United States Patent Office

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ALKALINE, CYANIDE ZINC ELECTROPLATING BATH PROCESS, AND ADDITIVE THEREFOR

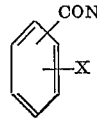
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No Drawing. Continuation-in-part of application Ser. No. 393,777, Sept. 1, 1964. This application July 17, 1967, Ser. No. 653,619

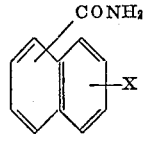
13 Claims. (Cl. 204—55)

ABSTRACT OF THE DISCLOSURE

A process of electrodepositing bright zinc from an aqueous alkaline cyanide solution. The solution contains as a brightener an aromatic amide of the formula



and



wherein x is —OH, —COOH or —SO_3H. The solution may also contain organic polymers such as polyvinyl alcohol, polyethyleneimine, glue, gums, and protein substances.

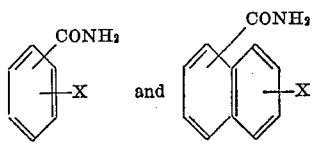
Cross reference to related applications

This application is a continuation-in-part of U.S. application Ser. No. 393,777 filed Sept. 1, 1964, now abandoned.

Background of invention

Solutions for the electrodeposition of zinc are broadly classified into two general categories, namely, acid zinc baths such as those containing zinc sulfate, chloride or fluoroborate, and alkaline zinc baths which contain zinc cyanide. Additives which are suitable for one category are seldom suitable for use in the other type of bath. The mode of plating is further classified into two groups, i.e., still plating and barrel plating. In both groups, electrodeposited zinc generally has a dull appearance unless a brightening agent is added. A wide variety of such agents have been successfully used; however, most have not been fully acceptable for all types of plating. Some work well for still plating while others are only suitable for barrel plating. In addition, some are extremely expensive or must be used in large quantities and others suffer from instability in the plating bath. Others yield bright deposits but the deposits are not responsive to post-treatment with protective agents.

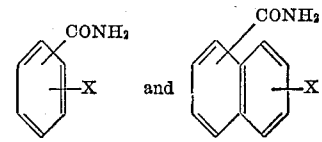
According to the present invention there is provided an aqueous, alkaline, cyanide zinc electroplating bath containing as a brightening agent therefor from about 0.1 to 10 grams per liter of bath of a bath-soluble aromatic amide selected from the group consisting of:



wherein X is —OH, —COOH or —SO_3H.

Detailed description of invention

The aromatic amides of the formulas



wherein X is —OH, —COOH or —SO_3H are particularly effective as brightening agents in an aqueous cyanide zinc plating bath. These compounds are soluble in the plating bath. By the term "soluble" it is meant having a solubility of at least about 0.1 gram per liter at a temperature of about 25° C. in an alkaline cyanide zinc plating bath.

Included among the suitable compounds are monomeric compounds such as isophthalamic acid, salicylamide, p-hydroxybenzamide, terephthalamic acid, p-sulfonic acid benzamide, and 1-naphthoamide 4-carboxylic acid. Of these representative compounds, isophthalamic acid is a preferred species.

The aromatic amides may be used alone in the usual commercial plating baths but are preferably used in combination with an organic polymer which is also soluble in the bath. Examples of suitable polymers include synthetic polymers such as polyvinyl alcohol and polyethyleneimine, and natural polymers such as gelatin and peptone. The polyvinyl alcohol may be modified, e.g., a partial ether formed by condensation with ethylene oxide or glycidol.

The polyvinyl alcohols prepared by alcoholysis (hydrolysis) of polyvinyl acetate are a preferred type of organic polymer. Those having molecular weights from about 5,000 to 20,000 when used in combination with the aromatic amide are generally preferred.

