification and in the claims.

The present invention is believed to find its best application in the decorative arts such as the production of silverware (flatware and holloware), jewelry, decorative surfaces of appliances, instruments and machines, and for corrosion protection where appearance is important, for example in instruments and the like.

In the prior art electrodeposited coatings including noble metals such as rhodium have been extensively developed as embodied in Keitel U.S. Pat. 1,779,436, granted Oct. 28, 1930 for Process of Electrodepositing Metals of the Platinum Group; Zschiegner U.S. Pat. 1,779,458, granted Oct. 28, 1930, for Electrodeposition of Platinum Metals; Bart U.S. Pat. 1,947,180, granted Feb. 13, 1934 for Tarnish-Resisting Silver; and Zimmermann U.S. Pat. 1,981,820, granted Nov. 30, 1934 for Process of Electrodepositing Rhodium, Bath and Method of Preparing the Same. In my U.S. Pat. 3,547,626, granted Dec. 15, 1970 for Plating Tarnish-Resistant Bright White Alloy, I have described an alloy of cadmium, silver and nickel which is tarnish-resistant and resembles rhodium.

The present invention is concerned with the production of a bright silver alloy which resembles platinum or white gold, is much less expensive than a noble metal, and which has improved resistance against tarnishing in industrial atmospheres, provides corrosion resistance, firm adherence to the base metal and resists scuffing and abrasion encountered in silverware (flatware and holloware), jewelry, instrument parts and the like. As compared with the surface of silver, applied for example in flatware or holloware, the alloy of the invention is much more resistant from tarnishing, and requires treating or burnishing less often. In addition the alloy of the invention is produced in a single step from an electroplating bath of high speed, with a high rate of deposition if desired and of uniformly good appearance when the plating is controlled as explained in this application.

The electrodeposited layer can be applied with adequate appearance for many jewelry parts in a matter of a minute or less to obtain a plating layer having a thickness of 0.0001 inch, or it can be applied for the purpose of electroforming in order to make a thick deposit, even a deposit having a thickness for example as great as ¼ inch or more.

The alloy of the invention lends itself to deposition on the common metals used in making inexpensive silverware, jewelry, appliances and instruments such as carbon and alloy steel, copper and copper base alloys such as brass and bronze, and the like. The coating of the invention can be applied over prior electrodeposited layers which are employed for example for corrosion protection or to obtain a favorable color background, as copper or nickel plate on steel.

One of the advantages of the alloy of the invention is that it has a whiteness and reflectance which resembles platinum or white gold and particularly resembles pure silver.

The alloy in the invention is tarnish-inhibitive. For example, it has been subjected to 10% solution of polysulfide at room temperature for 20 minutes without visible impairment in the brightness of the plated surface.

An unusual advantage which makes the alloy of the invention especially suited to silverware is that it resists attack of food acids such as acetic acid, citric acid and other constituents of fruits and vegetables, making it peculiarly suited for exposure to such materials in the

ordinary process of serving food and storing the food in a refrigerator.

The electroplating according to the invention is carried out in a cyanide water bath which of course is maintained alkaline, for example, in the presence of sodium or potassium hydroxide, that is in the concentration of 7 to 20 grams per liter. The pH of the plated bath is preferably maintained at about 11.5 to 12.5.

The electrolyte has dissolved in it soluble salts providing tin ion, silver ion and nickel ion. In order to create such ions in the bath, the respective cyanides may be introduced or any well-known techniques may be used. For example stannous chloride may be placed in the bath and dissolved by adding sodium cyanide. It will, of course, be evident that the conductivity of the bath can be increased if desired by adding sodium cyanide or other alkali conducting salts.

It is very desirable to maintain a proper balance of the concentration of tin ion, the concentration of silver ion and the concentration of nickel ion as suggested below.

The bath temperature can vary widely, but good results are obtained by plating in a temperature range between 125° F. and 155° F.

The voltage employed will suitably be in the range of 2 to 12 volts direct or unidirectional current. The current density will typically vary between 5 and 60 amperes per square foot, and preferably between 25 and 60 amperes per square foot. For best results a combination of insoluble and soluble anodes may be used, such as soluble anodes of silver and tin and an insoluble anode of stainless steel, platinum, titanium or carbon (graphite). The ratio of areas of anode to cathode should not exceed 1 to 1.

