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BRIGHT ALLOY PLATING

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2 Claims. (Cl. 204—44)

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This invention relates to the electroplating of bright coatings composed of a plurality of metals to provide uniform deposits having bright surfaces free from pitting and possessing other desirable characteristics.

This application is a continuation-in-part of our copending patent application Serial No. 513,178, entitled "Bright alloy plating" and filed December 6, 1943, which has become abandoned.

Considerable difficulty is encountered in electroplating deposits composed of the homogeneous combination of two or more metals. The conditions necessary to plate such deposits are quite critical; and, if the conditions of plating are varied to an extent that would be considered only minor in plating a single metal, the electrodeposit composed of two or more metals may be subject to disproportionate changes so that it is relatively unsatisfactory. In particular, it has been found that binary and ternary metal deposits tend to plate out quite dull and often exhibit considerable pitting and non-uniformity in the plate. Oftentimes, the plating becomes progressively duller and less satisfactory in other respects as a new bath is operated. Therefore, considerable difficulty is encountered in producing binary and ternary metal electrodeposits of a quality comparable to most of the single metal electroplated coatings.

This invention relates to improving the electrodeposition of binary and ternary electrodeposits composed of copper and tin. In the ternary alloy, zinc is the third component. In particular, we have found that these deposits, which are composed of copper and tin, may be electroplated under predetermined conditions from electrolytes containing a particular addition agent. The presence of the addition agent assures the production of a silvery white electrodeposit at all times. The high quality of the electrodeposit is maintained even when the electrolyte accumulates large quantities of carbonates and other impurities which would ordinarily tend to deteriorate the quality of the electrodeposit.

The object of this invention is to provide for producing a brilliant silvery electroplate of an alloy containing copper and tin by applying to the electrolyte certain quaternary ammonium compounds.

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A further object of this invention is to provide an electrolyte containing copper and tin, with or without zinc, suitable for electrodepositing an alloy therefor, and an addition agent composed of a quaternary ammonium compound to provide for a bright and homogeneous electrodeposit.

Other objects of the invention will, in part, be obvious and will, in part, appear hereinafter.

According to the present invention, electrolytes suitable for producing deposits composed of an alloy of copper and tin, or copper, tin and zinc, are improved by adding thereto surface-active water-soluble quaternary ammonium compounds having a minimum of 15 carbon atoms of which at least 12 carbon atoms are in a long chain. The addition of these compounds, more fully described hereinafter, has been found to increase the luster and brightness of the electrodeposited alloy of the metals set forth. The agents have been found to prohibit or prevent the formation of pitting in the electrodeposits. The throwing power is increased by the use of the addition agents. The deposited alloy coating is of more uniform thickness and has greater corrosion resistance when applied from an electrolyte containing the addition agents.

Particularly good results have been obtained with the addition agents composed of quaternary ammonium compounds of this invention, when applied to electrolytes capable of electrodepositing an alloy composed of from 50% to 75% by weight of copper, 15% to 30% by weight of tin and from 5% to 20% by weight of zinc. In some cases, these proportions may be departed from to a slight extent. The presence of minor amounts of other metals or impurities will affect the nature of the electroplated product.

The electrolyte for producing the ternary alloy of copper, tin and zinc, consists of the following:

	Ounces per gallon
Free cyanide	0.5 to 5.0
Copper	0.2 to 0.50
Tin	0.05 to 0.20
Zinc	0.1 to 0.5
Sodium carbonate	2.0 to 12.0
Sodium hydroxide	about 0.25 to 0.8 ounces per gallon to give a pH of from about 12 to 13.

When the composition is maintained within the

limits indicated, plating may be accomplished with satisfactory results. To secure an electroplating bath of the above-composition, the following chemicals in the indicated quantities by weight may be added per 1000 parts of water:

	Parts
Copper cyanide	2 to 5
Sodium cyanide	10 to 80
Zinc cyanide	1 to 6
Sodium stannate	¾ to 4
Sodium carbonate	15 to 90

and sufficient sodium hydroxide (roughly 3 to 6 parts) to give a pH of from 12 to 13.5.