The aromatic amide brightening agents of this invention may be used in conventional aqueous cyanide zinc plating baths in amounts ranging from about 0.1 gram per liter to an amount approaching saturation. Optimum amounts will vary, depending on the specific compound used, the current density employed, and the type of plate desired. It is generally preferred that from 0.5 to 10 grams per liter be used. When used in combination with an organic polymer, the amount of the aromatic amide should be in the range from 0.1 to 10 grams per liter, with from 0.02 to 10 grams per liter of the polymer being present in the bath. Preferably, 0.05 to 0.5 gram per liter of the polymer is used.

In one embodiment of this invention, a plating bath containing zinc cyanide, sodium cyanide, sodium hydroxide, an aromatic amide, and a bath-soluble organic polymer is prepared by dissolving the constituents in water. The aromatic amide and organic polymer may be added separately but are preferably added together in the form of a concentrated aqueous brightener solution. This solution may contain from 1:1 to 50:1 parts by weight of aromatic amide to polymer. If the aromatic amide is in acid form, it may be converted to the sodium salt by addition of sodium hydroxide. This solution can be more readily formulated in concentrated form. The concentrate may be diluted to provide an aqueous solution containing from about 20% to 35% solids.

The invention will be further illustrated by the following examples in which parts and percentages are by weight unless otherwise specified.

EXAMPLE I

An aqueous plating bath having the following composition was prepared:

	Grams per liter
Sodium cyanide	40
Sodium hydroxide	90
Zinc cyanide	60
Sodium carbonate	75

The bath was used in a conventional Hull-type plating cell to plate steel panels. In conducting the experiment, about 267 ml. of the plating solution, to which 4 grams per liter of isophthalamic acid had been added, was placed in the cell. The electrolysis was conducted at room temperature, between about 25° and 30° C., using a current of 2 amperes for five minutes. The cathode panel was then removed from the cell, washed in water, dipped in 0.5 weight percent nitric acid to remove stains, and washed with water. An extremely bright plate was obtained over a current density range from 20–150 amps./sq. ft.

In a control experiment conducted in the manner just related, but in which the isophthalamic acid was not added to the bath, a uniformly dull plate was obtained over the entire face of the steel panel.

EXAMPLE II

A plating bath containing 650 cc. of the solution described in Example I was prepared. The bath contained 3 grams per liter of isophthalamic acid. A six-link length of steel chain, each link being about 1 inch long by 5/8 inch wide and having a thickness of 3/16 inch was suspended in the bath. The chain was plated at 2.5 amperes (a current density of approximately 40 amps./sq. ft.) for fifteen minutes. The chain was then washed in water and dipped for ten seconds in 0.5 weight percent nitric acid to remove stains. After washing and drying, the product was found to be bright and lustrous on all surfaces.

In a control experiment carried out as related above, but in which no isophthalamic acid was included in the bath, the surface of the chain was dull and lacked luster.

EXAMPLE III

1.3 liters of the aqueous plating bath described in Example I was used in plating an automobile crank-hole cover. The bath contained 1.5 grams per liter of isophthalamic acid. The crank-hole cover, which had a total surface area of one-ninth square foot, was suspended as the cathode in the bath and plated between two zinc anodes for fifteen minutes, using a current of 3.5 amperes, i.e., a current density of about 40 amps./sq. ft. The crank-hole cover used had an outer surface comprised of a series of convex surfaces and an inner surface comprised of a series of concave surfaces presenting ridges and valleys to be plated. After removal of the crank-hole cover from the plating bath and washing with water and a dip in 0.5 weight percent nitric acid. the cover exhibited a bright plate on all surfaces. The plate was particularly bright on the concave surfaces.

EXAMPLE IV

A barrel plating experiment was conducted using a plating bath having the composition of that described in Example I and containing 2 grams per liter of isophthalamic acid. One hundred (100) grams of #8 x 3/4 inch mild steel screws were plated using a current of 5 amperes for thirty minutes. After washing and dipping the plated screws in 0.5 weight percent nitric acid for three to five seconds, the screws were found to be smooth and semi-bright. The appearance of the screws was decidedly improved over screws plated in a similar fashion but in the absence of isophthalamic acid.

