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ELECTROPLATING OF ZINC AND ELECTROLYTE THEREFOR

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This invention relates to a new and improved method of electroplating zinc from an alkaline zinc cyanide bath, and to a new and improved electrolyte therefor.

One of the objects of the invention is to provide a new and improved type of electrolyte for electroplating zinc from alkaline cyanide baths.

A further object of the invention is the provision of new and useful electrolyte baths which do not form precipitates and do not tend to coagulate on standing over long periods of time.

Another object of the invention is to provide a new and improved method of electroplating zinc wherein electroplated articles having a very bright finish are produced.

An additional object of the invention is to provide a new and improved method of incorporating into alkaline zinc electrolytes organic substances capable of forming complex metallo organic compounds with the metallic ions present in the bath.

Another object of the invention is to provide a new and improved method of adding to alkaline zinc cyanide baths for specific purposes certain types of compounds or derivatives thereof in a form in which the compounds or their derivatives remain in solution in the bath and can be added in relatively larger proportions than has heretofore been practical with the compounds per se. Other objects will appear hereinafter.

These objects are accomplished in accordance with this invention by incorporating into alkaline zinc cyanide electrolyte baths reaction products of a gelatin and an aldonic acid, preferably the reaction product of gelatin with gluconic acid. When zinc is electroplated from such baths on the customary base materials, the resultant electroplated products have a greatly improved brightness of finish. Especially good results are obtained with current densities up to 30–40 amperes per square foot, although bright finishes can be obtained at higher current densities without burning.

One of the important features of the invention is the great stability of the electrolyte baths and of the aldonic acid-gelatin derivatives which are added to these baths. The baths may be used over long periods of time at temperatures such as are ordinarily employed in electroplating without substantial coagulation or precipitation due to the presence of the protein derivatives. Relatively large amounts of the aldonic acid-protein derivatives may be employed as

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distinguished from gelatin per se which, when added to a similar type of electrolyte bath, merely floats around in masses or blobs.

For the purpose of the invention it is preferable to add an excess of the aldonic acid to the bath as a part of the solution produced by the treatment of a gelatin with the aldonic acid. The excess of the aldonic acid, as previously indicated, forms with the zinc ions present in the bath a complex metallo organic compound, and in the practice of the invention it has been found that the electrolyte baths used have a very high initial cathode efficiency, which is apparently due to the presence of the complex metallic ions of the aldonic acid.

In the preparation of compositions to be used in electroplating zinc in alkaline cyanide baths a further feature of the invention is the addition of furfural to the gelatin-aldonic acid derivative. Furfural forms with the solution of this derivative a clear stable solution of a somewhat deeper yellow color than that of the gelatin-aldonic acid derivative. Ordinarily, it is very difficult to add substantial amounts of furfural to electroplating baths, but by adding the furfural to the gelatin-aldonic acid derivative first, no such difficulty is encountered. The composition containing furfural has the added advantage in electroplating baths of the alkaline zinc cyanide type that it enhances the smoothness of the deposit as compared with gelatin-aldonic acid compositions not containing the furfural. The latter compositions, however, will nevertheless produce very bright finishes.

The invention is illustrated but not limited by the following examples:

Example I

The gluconic acid-gelatin derivative was prepared by mixing together 34 grams of gelatin and 100 cc. of 50% gluconic acid. The reaction mixture was digested from ½ to 1 hour at a temperature of from 80 to 120° F. The mixture was then stirred vigorously and the temperature gradually raised to 180° F. with the addition of 490 cc. of water. The gluconic acid forms a gel with the gelatin, and the addition of the water with vigorous stirring and heating converts this gel into a solution. The resultant product is stable and does not tend to precipitate or coagulate on standing. It is clear and has a yellowish color. This product can be added directly to an alkaline zinc cyanide electroplating bath with excellent results.

Example II

A gelatin-gluconic acid derivative was prepared as in Example I, except that 15 cc. of furfural was added to the solution after it had been heated to 180° F. and while it was still hot. The furfural may also be added after the solution is cool. This produced a clear stable solution having a somewhat deeper yellow color, which gave excellent results both as to brightness and smoothness of finish in alkaline zinc cyanide electroplating baths.

Example III

This example illustrates the application of the products of Examples I and II and the preparation of alkaline zinc cyanide electrolytes.

An electrolyte was prepared by mixing together the following ingredients:

90–100 grams sodium cyanide

36–40 grams zinc metal (added in the form of zinc oxide)

100–115 grams sodium hydroxide and enough water to make 1 liter of solution

2 grams per liter of zinc dust was stirred into the electrolyte and the entire mixture was filtered in order to remove traces of heavy metals.

This electroplating bath when employed in a conventional manner ordinarily produces zinc electroplated articles with a dull gray finish. Upon the addition of either of the products of Examples I or II, however, preferably in amounts corresponding to from 60 to 80 cc. of either of said products per gallon of the above described alkaline zinc cyanide electrolyte, bright finishes are obtained.

In electroplating operations with these electrolytes especially good results with respect to the brightness of the finish are obtained with current densities up to 30–40 amperes per square foot. At greater current densities bright zinc coatings are still obtained, but in general the coatings are not quite as bright as those obtained at the lower current densities. The products are especially useful in barrel plating operations but can be used in other types of operations without burning of the coating even at the higher current densities.

The invention is susceptible to some variation and modification in the manner of its practical application. In general, it is preferable to employ gluconic acid because it is the most cheaply and readily available of all of the aldonic acids. The gluconic acid is ordinarily employed in the form of an aqueous solution and usually has a concentration not substantially greater than 50%, because at the higher concentrations it tends to go into the crystalline lactone form. The minimum concentration of aldonic acid employed is that which will form a gel with the gelatin. As examples of other aldonic acids which may be used, mention is made of the following: mannonic, arabonic, galactonic, and xylonic. These acids are obtained by the oxidation of the corresponding aldoses and all have alpha and beta lactone forms.

