

[54] **ACID ZINC GALVANIC BATH**

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[58] Field of Search..... 204/55 R, 432, 44, 114

[56] **References Cited**

UNITED STATES PATENTS

3,537,959 11/1970 Korpion et al. 204/55 R

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[57] **ABSTRACT**

A novel aqueous acid galvanic zinc plating bath contains luster formers, and as its active ingredients a soluble zinc salt and an amount of a polycondensation product of formaldehyde and naphthalene sulfonic acid effective to impart ductility and malleability to the zinc coating, but free from complexing agents so that said bath upon dilution and neutralization with alkali is capable of retaining not more than about 3 mg per liter of zinc ion, expressed as zinc hydroxide.

3 Claims, No Drawings

ACID ZINC GALVANIC BATH

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 162,272, filed July 13, 1971, now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to a novel acid galvanic bath for the electroplating of zinc which contains luster formers and an agent for promoting ductility and malleability of the zinc coating, but does not contain any complexing agent which would combine with the zinc, and interfere with its subsequent removal when the used bath is discharged for waste treatment.

With the increased incidence of stream pollution, the various industrial countries of the world have adopted and are adopting stringent limitations on the amounts of chemical and metallic compounds which may be discharged into rivers and other bodies of water in order to minimize the deleterious effects of such pollution upon the ecological environment. For example, in West Germany, the permissible limit for zinc ion is now set at 3 mg. per liter in the discharged waste.

A result of these new pollution control requirements has been that the art has sought a type of zinc plating bath which upon proper treatment would be capable of retaining only a very small zinc content, so that it could be safely discharged into a public waterway and at the same time meet governmental residue limits.

The zinc electrolytic plating baths of the prior art have not been capable of meeting the new standards. Thus, a typical prior art zinc plating bath of the acid type is that described in U.S. Pat. No. 3,537,959, in which there are incorporated as agents for brightening and increasing throwing power, primary amines or polyamines. These ingredients have, however, the drawback that if present, they form complexes with the zinc ions so that upon dilution and neutralization of the solution after use in plating, or recovered in rinsing the plated articles, so large an amount of zinc is retained in the liquor, that it cannot be discharged into public waterways such as rivers and streams.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a novel zinc electroplating bath of the acid type which may contain conventional luster formers and agents effective to impart ductility and malleability

to the deposited zinc coating, but which is free from complexing agents which would interfere with subsequent zinc removal when preparing the waste bath for discharge into public bodies or streams of water. The bath of the invention does, however, provide zinc deposits having a high polish, and exhibiting great durability and ductility.

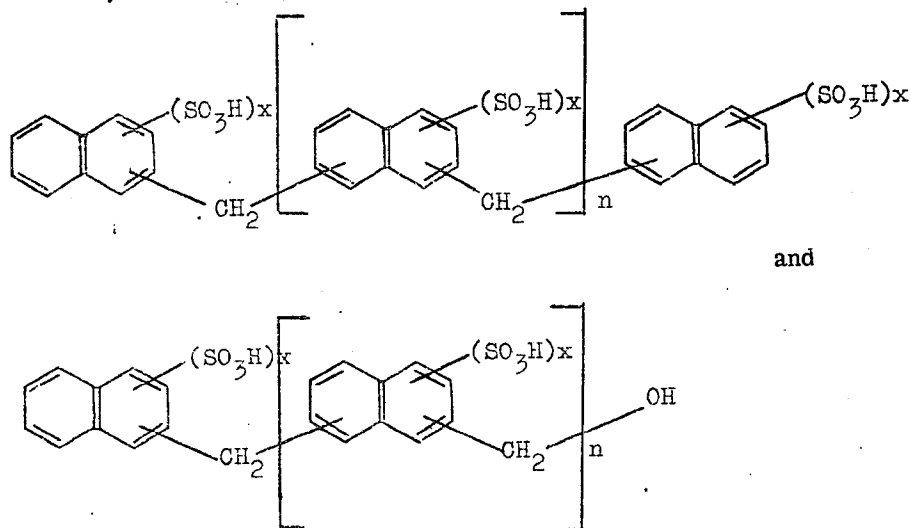
As distinguished from alkaline cyanide baths which involve extremely important detoxification measures, the acid zinc baths of the present invention possess greatly increased industrial importance. They possess the advantage that they do not contain any complex formers which would render the precipitation of zinc difficult or even impossible. In the absence of these complex formers, a simple neutralization with an alkali suffices to precipitate the zinc virtually quantitatively as the hydroxide.

