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CHROMIUM REDUCER FOR CYANIDE PLATING BATHS

Paul W. Moy, Gates Mills, Ohio, assignor to The Harshaw Chemical Company, Cleveland, Ohio, a corporation of Ohio

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This invention relates to the electrodeposition of metals from cyanide plating baths which are subject to contamination with chromium.

Metals such as copper and copper alloys are commonly used as undercoats for subsequent electrodeposits of nickel and chromium. When copper is employed as an undercoat, the object to be plated may be held on the same plating rack through a plurality of plating operations; that is, a common plating rack may be used in successive copper, nickel and chromium plating cycles. The result of this type of operation is that the copper plating bath becomes contaminated with chromium. While various mechanical means have been employed to prevent the introduction of chromium impurities through plating racks, none of these mechanical means have been entirely successful. Procedures such as, for instance, scrubbing plating racks after each electrodeposition and employing new racks for each electrodeposition have been tried, but the economies of these systems did not warrant their adoption.

The chromium contaminant which has a detrimental effect on electrodeposited coatings is hexavalent chromium. It has been found that hexavalent chromium when present in plating baths in concentrations as low as 1 p.p.m. will cause lower efficiency. The effect at 5 p.p.m. and higher is to cause lower throwing power, misplating and mottled deposits. If the solution is operated, and especially if it contains brightening agents, most of the hexavalent chromium will become reduced to trivalent chromium which is relatively harmless. This method, however, is too slow. Various reducing agents have been used, and are used for quickly reducing the chromium to the harmless trivalent form. These agents are (1) sodium hydrosulfite, (2) stannous tin compounds, and (3) various sugars, such as, for instance, glucose. The foregoing agents, however, have the following disadvantages:

(1) Hydrosulfite cannot be dissolved to form a stable solution either in aqueous or acid solution. Consequently, it is frequently added as a dry powder on top of the cyanide solution. One difficulty when it is added in solution or in the dry form is that frequently it causes roughness of the deposit. The exact cause of this is unknown. It is known that if the free cyanide is low, some copper metal powder is formed. If too much hydrosulfite is added it causes dullness of the copper deposit at intermediate current density areas. With solutions using selenium-containing brighteners, this is especially true.

(2) Stannous tin, such as $SnCl_2$, $SnSO_4$ and Na_2SnO_2, will reduce hexavalent chromium and precipitate the reduced chromium from the bath, but has the disadvantage of causing small blisters to form especially if the deposit is heated. It also alloys with the copper giving a bronze deposit which is not always desirable.

(3) Sugars, such as glucose, will reduce hexavalent chromium, but have the disadvantage that they, or their oxidation products, will complex with the trivalent chromium and hold it in solution. At first this is not harmful, but eventually a high concentration of Cr^{+3} is built up, and this is harmful. Also, an oxidation product of the sugar causes the solution to become quite dark in color, and eventually a high concentration of the sugar and oxidized sugar causes dull copper deposits. If complexing agents, such as for instance rochelle salts, citrates and

ethylenediaminetetraacetic acid are a required component of the plating solution, the use of sugars is not so objectionable. The complexing agents, however, will also hold the sugar reduced Cr^{+3} in solution. The build up of complexed chromium compounds continues throughout the operation of the bath and ultimately the bath becomes inoperable.

It is, therefore, an object of this invention to reduce contaminating hexavalent chromium in cyanide plating baths to harmless trivalent chromium.

It is a further object of this invention to precipitate reduced chromium from cyanide plating baths.

It is still another object of this invention to reduce contaminating hexavalent chromium and precipitate the reduced chromium from cyanide plating baths without producing detrimental effects on the electroplated coatings.

I have now discovered a class of addition agents suitable for the reduction and precipitation of contaminating hexavalent chromium from cyanide plating baths, said class of addition agents consisting of glyoxal and pyruvic aldehyde. The cyanide plating baths are preferably any of the plating baths employed for the electrodeposition of a metal selected from the group consisting of copper, cadmium, zinc and brass. While the addition agents of this invention have the ability to precipitate chromium which has been reduced to its trivalent form, it should be understood that the addition agents of this invention are also compatible with cyanide electroplating baths which contain complexing agents. When complexing agents are present, the addition agents of this invention will still reduce Cr^{+6} to Cr^{+3} which then remains in the bath in complexed form.

