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WHITE BRASS PLATING

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12 Claims. (Cl. 204—44)

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This invention relates to the electroplating of a white zinc copper alloy from an electrolyte containing the cyanides of zinc and copper.

Wernlund U. S. P. 2,181,773 describes the electrodeposition of a "white brass" from a cyanide electrolyte. This white zinc copper alloy electrodeposit may be electroplated in accordance with the Wernlund patent to produce a semi-bright or bright electrodeposit which is useful as undercoating for chromium plating and which, without a chromium overdeposit, forms an excellent, corrosion resistant, decorative finish for articles made of steel, copper, yellow brass and zinc. As undercoat for chromium plating, the white brass may be used in place of nickel.

However, some difficulty has arisen in producing a satisfactory bright and smooth white brass electrodeposit suitable, without buffing or polishing operations, to serve as an undercoat for the production of brilliant chrome plate, because of the relatively narrow current density range within which bright electrodeposits of the white brass may be consistently obtained. This difficulty has limited the utilization of the white brass electroplating method, particularly for electroplating particles of irregular shape, which have inherently areas of low and high current density.

An object of the present invention is an improved white brass electroplating process. A further object is to improve the process of the above-mentioned Wernlund patent whereby smooth, bright, white brass electrodeposits may be obtained uniformly on irregularly shaped objects and over a wide range of current density. Still other objects will be apparent from the following description of the invention.

The copending application of Robert R. Bair, S. N. 231,910, filed June 15, 1951, now abandoned, discloses the electrodeposition of white brass from a cyanide solution containing small amounts of a benzaldehyde-aliphatic ether and a water soluble molybdenum compound, together with the addition of hydrogen peroxide. In the Bair process, the addition of hydrogen peroxide is required to produce a satisfactorily bright electrodeposit over a wide current density range. Without the peroxide, bright electrodeposits are obtained within a rather narrow range of current density. A further object of the present invention is to obtain bright white brass electrodeposits over a wide range of current density without the necessity of adding a peroxide or equivalent oxidizing agent.

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The foregoing objects may be attained in accordance with the present invention by electroplating a white zinc copper alloy from an aqueous cyanide-containing electrolyte which contains a small amount of a vanadium compound and preferably also a benzaldehyde-aliphatic ether. Employing both of the above-mentioned addition agents, white brass electrodeposits are obtained with excellent brightness over a wide range of current densities without the addition of hydrogen peroxide. For example, by the herein described process I have been able to electrodeposit excellent bright white brass within the current density range of from 5 to 90 amps. per square foot.

The invention is illustrated by the following examples:

Example 1

The following ingredients were dissolved in water at a temperature of 80° C.:

	Grams per liter
Zinc cyanide	60
Copper cyanide	15
Sodium cyanide	52.5
Sodium hydroxide	60
Sodium sulfide	0.5

The hot solution was filtered and portions of the filtered solution were utilized as electrolyte to electrodeposit white brass onto steel panels. The steel specimens were plated from this electrolyte in a conventional Hull cell made of hard rubber, under the following conditions:

Volume of electrolyte	cc.	250
Cathode surface area	sq. in.	8
Anode surface area	sq. in.	5
Electrolyte temperature	°C.	25–35
Average current density	amps./sq. ft.	36
Over-all cathode density range	amps./sq. ft.	4–90
Time of plating	minutes	10

A separate portion of the plating solution was employed to electroplate each steel specimen and for plating certain specimens small amounts of piperonal bisulfite or sodium ortho-vanadate (Na_3VO_4), or both, were added to the electrolyte, as indicated below. The following tabulation shows the current density range within which excellent bright electrodeposits (indicated

as "very bright") were obtained for each specimen:

Trial	Addition Agts. (g./l.)		Current Density (amps./sq. ft.)	Electrodeposit Appearance
	Na_3VO_4	Piperonal Bisulfite		
A	None	None	4 to 8	Gray.
			8 to 20	Semi bright.
			20 to 90	Gray.
B	0.4	None	4 to 31	Semi bright.
			31 to 90	Gray.
C	None	3	4 to 9	Hazy bright.
			9 to 90	Dull gray.
D	0.1	3	4 to 5	Dull.
			5 to 78	Very bright.
			78 to 90	Hazy bright.
E	0.2	3	4 to 5	Dull.
			5 to 90	Very bright.
F	0.4	3	4 to 5	Dull.
			5 to 90	Very bright.
G	1.0	3	4 to 8	Hazy bright.
			8 to 90	Very bright.
H	1.6	3	4 to 9	Dull.
			9 to 47	Bright.
			47 to 90	Exfoliated.
I	2		4 to 12	Grayish black.
			12 to 40	Dull gray.
			40 to 90	Bright but blistered.