German display documents DOS No. 1,521,029 suggest an acid galvanic bath to which an aromatic carbonyl compound, a nonionogenic surface-active polyoxyethylene compound, ammonium chloride, and complexing agents forming salts with the zinc salts present and soluble in the pH range of 2.5 to 5.5, are all added. Also, it is proposed in Belgian Pat. No. 737,280, to incorporate N-polyvinyl-pyrrolidone and certain ketones in zinc electrolytes in acid media. A disadvantage of the bright coats deposited from these baths, however, is their brittleness, which results in the formation of hair cracks in a layer thickness of about 20 μm or more. Upon deformation of the zinc-plated part, these cracks appear even in much small layer thicknesses, so that the corrosion resistance of the coats is greatly reduced.

In accordance with the present invention, it has been found, surprisingly and unexpectedly, that in an acid plating bath, these disadvantages of prior art baths are eliminated by including in the bath only conventional luster formers, and, as an agent for promoting the formation of ductile and malleable zinc coatings, a water-soluble condensation product of formaldehyde with a naphthalene sulfonic acid. All complexing agents for zinc are omitted.

The polycondensation products of formaldehyde and naphthalene sulfonic acids are known compounds, and their production is described, for example, in Houben-Weyl, "Methoden der organischen Chemie," Vol. XIV/2, at page 316.

The formaldehyde-naphthalene sulfonic acid condensation products employed in the practice of the present invention have the general formula:



wherein X is an integer from 1 to 3, and n is an integer from 1 to 14, preferably from 2 to 6.

The general method of preparation of these polycondensation products is to react a 30% formaldehyde solution with a naphthalene sulfonic acid produced from 98.5 g concentrated sulfuric acid and naphthalene, at a temperature of 60° to 100°C for a period of time until the formaldehyde odor has disappeared. Similar products can be obtained by sulfonation of a naphthalene-formaldehyde resin. The condensation products contain two or more naphthalene sulfonic acids, linked by methylene bridges which can have from 1 to 3 sulfonic groups.

The amounts in which these polycondensation products are added to the zinc plating electrolyte in order to obtain a marked improvement in the properties of the resulting zinc coat, may vary within wide limits from about 0.2 to about 25 g per liter, preferably about 2.0 g per 15 g per liter.

DETAILED DESCRIPTION OF THE INVENTION

The zinc plating bath according to the invention contains the following principal ingredients, in the ranges indicated:

a. a soluble zinc salt, such as zinc chloride, sulfate, acetate, or fluoborate. The zinc chloride is present in a concentration between about 30 and about 200 g per liter, the other zinc salts in equivalent amounts.

b. an ammonium salt, such as ammonium chloride or sulfate, which acts to improve conductivity. Surprisingly, however, the ammonium salt does not interfere with the subsequent substantially complete removal of zinc ion by alkaline precipitation prior to waste discharge, even through the ammonium salts might be regarded as complex formers. In this respect, they differ in activity from the amines used in the prior art baths as specific complex formers, which do interfere with zinc removal. This difference in mode of action is demonstrated by the comparative test data set forth below.