The gelatin employed may be any of the ordinary types of gelatins obtained from animal tissues in the usual way, by boiling them under pressure with water. The term "gelatin" is used herein in its ordinary sense, as defined in Hackh's Chemical Dictionary, 1929, page 326.

It will be understood that the electroplating baths of the present invention may be employed for direct current electroplating in the usual manner, and also give excellent results when employed in electroplating zinc from alkaline zinc cyanide electroplating baths using alternating current superimposed upon direct current.

The term "cyanide-zinc plating bath," as employed herein, is used generically to cover any alkaline cyanide plating baths for electroplating zinc, which may or may not contain other substances added for special purposes. Electroplating baths of this type are so well known in the art that further description of them is considered unnecessary. The plating baths of the present invention apparently contain zinc ions in several forms, including complex inorganic ions such as zincate ions due to the presence of the alkali and complex metallo organic ions due to the presence of zinc gluconate.

The method of electroplating herein described provides a new and improved way of obtaining bright zinc finishes. The electroplating baths produced in accordance with the invention are characterized by excellent stability. Furthermore, as previously indicated, the incorporation into the bath of gelatin-aldonic acid derivatives containing excess aldonic acid produces results which cannot be obtained by adding the gelatin alone or the aldonic acid alone. Likewise, the incorporation into the baths of gelatin-aldonic acid-furfural derivatives gives results that are not obtained from the separate components added as such.

The invention is hereby claimed as follows:

1. An aqueous cyanide-zinc plating bath comprising an alkaline cyanide-zinc electroplating bath and the bath soluble chemically combined reaction product of a gelatin with an aldonic acid.

2. An aqueous alkaline cyanide zinc electroplating bath comprising an aqueous alkaline cyanide solution containing zinc in the form of an aldonate and the water soluble chemically combined reaction product of a gelatin with an aldonic acid.

3. An aqueous cyanide-zinc plating bath comprising an alkaline cyanide-zinc solution containing the chemically combined bath soluble reaction product of a gelatin, an aldonic acid, and furfural.

4. An aqueous cyanide-zinc plating bath comprising an alkaline cyanide-zinc electroplating solution and the chemically combined bath soluble reaction product of a gelatin with gluconic acid.

5. An aqueous cyanide-zinc plating bath comprising an alkaline cyanide-zinc electroplating solution and a solution of the chemically combined reaction product of gelatin, gluconic acid and furfural.

6. An aqueous zinc electroplating bath comprising a major proportion of an alkaline cyanide-zinc solution and a minor proportion of a solution of the chemically combined reaction product of gelatin with an aldonic acid.

7. An aqueous zinc electroplating bath comprising a major proportion of an alkaline cyanide containing complex zinc ions and a minor proportion of a solution of the chemically combined reaction product of gelatin with gluconic acid.

8. An aqueous zinc electroplating bath comprising an alkaline cyanide solution containing complex zinc ions and a solution of the chemically combined reaction product of gelatin and gluconic acid in proportions of about 60 to 80 cc. per gallon of plating bath.

9. An aqueous zinc electroplating bath comprising an alkaline cyanide solution containing complex zinc ions and a solution of the chemically combined reaction product of gelatin, glutonic acid and furfural in proportions of about 60 to 80 cc. per gallon of plating bath.

10. In a process for the electrodeposition of zinc, the step which comprises depositing zinc from an aqueous cyanide-zinc plating bath in the presence of the chemically combined reaction product of a gelatin and an aldonic acid, said reaction product being bath soluble.

11. In a process for the electrodeposition of zinc, the step which comprises depositing zinc from an aqueous cyanide-zinc plating bath in the presence of a solution of the chemically combined reaction product of a gelatin, an aldonic acid, and furfural.

12. In a process for the electrodeposition of zinc, the step which comprises depositing zinc from an aqueous cyanide-zinc plating bath in the presence of the chemically combined reaction product of a gelatin and gluconic acid reacted in gel-forming proportions and dissolved in water.

13. In a process for the electrodeposition of zinc, the step comprising depositing zinc from an aqueous cyanide-zinc plating bath in the presence of the chemically combined reaction product of gelatin, furfural, and gluconic acid, said reaction product being bath soluble.

14. In a process for the electrodeposition of zinc from a cyanide-zinc plating bath, the step which comprises depositing zinc from an aqueous cyanide-zinc plating bath containing zinc gluconate and the water soluble chemically combined reaction product of gelatin and gluconic acid.

15. In a process for the electrodeposition of zinc from a cyanide-zinc plating bath, the step

which comprises depositing zinc from an aqueous cyanide-zinc plating bath containing zinc gluconate and the water soluble chemically combined reaction product of gelatin, gluconic acid and furfural.

16. The process for electrodepositing zinc from a cyanide-zinc plating bath which comprises depositing zinc from an aqueous cyanide-zinc plating bath containing zinc gluconate and a quantity of the water soluble chemically combined reaction product of gelatin and gluconic acid resulting from the reaction of gelatin with gluconic acid in proportions corresponding to about 34 grams of gelatin and 100 cc. of 50% gluconic acid digested together from one-half hour to one hour at a temperature of from 80 degrees F. to 120 degrees F. to form a gel followed by the addition of an amount of water sufficient to dissolve said gel, said quantity corresponding to about 60 cc. to 80 cc. of the resultant solution of the gelatin-gluconic acid reaction product in water per gallon of aqueous cyanide-zinc plating bath.

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