The reducing addition agents have been found to produce beneficial results when present in the plating bath in amounts of at least .01 g./l. The reducing addition agents, however, should be present in the plating bath in quantities sufficient to keep the concentration of hexavalent chromium below 5 p.p.m. The hexavalent chromium bath content may be controlled by maintaining a ratio of at least about 4 parts of reducing addition agent per one part of hexavalent chromium. No adverse effects are experienced by the bath on the addition of large quantities of reducing agent, the only upper limit being, of course, the economics of the situation.

The following examples are given to illustrate the practice of this invention, but should not be considered as limiting the spirit and scope thereof:

Example 1

One liter of copper plating solution was made up having the following formulation:

CuCN	g./l.	60
KCN	g./l.	100
KOH	g./l.	24
K_2CO_3	g./l.	35
Dithio-ammelide	g./l.	0.15
pH		12.8

Electrodeposits were made on steel panels at current density of 40 amperes per square foot, at an operating temperature of 150° F. The bath operated under these conditions produced smooth, mirror bright copper deposits. 0.025 g./l. of hexavalent chromium was then introduced into the bath. The resulting electrodeposits produced from this bath were badly blistered and blotchy. 0.11 g. of glyoxal was then added to the hexavalent contaminated bath. After two minutes test panels showed that the chromium interference had completely disappeared and the bath had reduced to its original plating condition. After one hour, chromium was visibly precipitated out as chromium hydroxide. It was noted that the glyoxal, which initially produced a brown coloration and later a dark flocculent precipitate, did not at any time interfere with

the electrodeposited material. It was also noted that after four hours the brown coloration and the fluocculent precipitate disappeared.

Example 2

One liter of zinc plating solution was made up according to the following formulation:

	G./l.
$Zn(CN)_2$	75
NaCN	45
NaOH	90
Na_2S	.75
Hypo	.75

Electrodeposits were made on steel sample panels at a current density of 25 amperes per square foot and at operating temperature of 77° F. The bath when operated under the formulation as initially given produced smooth, almost bright deposits of zinc. 0.025 g./l. of hexavalent chromium was then added to the bath. The resulting deposits from this bath were badly blistered and blotchy. 0.75 cc. of a 15% solution of glyoxal was then added to the bath. After two minutes test panels showed that the chromium interference had completely disappeared and the bath had returned to its original plating condition. After one hour, the chromium was visibly precipitated out as chromium hydroxide.

Example 3

A liter of copper plating solution was made up according to the following formulation:

CuCn	g./l.	60
KCN	g./l.	100
KOH	g./l.	24
K_2CO_3	g./l.	35
Dithio-ammelide	g./l.	0.15
pH		12.8

Electrodeposits were made on sample steel panels at a current density of 40 amperes per square foot, and at an operating temperature of 150° F. Electrodeposits prepared from the bath in its original starting condition were smooth and mirror bright. 0.025 g./l. of hexavalent chromium was then introduced into the bath. The resulting copper deposits from this bath were badly blistered and blotchy. 0.225 g./l. of pyruvic aldehyde was added to the bath. After two minutes the test panels showed that the bath had returned to its original condition. After one hour the chromium was visibly precipitated out as chromium hydroxide.

Example 4

7.5 liters of copper plating bath were prepared having the following formulation:

CuCN	g./l.	60
KCN	g./l.	100
KOH	g./l.	24
K_2CO_3	g./l.	35
Dithio-ammelide	g./l.	0.15
pH		12.8

Daily additions of glyoxal in quantities of ¾ of a cc./l. were made to the bath, as well as daily additions of 0.025 g./l. of hexavalent chromium. These additions were continued over a five day period. The daily additions of glyoxal and hexavalent chromium were then quadrupled and the additions continued for a period of two weeks. Electroplating operations were carried out continuously at a current density of 25 amperes per square foot and at operating temperatures of 145° F. to 160° F. In spite of the fact that heavy precipitates of $Cr(OH)_2$ were produced, the electroplated samples were found to be excellent bright deposits, having a high degree of uniformity in color and ductility. An analysis of the bath after 720 ampere hours of continuous operation showed .002 g./l. of chromium to be present.

In another test run at the same time a proprietary agent containing a reducing sugar was used instead of glyoxal. At the end of the test, this solution was very dark in color and satisfactory deposits could not be obtained.

Example 5

One liter of a proprietary copper solution containing selenium type brighteners and other additives including a complexing agent similar to Rochelle salts was found to give bright copper deposits at 30 amperes per square foot and 150° F. Hexavalent chromium (25 p.p.m.) was added and the resulting deposit was blotchy and misplated. Glyoxal (0.11 g./l.) was then added. After two minutes test deposits showed the deposit to have its normal brightness with no defects due to hexavalent chromium. In this case, however, the trivalent chromium remained in solution due to the complexing agent.

