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ELECTRODEPOSITION BATH FOR BRIGHT ZINC

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This invention relates to electroplating baths for bright plating zinc and, more particularly, to aqueous acid zinc sulfate plating baths containing addition agents which have a brightening action.

There are two principal types of zinc baths now in use for producing so-called "bright" zinc plate. One is an acidic zinc salt bath and the other is a cyanide zinc bath. Neither imparts to the electrodeposited zinc the degree of brightness which the bath herein described is capable of doing. Generally speaking, acidic zinc baths have a low throwing power and tend to produce crystalline deposits. The cyanide zinc bath is a relatively hazardous bath to operate, because of the danger of cyanide poisoning.

A primary object of this invention is to provide an electroplating bath for electroplating bright zinc.

Another object of this invention is to provide a method for producing lustrous, ductile zinc coatings which retard corrosion and protect the surface under the plated metal.

Still another object of this invention is to provide a bright, durable zinc coating which is pleasing to the eye.

Other and further important objects and advantages of this invention will become apparent from the following description and appended claims.

It has now been found that sulfonated heterocyclic nitrogen compounds can be used effectively as brighteners in aqueous acidic zinc plating baths.

Substances which have been found to be effective as addition agents are the sulfonated products of compounds selected from the group consisting of pyridine, polynuclear compounds containing a pyridine ring, and their substitution products. Specific examples of heterocyclic nitrogen compounds which may be sulfonated and employed as addition agents are quinoline, isoquinoline, quinaldine, benzalquinaldine, betanaphthoquinoline, beta - naphthoquinoline, 8 - phenylquinaldine, p - dimethylaminobenzalquinaldine, 2 - chloro - 4 - methyl - quinoline, 2 - hydroxy - 4 - methyl - quinoline, 2,4 - dimethylquinoline, 2 - styrylpyridine, 2,6 - distyrylpyridine, 2,4,6 - tristyrylpyridine, 2,4 - distyrylquinoline, quinophthalone, and quinonaphthalone. All of the preceding compounds have been found to give sulfonation products which are effective in small amounts in producing bright plates from an acidic zinc sulfate bath.

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It will be obvious to those skilled in the art that numerous other sulfonated heterocyclic nitrogen compounds selected from the group consisting of pyridine, polynuclear compounds containing a pyridine ring and substitution products of pyridine and of such polynuclear compounds may be employed in the practice of this invention. It is further evident that these addition agents may be employed singly or in combination.

A preferred addition agent is sulfonated 8-phenylquinaldine. Incorporation of a small amount of this material in an aqueous acidic zinc sulfate bath containing a buffering agent, such as boric acid, makes it possible to obtain bright and ductile zinc plates by electrodeposition.

In the operation of the plating bath containing brighteners, care must be taken to plate over clean metal surfaces since otherwise coatings will be patchy. Any conventional method, known to the art, may be used to obtain clean metallic surfaces.

The composition of one type of bright zinc plating is indicated below:

Approximate limits

Material	Lower	Upper	Preferred
ZnSO ₄ · 7H ₂ O.....grams per liter..	300	800	450
H ₃ BO ₃grams per liter..	15	45	30
8-phenylquinaldine (Sulfonation mixture of Example 1).....grams per liter..	0.02	5	0.04

Other buffering agents such as acetates or citrates may be used in place of the boric acid, although the latter is preferred. Any water soluble acetate or citrate of a non-depositing metal can be used satisfactorily. Normally, the sodium or potassium salts would be used.

The maintenance of the pH within a relatively narrow range is important with this preferred bath. This is accomplished by the use of a buffer and the addition of sulfuric acid, is necessary. The electrodeposited zinc is not ductile if the pH of the bath is too low, and the plate is not bright if the pH of the bath is too high. The approximate lower pH limit for the bath is 3.3, and the approximate upper pH limit for the bath is 4.3. The optimum pH values for different specific addition agents will vary. For an 8-phenyl quinaldine sulfonation mixture, the optimum pH range will be between 3.9 and 4.3, with 4.1 as the preferred pH value, whereas for the benzal

quinaldine sulfonation mixture the optimum pH value is about 3.3.

The temperature of the bath may vary from about 85° F. to 115° F. but the preferred temperature is 95° F. The current density may vary from 150 to 400 amperes per square foot, or, preferably, from 200 to 300 amperes per square foot. The preferred bath has a zinc sulfate content high enough to allow plating at high cathode current densities without fear of burning of the deposits. The boric acid concentration is high enough to provide a good control of the pH of the bath, yet not so high as to cause difficulty due to its limited solubility.