An electrolyte that has been satisfactory for both barrel and still-tank plating has the following composition:

	Ounces per gallon
Copper cyanide	0.5
Zinc cyanide	0.27
Sodium stannate ($Na_2SnO_3.3H_2O$)	0.22
Sodium cyanide	3.75
Sodium carbonate	4.0
Sodium hydroxide	0.6

The pH of this electrolyte, when maintained in the range of from about 12.6 to 13.5, produces excellent electroplate. The anodes were composed of from 52% to 65% copper, 25% to 35% tin and 10% to 20% zinc. Analysis of the ternary alloy electroplate produced by this last electrolyte in combination with the anodes shows copper from 55% to 60%, tin 25% to 28% and zince 14% to 18%.

In all of the above compositions zinc may be added as zinc sulfate. Other zinc, tin and copper salts, which are soluble in a cyanide solution may be employed in preparing the electrolyte. It will be understood that potassium salts may be used instead of sodium salts, allowance being made for the difference in molecular weight. The electrolyte is prepared by dissolving the finely powdered salts in the predetermined quantity of water. The solution may be filtered before introducing it into the plating tank.

The ternary alloy electroplating bath employs anodes composed of the alloy. The tin content of the anodes may be somewhat higher by two or three percent than the electrodeposit itself, since a small proportion of the tin precipitates out of the electrolyte during electroplating. For example, the anodes may contain from 15% to 35% tin, from 50% to 75% copper, and from 5% to 20% zinc.

The electroplating tank may be of glass, wood, or rubber covered metal, or even stainless steel. It is desirable to provide a source of heat, such as a steam coil, since plating has been found to be more efficient when the operation is conducted in a temperature range of from about 140° F. to 160° F.

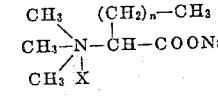
It is possible to obtain ternary alloy coatings 0.0001 to 0.0005 inch thick in a short time, about 12 minutes at a current density of 15 amperes per square foot per 0.0001 inch thickness of deposit is required. For most purposes, coatings of this thickness have adequate covering power and corrosion-resistance. In some cases where it is desirable to have a thicker coating, plates varying from 0.001 to 0.002 inch thick and even heavier and which are quite bright have been obtained by electroplating for greater periods of time.

Since the anode efficiency is about 100% while the cathode efficiency is about 35%, it is necessary, under most conditions, to employ a number of insoluble anodes of steel or carbon in combination with ternary alloy anodes. Satisfactory results have been obtained if from 15% to 30% of the total anode area consists of alloy anodes and the remaining alloy area is provided by insoluble anodes.

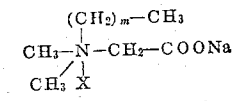
In electroplating an alloy composed of 55% to 65% copper, 20% to 30% tin, and 5% to 20% zinc, for example, as a bright silvery plate, the voltage between the anode and cathode should be maintained within the limits of 3 to 5 volts where the anodes and cathodes are separated at standard plating distances of from six to eight inches. Maintaining still tanks at a voltage of from 3½ to 4½ volts for the standard plating distances has given excellent plating. A higher voltage will be required if the anodes and cathodes are separated by more than the standard distance.

In order to produce bright smooth deposits of silvery white ternary alloy, it has been found that the addition of from 0.01% to 5% of the weight of the electrolyte, or 0.01 ounce to 5 ounces per gallon of water-soluble surface-active quaternary ammonium compounds having at least 15 carbon atoms should be present. The quaternary ammonium compounds which have been found to be highly satisfactory in the practice of the invention may have either of the following chemical formulas:

I.



II.



In Formula I, X is a halide and n is 12 or greater. In Formula II, X is a halide and m is 14 or greater. The halide, for example, may be bromine. Instead of sodium compounds, potassium and other alkali metal quaternary ammonium compounds may be employed. The quaternary ammonium compounds may occur as a byproduct constituent in the preparation of long carbon chain betaines though they may be produced directly. Particularly good results have been obtained when the quaternary ammonium compounds contain 17 carbon atoms or more.

While other long carbon chain compounds have exhibited some benefits in electrolytes capable of producing alloy electrodeposits, the quaternary ammonium compounds have been found to be markedly more stable in an alkaline cyanide solution than any other addition agent tried. Furthermore, the optimum brightness has been secured by the use of the quaternary ammonium compounds set forth above.