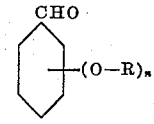
Example 2

The process of Example 1 was repeated in a series of plating tests, employing the vanadium compounds and aldehyde ethers indicated in the table below. To use vanadium pentoxide, it was dissolved in a caustic soda solution and the solution added to the electrolyte. Vanadium trioxide (V_2O_3) (4. grams) was digested in 40 cc. of 10% caustic soda solution at 100° C. and the resulting filtered solution added to the electrolyte. Vanadyl sulfate ($VOSO_4$) was dissolved in the electrolyte. The results obtained are tabulated below:

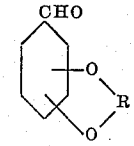
Trial	Addition agents (g./l.)		Current Density (amps./sq. ft.)	Electrodeposit Appearance
	Vanadium Compound	Aldehyde Ether		
A	None	Anisaldehyde Bisulfite (3 g./l.)	4 to 7	Bright.
			7 to 20	Hazy bright.
			20 to 90	Gray.
B	0.20 g./l. V_2O_5 dissolved in NaOH	do	4 to 5	Gray.
			5 to 20	Hazy bright.
			20 to 90	Very bright.
C	None	Vertraldehyde Bisulfite (3 g./l.)	4 to 6	Moderately bright.
			6 to 13	Semi-bright.
			13 to 90	Gray.
D	0.20 g./l. V_2O_5 dissolved in NaOH	do	4 to 13	Bright.
			13 to 90	Very bright.
E	0.08 g./l. $VOSO_4$	Piperonal Bisulfite (3 g./l.)	4 to 8	Hazy bright.
			8 to 90	Very bright.
F	0.32 g./l. $VOSO_4$	do	4 to 12	Hazy bright.
			12 to 90	Very bright.
G	4.0 g./l. V_2O_3 digested in 40 ml. of 10% NaOH at 100° C. (filtered).	do	4 to 6	Hazy bright.
			6 to 90	Very bright.

In addition to the vanadium compounds disclosed in the foregoing examples, any of the inorganic vanadium compound which can be dissolved in the electrolyte to the extent stoichiometrically equivalent to approximately 0.01 gram per liter or more of elemental vanadium may be utilized in the practice of my invention. Vanadium compounds soluble in alkaline solutions, including those, like vanadium trioxide, which require strong alkali concentration and heating to effect solution, are generally suitable. I generally prefer to dissolve vanadium pentoxide in a solution of sodium or potassium hydroxide and add the resulting solution to the electrolyte. As illustrated by the examples, the concentration of the vanadium compound may vary from the stoichiometrical equivalent of about 0.01 to 0.5 gram per liter of elemental vanadium. The preferred concentration is in the neighborhood of 0.1 gram per liter of vanadium; and as the concentration of vanadium is decreased below that value, the brightening effect becomes correspondingly less. While some slight brightening effect occurs at concentrations even below 0.01 gram per liter of vanadium, generally such small amounts of vanadium have little or no commercial importance. The vanadium concentration generally should not be increased to beyond about 0.5 gram per liter, as higher concentrations tend to cause exfoliation or blistering of the electrodeposit in the bright areas. Also as the vanadium concentration is increased above around 0.1 gram per liter, the extent of the bright range tends to decrease.

The aliphatic-aromatic ether aldehydes suitable as addition agents are benzaldehyde-aliphatic ethers, that is, ethers having an aliphatic group joined through ether oxygen linkage to a benzene ring with an aldehyde group on the ring. They may be represented by the generic formulas:



and



where R is an aliphatic hydrocarbon radical, and n is a whole number of from 1 to 3. Preferably, R contains a single carbon atom and n is 1 or 2. Examples are: piperonal, vanillin, veratraldehyde, anisaldehyde, 2,3-dimethoxybenzaldehyde and o-methoxybenzaldehyde. In order to obtain suitable solubility in the electroplating bath, the aldehyde is preferably added in the form of its bisulfite compound. The amount of the aldehyde addition agent may vary from 0.2 to 7.5 grams per liter of the bisulfite compound and generally best results are obtained at a concentration of from 0.4 to 4 grams per liter.

The presence of other addition agents generally suitable for electroplating white brass from cyanide solutions ordinarily is not deleterious in the practice of my invention. More specifically, a small amount of a water-soluble molybdenum compound as described in the aforesaid Bair application, with or without the addition of a peroxide or other oxidizing agent, may be added, if desired; and good results are thereby obtained.

The addition of peroxide to my electrolyte generally produces little or no significant change in the quality of the electrodeposit.

