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ACID ZINC ELECTROPLATING AND ELECTROLYTE THEREFOR

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This invention relates to an acid zinc electrolyte and to a method of electrodepositing zinc from acid zinc plating baths.

This application is a continuation-in-part of my application Ser. No. 441,694 filed May 4, 1942, which matured into U. S. Patent 2,443,599, June 22, 1948.

One of the objects of the present invention is to provide a new and improved method of electrodepositing zinc from an acid zinc electroplating bath.

Another object is to provide a method of producing bright zinc deposits from an acid zinc plating bath.

Still another object is to provide a method of producing image bright zinc deposits from an acid zinc plating bath at ordinary temperatures (e. g., 65 degrees F. to 95 degrees F.).

A further object of the invention is to provide a new and improved method of producing zinc deposits from an acid plating bath at high current densities without burning.

An additional object of the invention is to provide a new and improved method of producing brilliant zinc deposits directly out of an acid zinc plating bath.

Another object is to provide a simple type of acid zinc electrolyte characterized by excellent operating efficiency at higher current densities without burning the plated article.

A further object is to provide a new and improved electrolyte for producing image bright zinc deposits directly from an acid zinc plating bath. Other objects will appear hereinafter.

These objects are accomplished in accordance with this invention by incorporating with an acid zinc electroplating bath certain organic addition agents. According to one embodiment of the invention excellent results are obtained in the electrodeposition of the zinc to produce image bright zinc plates directly from an acid bath without the necessity for any subsequent chemical treatment. By another embodiment of the invention gray zinc deposits are obtained with better operating efficiency out of an acid bath and with less burning. Still another embodiment of the invention relates to the provision of simpler forms of improved electrolytes adapted for the purposes of the invention.

The primary organic addition agent which is employed for the purpose of the invention is an aldonic acid, preferably gluconic acid or a gluconate that is soluble in the acid zinc bath. The more or less water insoluble aldonates, e. g., calcium gluconate, also improve the plating characteristics of the acid zinc bath. The addition agent may be added in the form of an aqueous solution of the aldonic acid or as a salt thereof, the cation of which does not adversely affect the bath. The aldonic acid addition agent can be added in the form of a zinc aldonate previously prepared by the reaction of zinc oxide with an aldonic acid. The aldonic acid can be obtained by the oxidation of an aldose, or in any other suitable manner. If gluconic acid is used as such it is preferably employed in the form of an aqueous solution having a concentration of about 50% of gluconic acid. Other examples of acids and salts thereof which may be used are galactonic, arabonic, xylonic and mannonic. The aldonic acid, when used in sufficient amount, has a pronounced antiburn effect and produces improved plating efficiency.

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A second addition agent, which is essential for the production of bright plates in the practice of the invention, is an alkylated naphthalene sulfonic acid which may be added in the form of the free sulfonic acid or a soluble salt thereof. The preferred addition agent of this class is isopropyl naphthalene sulfonic acid sodium salt which is available in a commercial form of 95% purity. Neither the aldonic acid alone nor the alkylated naphthalene sulfonic acid alone will produce a bright zinc plate out of the acid bath. When these two addition agents are employed together, however, a specific and surprising result is obtained.

Excellent results have been obtained at room temperatures (75 degrees F.), and equally good results have been obtained at temperatures of 65 degrees F. to 95 degrees F. At temperatures above 100 degrees F. maintenance of a low lead content (below 5 milligrams of dissolved lead per liter) and agitation are important factors in obtaining a bright plate directly out of the bath, as described and claimed in the copending application of Chester, Main and Hansen, Ser. No. 34,129, filed of even date herewith. In commercial operations the bath becomes heated normally by the current which is passing through it, especially when high current densities are used. It is not ordinarily desirable to operate at temperatures above 160 degrees F. because of the operating hazards to the operators. This is especially true where the object being plated is a continuous strip which might break and have to be removed from the bath. The same difficulty arises in case individual articles are being plated, as in piece plating, and one or more of these drops from its rack into the bath. As will be apparent

if the bath were heated to a very high temperature it might be necessary to cool it before the strip could be repaired or the article could be removed from the bath, as the case might be.