Example 6

7.5 liters of copper plating bath were made up according to the following formulation:

CuCN	g./l.	60
KCN	g./l.	100
KOH	g./l.	24
K_2CO_3	g./l.	35
Dithio-ammelide	g./l.	0.15
pH		12.8

Daily additions of 15% aqueous solution of glyoxal in quantities of ¾ of a cc./l. were made to the bath. Daily additions were continued for five days and then the quantity of glyoxal was quadrupled and daily additions continued for a two week period. Continuous electroplating carried out at a current density of 25 amperes per square foot and at operating temperatures of 145° F. to 160° F. produced samples which were smooth and of excellent brightness. Excellent samples were continuously obtained in spite of the heavy build-up of glyoxal; the plating bath itself remaining clear with light brown coloration. The results show that an excess of glyoxal is not harmful even when hexavalent chromium is absent.

The aldehyde reducing agent additives of this invention may be added before or after hexavalent chromium contamination of the cyanide plating bath. The cyanide plating baths themselves may be any of the cyanide plating baths ranging from dilute baths, such as are used for strike plating, through the more concentrated solutions used in heavy electrodeposition. Regardless of the point of addition or the cyanide bath to which the addition is made, the glyoxal and pyruvic aldehyde reducing agent additives of this invention function in the same manner, that is, the additives reduce hexavalent chromium to trivalent chromium, which subsequently precipitates out as chromium hydroxide if no complexing agent is present.

Reasons for the beneficial reducing properties of the aldehyde reducing agent additives of this invention are not known. It is known, however, that hexavalent chromium reducing properties suitable for application in cyanide plating baths are not a common feature of organic aldehydes.

Having thus disclosed my invention, what I claim is:

1. A method of electroplating a metal selected from the group consisting of copper, cadmium, zinc and brass from a cyanide plating bath comprising adding to said bath a reducing agent in quantities of at least 0.1 gram per liter selected from the group consisting of glyoxal and pyruvic aldehyde.

2. The method of claim 1 wherein said metal is copper.

3. The method of claim 1 wherein said reducing agent is glyoxal.

4. The method of claim 1 wherein said reducing agent is pyruvic aldehyde.

5. A method of electroplating a metal selected from the group consisting of copper, cadmium, zinc and brass

from a cyanide plating bath subject to hexavalent chromium contamination comprising adding to said bath a reducing agent selected from the group consisting of glyoxal and pyruvic aldehyde, said reducing agent being present in quantities such that there is at least four parts of reducing agent present per part of hexavalent chromium.

6. The method of claim 5 wherein said metal is copper.

7. The method of electroplating a metal selected from the group consisting of copper, cadmium, zinc and brass from a cyanide plating bath containing hexavalent chromium contaminants comprising adding to said bath at least 0.1 gram per liter of a reducing agent selected from the group consisting of glyoxal and pyruvic aldehyde and maintaining said bath at a temperature of from 120° F. to 160° F., whereby said hexavalent chromium is reduced to trivalent chromium.

8. The method of claim 7 wherein said metal is copper.

9. The method of claim 7 wherein said reducing agent is glyoxal.

10. The method of claim 7 wherein said reducing agent is pyruvic aldehyde.

11. In a metal cyanide plating solution selected from the group consisting of copper, cadmium, zinc and brass cyanide plating solutions subject to hexavalent chromium contamination, an aldehyde reducing agent additive present in amounts of at least 0.1 gram per liter selected from the group consisting of glyoxal and pyruvic aldehyde.

12. In a copper cyanide plating solution subject to hexavalent chromium contamination, an aldehyde reducing agent additive present in amounts of at least 0.1 gram per liter selected from the group consisting of glyoxal and pyruvic aldehyde.

13. In a metal cyanide plating solution selected from the group consisting of copper, cadmium, zinc and brass cyanide plating solutions subject to hexavalent chromium contamination and containing a complexing agent, an aldehyde reducing agent additive present in amounts of at least 0.1 gram per liter selected from the group consisting of glyoxal and pyruvic aldehyde.

14. In a copper cyanide plating solution subject to hexavalent chromium contamination and containing a complexing agent, an aldehyde reducing agent additive present in amounts of at least 0.1 gram per liter selected from the group consisting of glyoxal and pyruvic aldehyde.

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