c. a luster former or formers, preferably polymeric substances which may contain hydroxyl groups, together with certain carbonyl compounds, such as aldehydes or ketones. As examples of polymeric compounds containing hydroxyl groups there are mentioned polyethylene glycols, polypropylene glycols, alkylaryl polyglycol ethers, fatty alcohol polyglycol ethers, and polyvinyl pyrrolidones, and amphoteric oxyethylation products. As examples of carbonyl compounds, there are mentioned acetophenone, benzalacetone, benzoylacetone, 3-acetyl cumarine, 3-acetylpyridine, and m-oxybenzaldehyde. As further additives, there may be included other luster formers, such as thio compounds or certain wetting agents. Benzoylacetone nitrile is another example of a carbonyl compound of different structure.

d. other additives, such as inorganic or organic acids, for example boric acid, aliphatic carboxylic acids such as acetic acid, or aromatic carboxylic acids, such as benzoic acid or salicylic acid.

The pH range of the zinc plating bath of the invention is between about 3.0 and about 6.0, preferably from 4.5 to 5.5.

The bath temperature employed will ordinarily range from about 15° to 45°C, preferably between about 20° and about 30°C.

The current density, at the cathode, is between about 0.1 and about 10.0 amperes per sq. dm., preferably

about 3 to 6 amperes per sq. dm.

The electrolyte may be agitated during application by air injection or by movement of the cathode bar.

In the luster galvanization of mass-produced parts in a drum apparatus, the current density is, on the average, about 0.2 to about 1.2 amperes per sq. dm., as related to the entire surface of the article arranged in the drum.

When the plating is completed, the zinc-coated articles are rinsed in flowing water prior to being dried, in order to remove residual electrolyte adhering to their surfaces. The rinse waters are collected and subjected to neutralization step by the addition of sodium hydroxide solution to attain a pH value of between about 8.5 and 9.0, which pH range is necessary in order to precipitate the zinc as zinc hydroxide substantially quantitatively.

In general, it is found that for each square meter of article surface about 0.1 liter of electrolyte is carried into the rinse water. Thus, with a zinc bath of approximately 10,000 liter content, with a throughput of 30 sq. meters per hour of article surface, the amount of electrolyte transferred into the rinse water is equivalent to about 3 liters of zinc electrolyte, for which an addition of 0.3 kg sodium hydroxide per hour is necessary to attain a pH value of 9.0 thereby precipitating all the zinc as hydroxide.

This ability of the baths of the invention to release zinc by precipitation as zinc hydroxide in the rinse water, constitutes one of the most important advantages of the present invention in connection with the industrial applications of acid zinc plating baths. In order to attain this goal, an acid zinc bath must contain either no complex former, or so little thereof as not to result in formation of any complex formation, which in the course of the usual dilution of the rinse water in a ration of about 500:1 with water, the zinc is nevertheless fully removed as zinc hydroxide by precipitation in the pH range of 8.5 to 9.0.

The following comparative tests serve to illustrate the unique results obtainable by the use of the bath of the present invention as compared with a conventional zinc plating bath, such as that disclosed in U.S. Pat. No. 3,537,959 alluded to above.

A bath was prepared corresponding to Example 2 below, having the composition:

	g/l
Zinc chloride	100.0
Ammonium chloride	150.0
Benzoic acid (potassium salt)	4.0
Amphoteric oxyethylation product	5.0
Benzalacetone	0.4
Formaldehyde-naphthalene sulfonic acid condensation product	10.0

A comparison bath was prepared according to Example 1 of U.S. Pat. No. 3,537,959, having the composition:

Bath B	g/l
Zinc sulfate	300.0
Ammonium chloride	20.0
Diethylenetriamine	40.0
Formaldehyde-naphthalene sulfonic acid condensation product	2.0

In order to determine the residual content of zinc ion upon dilution with water, followed by precipitation with sodium hydroxide at pH 9.0, simulated rinse waters were produced by addition of various ratios of water.

In the case of Bath A of the present invention, even at a dilution of only 200:1, substantially all the zinc was removed down to a residual content of zinc ion of 5 mg per liter. With further dilution at 500:1, the limit of 3 mg zinc ion per liter was achieved, and thereby the requirements of water discharge limits of pollution control regulations. The carboxylic acids and carbonyl compounds present in the bath do not act as complex formers and do not affect zinc removal.