While my process is generally applicable to cyanide plating baths for electroplating brass wherein the zinc content of the bath is sufficiently high to produce a white brass, the best results are obtained by employing the electrolyte compositions and plating conditions disclosed in the above-mentioned Patent No. 2,181,773. As disclosed in that patent the amount of zinc cyanide should exceed that of copper cyanide and generally the zinc cyanide concentration will be about 4 times that of the copper cyanide, by weight. To plate a white brass containing from 60 to 90% of zinc in the electrodeposit, the ratio of zinc cyanide ($Zn(CN)_2$) to copper cyanide (CuCN) should be within the range of 2 to 1 to 6 to 1. With smaller proportions of zinc cyanide, the electrodeposit will tend to have a yellow color.

The bath should contain an alkali metal hydroxide, preferably sodium hydroxide (although potassium hydroxide may be used if desired); and preferably the amount of alkali metal hydroxide should be equivalent to an amount of sodium hydroxide equal to 50 to 150% of the weight of the zinc cyanide present. The electrolyte also must contain sufficient alkali metal cyanide, preferably sodium cyanide (although potassium cyanide may be used if desired) to form the double cyanides of zinc and copper. Preferably, a small excess of the alkali metal cyanide is used so that the bath contains "free cyanide," in accordance with conventional practice in electroplating zinc, copper or brass from cyanide solutions.

My invention makes possible the production of excellent, smooth, bright electrodeposits of white zinc-copper alloys having a color closely approaching that of chromium electrodeposits. These white brass electrodeposits form an excellent undercoating for chrome plating or, without any overplating, serve to provide an excellent, bright, corrosion resistant finish of pleasing appearance. By means of the herein described improvement, electrodeposits of this character may be produced over a wide range of current density, to provide electrodeposits of uniform surface characteristics on various articles of irregular shape.

I claim:

1. The process which comprises electroplating a white brass from an aqueous solution containing the cyanides of zinc and copper and an amount of an alkali-soluble vanadium compound small but sufficient to impart a bright surface to brass deposited from the solution.

2. The process which comprises electroplating a white brass from an aqueous solution containing the cyanides of zinc and copper and an amount of an alkali-soluble vanadium compound stoichiometrically equivalent to about 0.01 to 0.5 gram per liter of elemental vanadium.

3. The process which comprises electroplating a white brass from an aqueous solution containing the cyanides of zinc and copper, an amount of an alkali-soluble vanadium compound stoichiometrically equivalent to about 0.01 to 0.5 gram per liter of elemental vanadium and 0.2 to 7.5 grams per liter of a benzaldehyde-aliphatic hydrocarbon ether.

4. The process of claim 3 wherein the vanadium compound is that resulting from dissolving vanadium pentoxide in an alkaline aqueous solution.

5. The process of claim 3, wherein said ether is added as piperonal bisulfite.

6. The process of claim 3, wherein said ether is added as vertraldehyde bisulfite.

7. The process of claim 3, wherein said ether is added as anisaldehyde bisulfite.

8. The process of claim 3 wherein the vanadium compound is added to the electrolyte in the form of a solution prepared by dissolving vanadium pentoxide in an alkaline solution selected from the group consisting of aqueous solutions of sodium and potassium hydroxides, the benzaldehyde-aliphatic hydrocarbon ether is piperonal bisulfite and the solution contains an alkali metal hydroxide in amount equal to 50 to 150% of the weight of zinc cyanide present.

9. The process of claim 3 wherein the vanadium compound is added to the electrolyte in the form of a solution prepared by dissolving vanadium pentoxide in an alkaline solution selected from the group consisting of aqueous solutions of sodium and potassium hydroxides, the benzaldehyde-aliphatic hydrocarbon ether is vertraldehyde bisulfite and the solution contains an alkali metal hydroxide in amount equal to 50 to 150% of the weight of zinc cyanide present.

10. The process of claim 3 wherein the vanadium compound is sodium ortho-vanadate, the benzaldehyde-aliphatic hydrocarbon ether is piperonal bisulfite and the solution contains an alkali metal hydroxide in amount equal to 50 to 150% of the weight of zinc cyanide present.

11. The process of claim 3 wherein the vanadium compound is vanadyl sulfate ($VOSO_4$), the benzaldehyde-aliphatic hydrocarbon ether is piperonal bisulfite and the solution contains an alkali metal hydroxide in amount equal to 50 to 150% of the weight of zinc cyanide present.

12. The process of claim 3 wherein the vanadium compound is added to the electrolyte in the form of a solution prepared by reacting vanadium trioxide with an aqueous solution of an alkali selected from the group consisting of sodium and potassium hydroxides, the benzaldehyde-aliphatic hydrocarbon ether is piperonal bisulfite and the solution contains an alkali metal hydroxide in amount equal to 50 to 150% of the weight of zinc cyanide present.

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