In a continuation of the experiment related above, the plating bath containing the isophthalamic acid was permitted to stand idle for twenty-four hours, after which it was again used to plate screws. The appearance of the screws was almost equivalent to that of the screws plated using the freshly prepared bath and far superior to screws plated with the bath containing no isophthalamic acid.

EXAMPLE V

The experiment of Example III was repeated except that 1.5 grams per liter of salicylamide was substituted for the isophthalamic acid. The plated crank-hole cover obtained exhibited improved brightness and luster over a crank-hole cover plated using a bath containing no salicylamide.

EXAMPLE VI

The experiment of Example III was repeated except that 1.5 grams per liter of p-hydroxybenzamide was substituted for the isophthalamic acid. Results similar to those of the preceding Example V were obtained.

EXAMPLE VII

Example IV was repeated except that 1.5 grams per liter of isophthalamic acid and 0.075 gram per liter of "Elvanol" [1] 51–03 were substituted for the isophthalamic acid. After washing and dipping the screws in 0.5 weight percent nitric acid for three to five seconds, the screws were found to be extremely brilliant and lustrous.

In comparative experiments, in which plating baths contained either isophthalamic acid or "Elvanol" 51–03 alone, it was not possible to obtain screws which exhibited the bright and lustrous plate described above.

EXAMPLE VIII

Example I was repeated except that 0.08 gram per liter of "Elvanol" 51–03 was added to the plating bath. A very bright plate was obtained over the range of current densities of the Hull cell plate in the range of 5 to 150 amps./sq. ft. By comparing the results of this experiment with the results of the experiment in which no "Elvanol" 51–03 was present in the bath, it was found that by using the mixture of additives the bright current density range was increased from 20 to 150 amps./sq. ft. to the above-mentioned 5 to 150 amps./sq. ft.

In a control experiment in which "Elvanol" 51–03 was used alone at a concentration of 0.08 gram per liter little improvement over a blank test was observed.

In practicing the present invention, other aromatic amides which are soluble in the plating baths may be substituted for those illustrated in the examples with similar results. Among these compounds are isomers of the illustrated compounds as well as such compounds as 1-naphthoamide 4-carboxylic acid and its isomers and 2-naphthoamide 5-sulfonic acid and its isomers. Other compounds within the general class described will be apparent to those skilled in the art. Other polymeric materials such as glue, gums such as gum arabic, gum tragacanth, gum ghatti, gum guaiac, as well as protein substances such as egg albumin and milk protein hydrolysate may be used in combination with the aromatic amides. While the preferred polymer is a polyvinyl alcohol having a molecular weight between about 15,000 and 20,000, those having molecular weights from 5,000 to over 100,000 provide beneficial results.

The plating baths exemplified may, of course, be modified to substitute for the sodium salts other salts, e.g., potassium and lithium compounds, which behave similarly in the bath. Also zinc oxide rather than zinc cyanide may be used. Details for preparing and using the baths are, of course, well known to those skilled in the art.

The primary advantage of the brightening agents of this invention resides in the excellent quality of bright zinc plate obtained. In addition, the compositions of this invention are stable both in storage and in the plating bath during use and periods of non-use. Their rate of consumption is low, thus making them economically attractive. Of particular importance is the fact that a for-

[1] Trademark for a water-soluble polyvinyl alcohol having an average molecular weight of about 16,800.

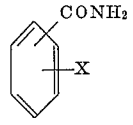
mulation containing an aromatic amide is usually equally effective both in still plating and in barrel plating operations.

A further advantage provided by the brightening agents of this invention is their superior "throwing" power. The combination of aromatic amide and organic polymer gives bright uniform coatings over a wide range of current densities, thus making it possible to coat intricately shaped articles. They are effective at low current densities where previously known compositions have failed to provide satisfactory coatings.

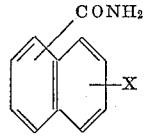
The bright zinc deposits provided by the present invention are also responsive to treatment with protective agents. Excellent results are obtained using a variety of available commercial products such as chromate conversion coating preparations.

