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CADMIUM PLATING

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1

This invention relates to the electrodeposition of cadmium, to electrolytes therefor, and to compositions adapted to be incorporated into cadmium plating baths.

One of the objects of the invention is to provide new and improved cadmium plating baths.

Another object of the invention is to provide new and improved cyanide-cadmium plating baths containing complex organic compounds which are soluble in the bath and which produce improved color and brightening effects.

An additional object of the invention is to provide a new and improved method for electrodepositing bright cadmium plates. Other objects will appear hereinafter.

In accordance with the invention, it has been found that greatly improved results in cadmium plating from cyanide-cadmium baths are obtained by electrodepositing the cadmium from an electrolyte containing an amine salt of an aldonic acid and/or a nickel salt of an aldonic acid. The term "amine salt of an aldonic acid" is employed herein to describe reaction products of amines with aldonic acids. In the practice of the invention it is preferable to employ amine salts derived from relatively high molecular weight amines. The preferred type of amine salt for the purpose of this invention is alpha naphthylamine gluconate. A preferred nickel salt for the purpose of the invention is nickel gluconate. It will be understood, however, that other types of amine salts may be employed, and that other nickel aldonates may be used.

The invention will be further illustrated, but is not limited, by the following example in which the proportions are given in parts by weight unless otherwise indicated:

Example

(A) A mixture of

	Grams
Alpha naphthylamine	20
and	
50% gluconic acid	120

was refluxed for 2 hours and then allowed to cool. The resultant reaction product herein referred to as alpha naphthylamine gluconate solidified on cooling.

(B) A nickel carbonate was prepared by dissolving 349 grams of single nickel salts

($NiSO_4.7H_2O$)

in a gallon of boiling water, separately dissolving 356 grams of sodium carbonate in a gallon of boiling water, and then mixing together the two

2

solutions with vigorous stirring. The mixture was allowed to settle for a few minutes and the freshly precipitated nickel carbonate was filtered off. The precipitate was washed several times with hot water until there was no more sulphate ion in the wash water. The precipitate was then sucked dry and dissolved in 970 grams of hot 50% gluconic acid. The resultant solution of nickel gluconate was then adjusted to 3 liters by the addition of water, thereby producing a solution containing 24 grams per liter of nickel.

(C) A cadmium electrolyte was prepared by dissolving 12 ounces of sodium cyanide and 5 ounces of cadmium oxide in a gallon of water.

(D) A stock solution was prepared by mixing together the following ingredients:

2 grams of the alpha naphthylamine gluconate prepared as in (A)
14 cc. of the nickel gluconate solution prepared as in (B)
50 cc. of the cadmium electrolyte solution prepared as in (C)
50 cc. of diethyleneglycolmonobutylether.

When cadmium is electroplated from the electrolyte prepared as in (C), a dull gray plate is obtained. However, if a small amount of the reaction product prepared as in (A) is added to this same electrolyte, a considerable brightening effect is produced. If (A) alone is used, a substantial brightening effect is obtained with as little as 0.25 gram of (A) per gallon of electrolyte. Larger amounts may be employed, although there is little point in adding more than about 1 gram of (A) per gallon of electrolyte because an excess beyond this amount does not produce a comparable improvement in result.

A considerable brightening effect is also obtained if a nickel gluconate prepared as in (B) is incorporated with the cadmium electrolyte (C) in small amounts, preferably within the range of 0.25 gram to 1 gram per gallon of electrolyte.

The alpha napthylamine gluconate produced as in (A) and the nickel gluconate produced as in (B) are both soluble in the bath of the cadmium electrolyte produced as in (C). As previously indicated, each of these substances alone, when added to the cadmium electrolyte (C), produces a brightening effect. In case each substance is added alone, however, the effective range of current density which will produce good results in the electrodeposition of cadmium is relatively narrow, being up to about 40 amperes per square foot in case (A) alone is added, and up to about 25 amperes per square foot in case (B) alone is

added. On the other hand, if both (A) and (B) are incorporated into the cadmium electrolyte, a remarkable brightening effect is obtained and the bright range is complete for current densities up to 100 amperes per square foot. Excellent results are obtained with current densities between 20 and 100 amperes per square foot, bright deposits being obtained without burning the metal. Even higher current densities may be used with very good results.

The alpha napthylamine gluconate and the nickel gluconate are preferably added in the form of the composition described under (D). Ten to 15 cc. of composition (D) per gallon of electrolyte (the electrolyte being similar to electrolyte (C)) will give a pronounced effect with respect to increased brightness of the electrodeposited cadmium, and brilliant deposits are obtained with as little as 57 cc. of composition (D) per gallon of cadmium electrolyte. Electrolytes prepared in this manner are also good barrel plating electrolytes.

In a similar manner, other amine salts of aldonic acids may be employed which may be prepared as described in our co-pending application Serial No. 546,438, filed of even date herewith. Amine salts of aldonic acids formed from relatively high molecular weight amines, and particularly arylamines, are preferred for the practice of the invention. Among said salts are those derived from alpha napthylamine and beta naphthylamine reacted with aldonic acids, such as for example gluconic acid, mannonic acid, galactonic acid, arabonic acid, and xylonic acid. All of these aldonic acids exist in alpha and beta lactone forms. The amine-gluconates are preferable for the practice of the invention because gluconic acid is less expensive and more readily available than the other aldonic acids. These acids are usually obtained by the oxidation of aldoses and are ordinarily prepared in the form of aqueous solutions.

Instead of nickel gluconate, other nickel salts of aldonic acids may be employed, including nickel salts of any of the aldonic acids previously mentioned. These are preferably prepared from freshly precipitated nickel carbonate in the manner described in the foregoing example.