The alloy obtained is an alloy of tin, silver and nickel. It may have the following weight proportions:

Component	Broad	Narrow	Preferred
Tin	20–45	25–45	25–30
Silver	45–70	50–70	65–70
Nickel and a small amount of impurity	Balance	Balance	Balance

The percent of impurities in these alloys is not in excess of 0.50% (by weight).

Example 1

The following electrolyte bath was made up in water:

	Grams per liter
Tin ion	5.3
Silver ion	0.65
Nickel ion	0.13
Sodium hydroxide	15
Sodium cyanide	100

Tin was added as tin hydroxide. The silver was added as silver cyanide. The nickel was added as nickel hydroxide.

Components suitable for jewelry and the like were made up consisting of low carbon steel, copper and brass. The components were cleaned of grease, foreign matter and oxide as well known in the procedure described in 2 Metals Handbook (8th Ed. 1964) 307 and following.

The bath was heated to 130° F. plus or minus 5° F., and maintained within that temperature range with constant stirring. An insoluble anode of stainless steel and a soluble anode of silver were used, with an anode to cathode ratio of 1 to 1. The work was inserted as cathode and direct current was supplied between the anode and the cathode under a direct voltage of 1 to 1.5 volts at a current density of 15.0 amperes per square foot. The work was electroplated for 60 seconds in the above bath under the above conditions, and a deposit was obtained which was silvery white and bright without burnishing. No porosity was visible, and the coating was tarnish-free after immersion in a 10% water solution of sodium sulfide for 5 minutes.

Spectrographic analysis showed that the electrodeposit had the following composition by weight:

Tin	percent	26
Silver	do	70
Nickel and impurities		Balance

Example 2

In order to make an alloy of higher tin content the preferred technique is to increase the bath temperature and plate at higher current density.

The procedure of Example 1 was followed except that the bath temperature was maintained at 140° F. plus or minus 5°, and the work was plated at a current density of 45 amperes per square foot. The alloy deposit in this case had the following composition by weight:

Tin	percent	45
Silver	do	45
Nickel and impurities		Balance

For a discussion of control of alloy content by temperature and current density see 1 Brenner Electrodeposition of Alloys (1963), p. 610, paragraph 19.2b.

Example 3

By adjusting the temperature and current density I have obtained alloys having intermediate tin contents. Using a bath temperature of 150° F. and a current density of 30 amperes per square foot I have obtained from this bath an alloy of the following composition by weight:

Tin	percent	29
Silver	do	30
Nickel and impurities		Balance

Example 4

By plating at a bath temperature of 120° F. and a current density of 20 amperes per square foot, I have obtained a coating having the following composition by weight:

Tin	percent	30
Silver	do	69
Nickel and impurities		Balance

In view of my invention and disclosure, variations and modifications to meet individual whim or particular need will doubtless become evident to others skilled in the art, to obtain all or part of the benefits of my invention without copying the composition and process shown, and I therefore claim all such insofar as they fall within the reasonable spirit and scope of my claims.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent is:

1. An electrolyte for electroplating a bright silver alloy essentially consisting of an alkaline cyanide water bath comprising 3.0 to 30.0 grams per liter of tin ion, 0.3 to 3.0 grams per liter of silver ion, and 0.13 to 1.35 grams per liter of nickel ion.

2. An electrolyte of claim 1, essentially consisting of 5.3 grams per liter of tin ion, 0.65 gram per liter of silver ion and 0.13 gram per liter of nickel ion.

3. A process of electrodepositing a tarnish-inhibited bright silver alloy which comprises establishing an alkaline cyanide water bath in which the concentration of tin ion is between 3.0 and 30.0 grams per liter, the concentration of silver ion is between 0.3 and 3.0 grams per liter and the concentration of nickel ion is between 0.13 and 1.35

grams per liter, without other substantial metal components, and passing a current unidirectionally through the bath between an electrode and the work as cathode to deposit an alloy of tin, silver and nickel, without substantial quantities of other metallic components.

4. The process of claim 3, in which the temperature of the bath is between 120 and 155° F.

5. The process of claim 4, in which the current density is between 5 and 60 amperes per square foot.

6. The process of claim 5, in which the concentration of tin ion is 5.3 grams per liter, the concentration of silver ion is 0.65 gram per liter and the concentration of nickel ion is 0.13 gram per liter.

References Cited

UNITED STATES PATENTS

1,404,156	1/1922	Marino	204—43
3,591,370	7/1971	Denereaz	75—173 R X

OTHER REFERENCES

Frederick A. Lowenheim, "Modern Electroplating," pp. 453–455 (1968).

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