In the case of Bath B of the prior art, the diethylene-triamine present is such a strong complex former that upon a dilution of 500:1 there still remains in the solution after neutralization with sodium hydroxide to pH 9.0, 50 mg per liter of zinc ion in the form of an amine complex, which is about 13 times the permissible limit. Even upon dilution in a ratio of 1,000:1, the solution still contains 25 mg per liter of zinc ion, and hence is unsuited for discharge into public streams.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples serve to illustrate the practice of the present invention, but are not to be regarded as limiting:

EXAMPLE 1

A zinc plating electrolyte was prepared and applied under the following conditions, having the composition:

Zinc chloride	125.0 g/l
Ammonium chloride	150.0
Boric acid	20.0
Polyethylene glycol	2.0
Acetophenone	0.3
Benzoylacetonitrile	0.01
pH value	5.0
Temperature	23°C
Mean cathode current density	4.0 A/dm ²

Bright, but very brittle zinc coats were deposited which formed numerous hair cracks on deformation. Because of its brittleness, the coat peels off on the edges of the parts being plated. However, adding to the electrolyte having the above composition, 15.0 g/l of a formaldehyde-naphthalene sulfonic acid condensation product of the above formula (a), wherein *n* is 4, the galvanized parts can be bent without formation of any cracks or without any peeling off of the coat from the substrate. At the same time, the malleability of steel plate strips, plated with a zinc coat of 12 μm (μm), increases from 14.8 to 19.6%, as determined by the method of Cashmore and Fellows.

Upon rinsing of the articles to a dilution of 500:1, followed by neutralization to pH 9.0 with sodium hydroxide, the zinc hydroxide precipitated to such an extent that residual zinc ion in the diluted electrolyte was reduced to less than 3.0 mg/liter, the permissible limit.

EXAMPLE 2

Galvanization of Mass-Produced Parts

A zinc plating electrolyte was prepared having the composition indicated below, and applied under the indicated conditions:

Zinc chloride	100.0 g/l
Ammonium chloride	150.0
Benzoic acid (potassium salt)	4.0
Amphoteric oxyethylation product	5.0
Benzal acetone	0.4
pH value	5.0
Temperature	25°C
Current density	0.4 A/dm ²
Speed of drum	6 rpm.

In mass-produced parts galvanized in this electrolyte, the deposit is partly cast off from the corners and edges of the object during galvanization due to its brittleness. However, if there is added to the electrolyte 100.0 g/liter of formaldehyde-naphthalene sulfonic acid condensation product of the above formula (b) wherein *n* is 2, there is obtained a uniformly adherent coating on the substrate.

What is claimed is:

1. An aqueous acid galvanic zinc electroplating bath containing (a) a water-soluble zinc salt in a concentration between about 30 and about 200 g per liter expressed as zinc chloride, (b) a water-soluble ammonium salt in a concentration sufficient to improve the bath conductivity but insufficient to interfere with subsequent zinc ion removal by dilution and alkaline precipitation, (c) a water-soluble condensation product of formaldehyde and at least two naphthalene sulfonic acids linked by methylene bridges and which contain from 1 to 3 sulfonic acid groups in an amount effective to impart ductility and malleability to the zinc coating produced from said bath, and (d) a luster former selected from the group consisting of polymeric organic glycols and glycol ethers, and organic carbonyl compounds in an amount effective to impart luster to the zinc coating produced from said bath, said bath containing no complexing agent for zinc and being capable upon dilution with water in a ratio of about 500:1 and neutralization with alkali of precipitating the zinc ion present to such an extent such that not more than about 3 mg per liter of zinc ion is retained in said bath.

2. The electroplating bath of claim 1 in which the pH range is between about 3 and about 6.

3. The electroplating bath of claim 1 in which the amount of said polycondensation product (c) is between about 0.2 and about 25 grams per liter.

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