What is claimed is:

1. An aqueous, alkaline, cyanide zinc electroplating bath containing zinc ions and as a brightening agent therefor from about 0.1 to 10 grams per liter of bath of a bath-soluble aromatic amide selected from the group consisting of



and



wherein X is —OH, —COOH or —SO_3H.

2. The bath of claim **1** wherein a bath-soluble organic polymer selected from the group consisting of polyvinyl alcohol, polyethyleneimine, glue, gums and protein substances is present in an amount from about 0.02 to 10 grams per liter.

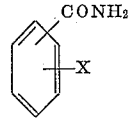
3. The bath of claim **2** wherein said organic polymer is a polyvinyl alcohol having a molecular weight from about 5,000 to 20,000.

4. The bath of claim **3** wherein the aromatic amide is isophthalamic acid.

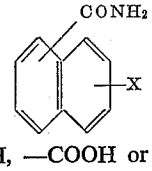
5. An aqueous, alkaline cyanide zinc electroplating bath containing zinc ions and from about 0.1 to 10 grams per liter of isophthalamic acid and from about 0.05 to 0.5 gram per liter of a bath-soluble polyvinyl alcohol having a molecular weight from about 5,000 to 20,000.

6. The bath of claim **5** wherein said polyvinyl alcohol has a molecular weight of about 16,800.

7. An additive for an aqueous, alkaline cyanide zinc electroplating bath consisting essentially of from about 1:1 to 50:1 parts by weight of a bath-soluble aromatic amide selected from the group consisting of



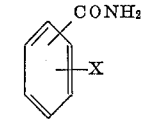
and



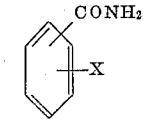
wherein X is —OH, —COOH or —SO_3H and a bath-soluble organic polymer selected from the group consisting of polyvinyl alcohol, polyethyleneimine, glue, gums and protein substances.

8. The composition of claim **7** wherein said aromatic amide is isophthalamic acid and said organic polymer is polyvinyl alcohol having a molecular weight of about 16,800.

9. In the process for electrodepositing zinc from an aqueous, alkaline, cyanide plating bath the improvement comprising having present in said bath from about 0.1 to 10 grams per liter of bath of a bath-soluble aromatic amide selected from the group consisting of



and

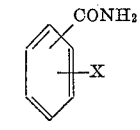


wherein X is —OH, —COOH or —SO_3H.

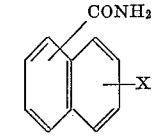
10. The process of claim **9** wherein a bath-soluble organic polymer selected from the group consisting of polyvinyl alcohol, polyethyleneimine, glue, gums and protein substances is added to said bath in an amount from about 0.02 to 10 grams per liter.

11. The process of claim **9** wherein said aromatic amide is isophthalamic acid.

12. In a process for electrodepositing zinc from an aqueous, alkaline, cyanide plating bath, the improvement comprising having present in said bath from about 0.5 to 10 grams per liter of a bath-soluble aromatic amide selected from the group consisting of



and



wherein X is —OH, —COOH or —SO_3H and from about 0.05 to 05 gram per liter of a bath-soluble organic polymer selected from the group consisting of polyvinyl alcohol, polyethyleneimine, glue, gums and protein substances.

13. In a process for electrodepositing zinc from an aqueous, alkaline cyanide plating bath, the improvement comprising adding to said bath a brightening composition consisting essentially of from about 1:1 to 50:1 parts by weight of isophthalamic acid and a bath-soluble polyvinyl alcohol having a molecular weight from about 5,000 to 20,000.

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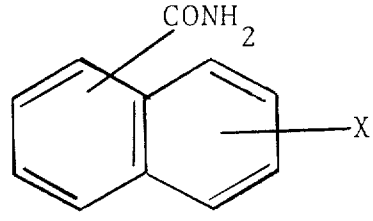
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,386,898 June 4, 1968

John D. Rushmere

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, lines 16 to 21, the formula should appear as shown below:



Signed and sealed this 21st day of October 1969.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents