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ZINC ELECTROPLATING COMPOSITIONS AND METHOD FOR THE ELECTRODEPO-SITION OF ZINC

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1

This invention relates to new and improved compositions for use in the electrodeposition of zinc, and to a new and improved method for electrodepositing zinc from alkaline zinc-cyanide

One of the objects of the invention is to provide new and improved compositions which, when added to alkaline cyanide-zinc plating baths in relatively small amounts, will produce new and improved results in the electrodeposition of zinc 10 from such baths.

A further object of the invention is to provide compositions of the type referred to which will produce new and improved results in the color of the electrodeposited metal.

Another object of the invention is to provide compositions of the type referred to which will increase the brightness of the electrodeposited metal.

An additional object of the invention is to provide compositions of the type referred to which increase the cathode efficiency of the electroplating bath.

Still a further object of the invention is to provide compositions of the type referred to which will widen the range of allowable current density for the electrodeposition of zinc as compared with an ordinary plating bath not containing these compositions.

Other objects of the invention are the provision of fast starting electrolytes and electrolytes of high striking power.

Another object of the invention is to provide a new and improved method of electrodepositing zinc at relatively high rates of deposit over a wide range of current densities. Other objects will appear hereinafter.

In accordance with the invention, it has been found that new and improved results in the electrodeposition of zinc are obtained by incorporating into cyanide-zinc plating baths compositions or concentrates containing a zinc aldonate, preferably zinc gluconate, and preferably also containing an alkali soluble protein derived from a vegetable seed meal, such as for example soy bean 45 meal.

A further feature of the invention in its preferred aspects is the incorporation into compositions or concentrates of the type described for addition to electroplating baths, ammonium 50 alginate and/or a naphthylamine salt of an aldonic acid, preferably the alpha naphthylamine salt of gluconic acid.

creasing the cathode efficiency and hence the speed of deposit, and to some extent of decreasing or lessening the burning tendency. The alkali soluble seed meal protein may also be used alone, but has the disadvantage of a tendency to coagulate and is preferably used in combination with the zinc aldonate. The presence of the seed meal protein in the bath increases brightness, but its biggest effect is to widen the range of allowable current density. Both the naphthylamine salt of the aldonic acid and the ammonium alginate contribute to an improvement in the color or snap of the electrodeposited zinc.

A concentrate or composition containing all 15 four of the aforementioned ingredients is clear and stable against precipitation on standing when added to a cyanide-zinc plating bath in relatively small amounts; it provides a very fast starting electrolyte with high striking power, fair nonburning tendencies, uniform color, and one which is useful through a relatively wide range of current densities. Electroplating baths containing the aforementioned ingredients are especially suited for plating operations at low current densities, for example in tumble barrels at densities within the range of about 3 to about 15 amperes per square foot, although satisfactory results are also obtained at medium current densities within the range of, say, 15 to 40 amperes per square foot, and at higher current densities within the range of 40 to 100 amperes per square foot or better.

The invention will be illustrated but is not limited by the following examples, in which the quantities are stated in parts by weight unless otherwise indicated:

Example I

A. Zinc gluconate is prepared by mixing together Parts Zinc oxide_ 50% gluconic acid______ 400 heating to the boil, and filtering. The filtrate may be incorporated in an alkaline cyanide-zinc electroplating bath as such, but is preferably employed in conjunction with other ingredients as hereinafter described. B. A substantially de-oiled soya bean flour containing about 46% protein nitrogen was treated to extract the alkali soluble protein by mixing together the following ingredients: Parts Soya flour_____ Sodium hydroxide_____ 40

3

and refluxing for 2 hours, cooling to room temperature, allowing to stand at room temperature for about a day, and then filtering to remove the residue. This filtrate may be added directly to a cyanide-zinc electroplating bath, but is preferably combined with the filtrate from A and with other ingredients hereinafter described under C and D.

C. A naphthylamine salt of gluconic acid is prepared by refluxing a 50% solution of gluconic acid with alpha naphthylamine in the following proportions:

Parts
Alpha naphthylamine________20
50% gluconic acid_______28

and refluxing for 2 hours, and thereafter pouring the reaction mixture from the reflux vessel while hot and allowing it to cool to form a solid.

The solid alpha naphthylamine salt of gluconic acid prepared as above described is then added to water in proportions of 14 parts per 190 parts of water, and the mixture is brought to the boil and filtered hot.

D. An ammoniacal solution of ammonium alginate is prepared by dissolving 0.9 part of ammonium alginate in approximately 150 parts of ammonium hydroxide.

According to a preferred embodiment of the invention, the ingredients prepared as above described are mixed in the following proportions:

30 cc. of A 90 cc. of B

3 cc. of C (if used hot, or 3 grams if used cold) 30 cc. of D.

A typical zinc electrolyte to which the foregoing composition is added is prepared by dissolving

Sodium cyanide	90–100	
Zinc metal (added as 45-50 parts zinc		
oxide)	36~40	
Sodium hydroxide	100-115	

in enough water to make a liter of solution, treating the resultant composition with 2 parts per liter of zinc dust, and then filtering to remove traces of heavy metals.

When the composition A, B, C, D prepared as above described is added to the electrolyte in proportions preferably within the range of 80–100 cc. per gallon of electrolyte, the resultant electrolyte is clear and no precipitate is formed on standing. It may be described as a very fast starting electrolyte with high striking power, fair non-burning tendencies, uniform color, and can be used through a wide range of current densities. Especially good results are obtained in tumble barrel operations at current densities within the range of 3 to 15 amperes per square foot.

Example II

A concentrate is prepared as in Example I except that the protein solution is prepared in a different manner. According to this second procedure, 2.8 pounds of a vegetable protein flour 65 of the type described in Example I is added to one gallon of the alkaline cyanide-zinc electrolyte described in Example I. This mixture is allowed to stand about 12 hours at room temperature (60° F.-80° F.) or until the soya protein goes into 70 solution. This concentrate is then diluted by adding 9 gallons more of water for each gallon of concentrate. The resultant stock solution can be used in the same proportions as solution B in Example I. It has the advantage that no separate filtra-75

tion step is necessary, the protein going into solution in the alkaline zinc electrolyte without a separate extraction step.

The invention is susceptible to some variation and modification in the manner of its practical application. While it is preferably in accordance with the invention to employ an alkali soluble protein derived from soya flour, the protein may also be derived from other proteinaceous vegetable seed meals, as for example peanut flour, cottonseed meal, and other beans or lupines rich in protein. Usually it is preferable to start with the flour from which most or all of the oil has been removed, as for example the so-called solvent soya flours or soya flours which have been subjected to an expeller treatment. However, full fat soya flours may also be employed. If soya flour is employed, the starting material usually contains around 43 to 56% protein. Likewise, it will be understood that more highly purified vegetable seed meal proteins may be used.

While it is preferable in accordance with the invention to employ caustic alkali for extraction of the protein, other alkalies, such as soda ash and/or lime, may be used. A separate extraction step can be avoided by following the procedure of Example II.

It is preferable to employ gluconic acid, although it will be understood that other aldonic acids may be used, such as for example mannonic, galactonic, arabonic, and xylonic. These acids are derived from the corresponding aldoses by oxidation. All of the aforementioned acids exist in alpha and beta lactone forms. The aldonic acids mentioned may be used in the preparation of the zinc aldonates and also in the preparation of arylamine salts, as in C. Gluconic acid and the corresponding gluconate derivatives are preferred for the practice of the invention because gluconic acid is more cheaply and readily available.

Instead of the alpha naphthylamine salt of an aldonic acid other alkali-soluble arylamine salts can be used, for example, the beta naphthylamine salt of gluconic acid.

Instead of ammonium alginate other alkalisoluble alginates can be used, for example, sodium alginate.