The recommended tank-lining material for a commercial installation is rubber or synthetic rubber using zinc bars as anode contacts. It is not advisable to use lead-lined tanks, for lead reduces noticeably the ductility of the plate. Some agitation of the work, or cathode, such as imparting thereto a simple oscillatory motion, is desirable to prevent pitting.

The amount of brightener added to the electroplating bath will vary with the nature of the heterocyclic nitrogen compound used as the starting material and with the conditions of sulfonation. In general, minor amounts ranging from 0.01 to 1.0 gram of sulfonation mixture per liter of plating bath are most satisfactory, but higher concentrations may be used under certain conditions.

The use of sulfonated 8-phenylquinaldine as a brightener, within such range, and preferably at a concentration of about 0.02 to 0.04 gram of sulfonation mixture per liter of bath, produces ductile plates with a high degree of brightness. Concentrations of sulfonated 8-phenylquinaldine as great as 5 grams of sulfonation mixture per liter of bath gave brilliant deposits if a second addition agent (surface-active agent) such as Solvadine NC (which is believed to be a sodium salt of the sulfonic acid of a petroleum hydrocarbon), or an alkylated aryl sulfonate, were used. The preferred range for consistently excellent results, however, is that previously stated. A bath employing the low concentration of brightener has been operated for 150 ampere-hours per liter with only occasional additions of brightener. Filtration was employed as required.

Lead, as stated before, has been found to reduce noticeably the ductility of the plate, although it enhances the brightness. In the case of accidental contamination of the electroplating bath with lead, it has been found that purification can be accomplished by agitation with about 1.5 grams of zinc dust per liter of bath at room temperature for one hour, followed by filtration.

Sulfonation of the heterocyclic nitrogen compounds listed above may be accomplished by conventional procedures such as by treatment with concentrated or fuming sulfuric acid or chlorosulfonic acid. The strength of acid used, the amount of acid, and the time and temperature of sulfonation will vary with the ease of sulfonation of the compound used and with the degree of sulfonation desired. Ordinarily the sulfonic acids of the heterocyclic nitrogen compounds of this invention are not isolated. The sulfonation mixture containing excess sulfuric acid may be added directly to the plating bath, preferably after dilution with water; or the diluted mixture may be neutralized with zinc carbonate or zinc oxide and added to the bath as the zinc salt of the sulfonated products. The sulfonated heterocyclic nitrogen compounds employed are of in-

definite composition with respect to the number and position of the sulfonic acid groups. Generally, mixtures of mono-sulfonic acids or mixtures of mono- and di-sulfonic acids are obtained by the sulfonation procedure, and these mixtures are suitable for addition, as such or after dilution and/or neutralization, to the plating bath.

The following examples serve to illustrate the preparation of the sulfonated heterocyclic nitrogen compounds of this invention.

Example 1.—Sulfonated 8-phenylquinaldine

Ten grams of purified 8-phenylquinaldine, prepared as described in U. S. Patent No. 2,211,662, issued to Lucas P. Kyrides August 13, 1940, entitled "Quinaldine Dye Intermediates and Quinophthalone Dyes Thereof," were added in small portions to 90 grams of fuming sulfuric acid (15% sulfur trioxide content) in a small flask provided with a stirrer and a thermometer. The addition rate was adjusted so that the temperature did not exceed 50° C. (122° F.). Subsequently the mixture was heated gradually to 125° C. (257° F.) and maintained at this temperature for 20 minutes. A test showed that the product was completely soluble in aqueous sodium carbonate, whereas the starting material was insoluble. This concentrated sulfonation mixture was added to the plating bath in the amounts indicated below. In order to increase the storage life of the addition agent it was found expedient to neutralize the acidic aqueous solution with zinc oxide or zinc carbonate. In any case, the amounts of addition agent added to the plating bath are expressed in this specification in terms of the concentrated sulfonation mixture resulting directly from the sulfonation procedure.

Example 2.—Sulfonated isoquinoline

Fifteen grams of isoquinoline were added dropwise during 20 minutes to 66 grams of fuming sulfuric acid (60% sulfur trioxide content) in a three-necked flask equipped with a mechanical stirrer, dropping funnel and thermometer. The flask was cooled externally during the addition, to keep the temperature below 80° C. (176° F.). Subsequently, the mixture was heated for two hours at 90–95° C. (194–203° F.) and allowed to cool to room temperature, at which time 5 cc. of water was cautiously added to react with excess sulfur trioxide. This sulfonation mixture was added in small amounts to a zinc plating bath as described elsewhere in this specification.

Example 3.—Sulfonated benzalquinaldine

Five grams of benzalquinaldine were added in small portions over a period of 15 minutes to 45 grams of fuming sulfuric acid (15% sulfur trioxide content) with agitation. The resulting mixture was heated for 20 minutes at 100° C. (212° F.). Before adding to the plating bath, this material was diluted with water, neutralized with sodium carbonate, and made up to a volume such that one cubic centimeter of the solution was equivalent to 0.05 gram of sulfonation mixture.