It will be understood that the proportions of the amine salt of the aldonic acid and the proportions of the nickel salt of the aldonic acid may be varied somewhat. In general, as previously indicated, relatively small amounts of the amine salt of the aldonic acid and of the nickel salt of the aldonic acid, either alone or in combination, will produce a pronounced brightening effect. Larger amounts may be used but ordinarily are not necessary to obtain the result, and therefore merely add to the cost of the operation. Thus, the amount of alpha napthylamine gluconate is preferably around 1 gram per gallon of cyanide-cadmium electrolyte, although a substantial brightening effect is obtained with as little as 0.25 per gallon. The addition of larger amounts, however, is not ordinarily justified by an increasing improvement in brightening effect. Similarly, the ultimate results with nickel gluconate, preferably when employed in combination with the alpha napthylamine gluconate, are obtained with about 7 cc. per gallon of electrolyte of the nickel gluconate solution containing around 24 grams per liter of nickel, but effective results can be obtained with as little as one-fifth of that amount.

As illustrated in the example, it is preferable to employ a water miscible organic solvent in the preparation of the stock solution. Among the suitable solvents are butyl Carbitol and methyl "Cellosolve" Formal, although it will be understood that many other types of water miscible organic solvents can be used.

The invention produces new and improved results in the electroplating of cadmium and makes it possible to obtain very bright cadmium plates over a wide range of current densities. The amounts of additional materials incorporated into the cadmium electrolyte in accordance with the invention, are so small that the expense of the operation is not greatly increased and the improved results with respect to brightness and current density range more than justify the cost.

The invention is hereby claimed as follows:

1. An aqueous cyanide-cadmium plating bath comprising a cyanide-cadmium electrolyte and an amine salt of an aldonic acid.

2. An aqueous cyanide-cadmium plating bath comprising a cyanide-cadmium electrolyte, an amine salt of an aldonic acid and a nickel aldonate.

3. An aqueous cyanide-cadmium plating bath comprising a cyanide-cadmium electrolyte and a nickel aldonate.

4. An aqueous cyanide-cadmium plating bath comprising a cyanide-cadmium electrolyte and an arylamine salt of gluconic acid.

5. An aqueous cyanide-cadmium plating bath comprising a cyanide-cadmium-electrolyte, an arylamine salt of gluconic acid and nickel gluconate.

6. An aqueous cyanide-cadmium plating bath comprising a cyanide-cadmium electrolyte and nickel gluconate.

7. An aqueous cyanide-cadmium plating bath comprising a cyanide-cadmium electrolyte and alpha naphthlyamine gluconate.

8. An aqueous cyanide-cadmium plating bath comprising a cyanide-cadmium electrolyte, alpha naphthylamine gluconate and nickel gluconate.

9. An aqueous cyanide-cadmium plating bath comprising a cyanide-cadmium electrolyte and alpha naphthylamine gluconate in proportions within the range of about 0.25 gram to 1 gram per gallon of the plating bath.

10. An aqueous cyanide-cadmium plating bath comprising a cyanide-cadmium electrolyte, about 1 gram per gallon of alpha naphthylamine gluconate and about 7 cc. per gallon of nickel gluconate solution with the amount of nickel per liter of nickel gluconate solution corresponding to about 24 grams.

11. A brightener solution for cyanide-cadmium electrolytes comprising an amine salt of an aldonic acid and a nickel salt of an aldonic acid.

12. A brightener solution for cyanide-cadmium electrolytes comprising an arylamine gluconate and nickel gluconate, said solution serving to increase the brightness of the electrodeposited cadmium and to extend the range of current densities over which bright deposits are obtained.

13. A brightener solution for cyanide-cadmium electrolytes comprising alpha naphthylamine gluconate and nickel gluconate, said solution, when added in small amounts to a cyanide-cadmium electrolyte, serving to increase the brightness of the electrodeposited cadmium and to extend the range of effective current densities.

14. A brightener solution for cyanide-cadmium electrolytes comprising an amine salt of an aldonic acid, a nickel salt of an aldonic acid, a water miscible organic solvent for said salts, and a

substantial proportion of a cadmium electrolyte.

15. A solution for addition to cyanide-cadmium plating baths to improve the plating characteristics thereof, particularly with respect to brightness and effective current densities range, said solution comprising approximately

2 grams alpha naphthylamine gluconate
15 cc. nickel gluconate containing about 24 grams per liter of nickel
50 cc. of a cyanide-cadmium electrolyte
50 cc. diethyleneglycolmonobutylether,

said solution producing marked increase in brightness of electrodeposited cadmium when added to a cyanide-cadmium electrolyte in proportions within the range of 10 to 57 cc. of solution per gallon of electrolyte and also serving to extend the effective current density range of said electrolyte.

16. In the electrodeposition of cadmium, the step which comprises electrodepositing cadmium from an aqueous cyanide-cadmium plating bath having dissolved therein an amine salt of an aldonic acid.

17. In the electrodeposition of cadmium, the step which comprises electrodepositing cadmium from an aqueous cyanide-cadmium plating bath having dissolved therein an amine salt of an aldonic acid and a nickel salt of an aldonic acid.

18. In the method of electrodepositing cadmium, the step which comprises electrodepositing cadmium from an aqueous cyanide-cadmium plating bath having dissolved therein a nickel salt of an aldonic acid.

19. In the electrodeposition of cadium, the step which comprises electrodepositing cadmium from an aqueous cyanide-cadmium plating bath having dissolved therein an aromatic amine gluconate and nickel gluconate.

20. In the electrodeposition of cadmium, the step which comprises electrodepositing cadmium from an aqueous cyanide-cadmium plating bath having dissolved therein alpha naphthylamine gluconate and nickel gluconate.

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