The invention has the advantage of providing clear electrolytes which do not form precipitates on standing, are very fast starting, have high striking power, high cathode efficiencies, fair non-burning tendencies, uniform color, and which can be used over a wide range of current densities. The electrodeposited metal is further characterized by improved brightness. One of the particular advantages of the invention is that the concentrates can be added to any standard alkaline cyanide-zinc plating bath, and only relatively small amounts are required in order to produce the desired results. Hence, the concentrates can be shipped and handled with the minimum of expense.

The invention is hereby claimed as follows:

- 1. The method of depositing zinc which comprises electrodepositing zinc from an aqueous alkaline cyanide-zinc plating bath containing a sufficient amount of dissolved zinc-aldonate to enhance the speed of deposit.
- 2. The method of depositing zinc which comprises electrodepositing zinc from an aqueous alkaline cyanide-zinc plating bath containing a sufficient amount of dissolved zinc gluconate to enhance the speed of deposit.
 - 3. The method of depositing zinc which com-

4

sentially an aqueous alkaline zinc-cyanide soluprises electrodepositing zinc from an aqueous altion containing sufficient amounts of dissolved kaline cyanide-zinc plating bath containing a zinc gluconate, an alkali soluble soya bean prosufficient amount of dissolved zinc aldonate to entein, and the alpha naphthylamine salt of gluhance the speed of deposit and a sufficient amount conic acid to enhance brightness and the speed of dissolved alkali soluble protein derived from a

of deposit.

vegetable seed meal to enhance brightness. 4. The method of depositing zinc which comprises electrodepositing zinc from an aqueous alkaline cyanide-zinc plating bath containing sufficient amounts of a dissolved zinc aldonate and a 10 dissolved alkali soluble protein derived from a vegetable seed meal and an arylamine salt of an aldonic acid to enhance brightness and the

speed of deposit.

5. The method of depositing zinc which com- 15 prises electrodepositing zinc from an aqueous alkaline cyanide-zinc plating bath containing sufficient amounts of dissolved zinc gluconate and dissolved caustic alkali soluble protein derived from soya flour, and the dissolved alpha naphthylamine salt of gluconic acid to enhance brightness and the speed of deposit.

6. The method of depositing zinc which comprises electrodepositing zinc from an aqueous alkaline cyanide-zinc plating bath containing suffi- 25 cient amounts of dissolved zinc aldonate and dissolved alkali soluble protein derived from a vegetable seed meal, a dissolved arylamine salt of an aldonic acid and a dissolved alginate to enhance brightness and the speed of deposit.

7. A zinc plating composition comprising essentially an aqueous alkaline zinc-cyanide solution containing dissolved zinc aldonate in sufficient quantity to enhance speed of deposit.

8. A zinc plating composition comprising es- 35 sentially an aqueous alkaline zinc-cyanide solution containing dissolved zinc gluconate in sufficient quantity to enhance speed of deposit.

9. A zinc plating composition comprising essentially an aqueous alkaline zinc-cyanide solu- 40 tion containing sufficient amounts of dissolved zinc aldonate, and a dissolved alkali soluble vegetable seed meal protein to enhance brightness and the speed of deposit.

10. A zinc plating composition comprising es- 48

11. A zinc plating composition comprising essentially an aqueous alkaline zinc-cyanide solution containing sufficient amounts of dissolved zinc aldonate, an alkali soluble vegetable seed meal protein, an arylamine salt of an aldonic acid and an alginate to enhance brightness and the

speed of deposit.

12. A zinc plating composition comprising essentially an aqueous alkaline zinc-cyanide solution containing sufficient amounts of dissolved zinc gluconate, an alkali soluble soya bean protein, the alpha naphthylamine salt of gluconic acid and ammonium alginate to enhance bright-

ness and the speed of deposit.

13. An electrolyte composition suitable for addition to aqueous alkaline zinc-cyanide plating baths comprising sufficient quantities of dissolved zinc aldonate, an alkali soluble vegetable seed meal protein and an arylamine salt of an aldonic acid to enhance brightness and the speed of deposit.

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