Good results have been obtained when 4 cubic centimeters of the quaternary ammonium compound have been added to each gallon of the electrolyte. The quaternary ammonium compound should be replenished from time to time in order to replace drag-out losses, lost due to decomposition or for other reasons.

Illustrative of the benefits of the quaternary ammonium compounds of this invention, a ternary alloy electrolyte was found to produce dull and pitted electrodeposits without the presence of the addition agent. On adding 4 cubic centimeters of the quaternary ammonium compounds to the bath, the electrodeposits immediately became a brilliant silvery white color. The quality of the deposited metal was noticeably improved in that pitting was entirely eliminated. The ad-

dition agent has been found to compensate for slight changes in the proportions of the constituents from those given above. Thus, if the concentration of some one of the metals is just above the desirable proportions, the plating will be dull and of poor quality. By adding the quaternary ammonium compound, the plating will immediately improve and become bright and sparkling.

The water-soluble surface-active quaternary ammonium compound has been found to markedly improve the deposition of a copper-tin alloy. An electrolyte for depositing an alloy of copper and tin may have the following constituents;

	Grams per liter
Copper cyanide	5 to 35
Sodium stannate	5 to 35
Sodium cyanide	10 to 40
Sodium hydroxide	5 to 30

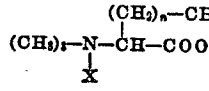
Without the addition agent, the electrolyte produces a relatively dull deposit, even under the best of conditions. By adding the quaternary ammonium compound in an amount of 5 cubic centimeters per gallon of electrolyte, the copper-tin alloy is plated out as a brilliant silvery white deposit at plating current densities of from 10 to 80 amperes per square foot, or even higher in some cases. A silvery white electrodeposit composed of 80% copper and 20% tin has been produced by plating at a current density of 20 amperes per square foot from an electrolyte containing 15 grams per liter of copper cyanide, 15 grams per liter of sodium stannate and one gram per liter of quaternary ammonium compound.

The addition agents of this invention appear to enhance the luster and brilliancy of the copper-tin binary and ternary alloy deposits. The electroplates appear to have a blue tinge when plated from an electrolyte containing the quaternary ammonium compound. This blue tinge is a desirable feature.

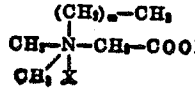
Since certain changes in carrying out the above processes and certain modifications in the compositions which embody the invention may be made without departing from its scope, it is intended that all the matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

We claim as our invention:

1. An alloy electroplating process which comprises electrolyzing an aqueous alkaline cyanide electrolyte containing from 0.01 to 5 ounces per gallon of at least one water soluble, surface active quaternary ammonium compound selected from the group consisting of compounds having the formulae:

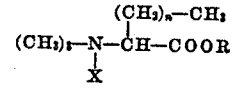


and



where X represents a halogen atom, R represents an alkali metal, n is a number greater than 11 and m is a number greater than 13, the balance of the electrolyte composed of from 0.5 to 5 ounces per gallon of free cyanide, from 0.2 to 0.5 ounce per gallon of copper, from 0.05 to 0.2 ounce per gallon of tin, from 0.1 to 0.5 ounce per gallon of zinc, anions associated with the copper, tin and zinc, from 2 to 12 ounces per gallon of alkali metal carbonate and from 0.25 to 0.8 ounce per gallon of alkali metal hydroxide, and the remainder being water.

2. An alloy electroplating process which comprises electrolyzing an aqueous alkaline cyanide electrolyte containing from 0.01 to 5 ounces per gallon of at least one water-soluble, surface active quaternary ammonium compound selected from the group of compounds having the formulae:



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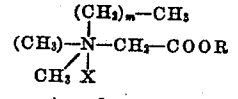

where X represents a halogen atom, R represents an alkali metal, n is a number greater than 11 and m is a number greater than 13, the balance of the electrolyte composed of from 5 to 35 grams per liter of copper cyanide, from 5 to 35 grams per liter of sodium stannate, from 10 to 40 grams per liter of sodium cyanide and from 5 to 30 grams per liter of sodium hydroxide, the balance being water.

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