Examples of the preparation of typical baths as defined by this invention are given below:

Example 4

ZnO	g./l.	124
H ₂ SO ₄ (sp. g. 1.86), C. P.	cc./l.	84.3
H ₃ BO ₃ , C. P.	g./l.	30

The sulfuric acid was added slowly to approximately 700 cc. of distilled water, then the zinc oxide was added in small batches to the sulfuric

acid solution, which was agitated by a motor stirrer. After the zinc oxide had reacted with the sulfuric acid, the boric acid was added and stirring was continued until it had all dissolved. To the bath as prepared above, the brightener consisting of the 8-phenylquinaldine sulfonation mixture (prepared as described in Example 1) was added in the concentration of 0.04 g./l. The bath was operated at a temperature of about 95° F., the cathode current density was about 290 amperes per square foot, and the pH of the bath was 4.1. Under these conditions, bright and ductile plates of zinc were obtained.

Example 5

The bath in this example was made up as described in Example 4 to the point of adding the brightener. In this example, 0.6 g./l. of the isoquinoline sulfonation mixture (prepared as described in Example 2) was added to the bath. The bath was operated at a temperature of about 95° F., and the pH of the bath was 4.05. Under these conditions, the zinc plate obtained possessed a high degree of brightness.

Example 6

The bath in this example was made up as described in Example 4 to the point of adding the brightener. In this example, 0.15 g./l. of the benzalquinaldine sulfonation mixture, or 3 cc. of the diluted sulfonation mixture (prepared as described in Example 3), was added to the bath. The bath was operated at a temperature of about 95° F., and the pH of the bath was 3.3. Under these conditions, the zinc plate obtained possessed a high degree of brightness.

In a similar way sulfonation mixtures of any other compound of the group consisting of pyridine, poly-nuclear compounds containing a pyridine ring and their substitution products may be prepared and such sulfonation mixtures used within the ranges of concentration specified herein to produce baths from which bright zinc electro-deposits can be obtained. In general, any basic metal or alloy capable of being zinc plated from any conventional acid zinc bath, such as ferrous metals and alloys, brass and copper, can be bright zinc plated by the method and from the baths herein described.

It is apparent from the above-detailed description that the present invention comprises an aqueous acid zinc sulfate electroplating bath to which has been added a sulfonated heterocyclic nitrogen compound. By practicing this invention, one obtains electrodeposited zinc which is bright and lustrous and provides a durable coating that retards corrosion of the basic metal or alloy. Moreover, the baths are non-hazardous and economical to operate.

We claim as our invention:

1. An electrodeposition bath comprising an aqueous acid zinc sulfate solution containing a buffering agent and sulfonated 8-phenylquinaldine in a sufficient amount to obtain a bright zinc plate, said bath having a pH between 3.3 and 4.3.
2. An electrodeposition bath for the production of bright zinc plate, said bath comprising an aqueous acidic zinc sulfate solution containing boric acid and a mixture of sulfonates of 8-phenylquinaldine in an amount ranging from about 0.01 to 5 grams per liter.
3. An aqueous acid electrodeposition bath for the production of bright zinc plate, said bath containing between 300 and 800 grams per liter of zinc sulfate heptahydrate, between 15 and 45 grams per liter of boric acid and between 0.01 and 5 grams per liter of a mixture of sulfonates of 8-phenylquinaldine.
4. An aqueous acid electrodeposition bath for the production of bright zinc plate, said bath containing between 300 and 800 grams per liter of zinc sulfate heptahydrate, between 15 and 45 grams per liter of boric acid, and between 0.02 and 5 grams per liter of a mixture of sulfonates of 8-phenylquinaldine, said bath having a pH between 3.3 and 4.3.
5. An aqueous electrodeposition bath operative for the production of bright zinc plate at current densities of 150 to 400 amperes per square foot, at a temperature of 85° F. to 115° F. and at a pH between 3.9 and 4.3, said bath containing between 300 and 800 grams per liter of zinc sulfate heptahydrate, between 15 and 45 grams per liter of boric acid and between 0.02 and 5 grams per liter of a mixture of sulfonates of 8-phenylquinaldine.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
733,028	Goldberg	July 7, 1903
905,837	Broadwell	Dec. 8, 1908
2,370,986	Nachtman	Mar. 6, 1945
2,407,489	Gray	Sept. 10, 1946

OTHER REFERENCES

- Blum and Hogaboom, Principles of Electroplating and Electroforming, 1930, page 321.
Metal Industry, November 29, 1940, pages 433, 436.