Very desirable plates can be obtained in accordance with the invention over a wide pH range of 1 to 5.5. The optimum pH range for bright plates is 2.5 to 4.0.

The invention can be practiced by adding one or more of the addition agents to any of the ordinary acid zinc electrolytes which may or may not contain other addition agents. Such zinc electrolytes and their method of preparation are generally well known.

Glucose in combination with the alkylated naphthalene sulfonic acid added in accordance with this invention will not produce bright zinc plates. Glucose or other aldose, therefore, is in no sense the equivalent of gluconic or another aldonic acid for the purpose of the present invention.

In the past it has been customary to prepare acid zinc electrolytes containing salts other than zinc salts, buffers, glucose or other reducing sugars and various types of organic colloids which have been alleged to have a beneficial effect in the bath. For the purpose of the present invention, however, it has been found that excellent results can be obtained by making the necessary additions to a simple electrolyte consisting of zinc sulfate and water. The zinc content of the bath for the purpose of this invention may vary rather widely, but in continuous plating it is preferably within the range of 50 to 150 grams of zinc per liter. In piece plating where speed of operation is not necessarily an important factor it is possible to use a bath having less than 50 grams per liter of zinc. The preferred range of zinc content in the electrolyte is 50 to 100 grams of zinc per liter of bath. Although a zinc content above 150 grams of zinc per liter may be used, it is not essential for the purpose of the invention and is undesirable where current densities in excess of about 100 amperes per square foot are employed.

The invention may be employed over a wide range of current densities. In continuous plating, in accordance with the invention, it is preferable to operate at current densities within the range of 100 to 250 amperes per square foot. Hull cell plates have been made, however, with electrolytes prepared in accordance with the invention showing the antiburn effects of gluconic acid alone and image bright surfaces with gluconic acid and an alkylated naphthalene sulfonic acid over a current density range from 2 to 60 amperes per square foot. There appears to be no particular limit on the current densities which may be employed, except as they are limited by the equipment used and the particular article plated. Because of the fact that high current densities may be used in the practice of the process, correspondingly high rates of zinc deposition may be obtained with resultant high production schedules.

Zinc plates may be obtained in accordance with the invention in a varying range of thickness of deposit. The preferred range of thickness in continuous plating of sheets or strips is within the range of 0.000025 to 0.0005. On the other hand, in the plating of wire it may be desirable to deposit much greater amounts of zinc, and this has been done in the practice of the invention. Thus, plates on wire were obtained in thicknesses from 0.002 inch to 0.004 inch (1.2 ounces to 2.5 ounces per square foot). It will be understood that where ductility is a factor there may be limits of thickness beyond which a deposit will tend to chip or crack. Such limits can readily be determined in any particular case by routine experiments. At the lower operating temperatures, i. e., below 100 degrees F., and with both types of the aforesaid addition agents bright deposits are obtained without agitation. In most continuous plating processes sufficient agitation is inherently present: If the amount of agitation is sufficient so that the desired brilliance is obtained without streaking, the rate of agitation can be increased while still maintaining the brilliance of the zinc deposit.

The invention will be further illustrated by the following examples in which the quantities are stated in parts by weight unless otherwise indicated.

Example I

An electrolyte was prepared by mixing the following ingredients:

450 grams zinc sulfate.
30 grams sodium acetate.
4 cc. of a 25% solution in water of Aerosol OS (a product of American Cyanamid Company containing 95% isopropyl naphthalene sulfonic acid sodium salt and 5% inerts).
32 cc. of 50% gluconic acid in water.
Water sufficient to make a liter of solution.

The bath was purified by electrolyzing it as described in Transactions of Electrochemical Society, vol. 80 (1941), pages 391 and 392. The pH of this electrolyte was maintained within the range of 2.5 to 4.0.

This electrolyte produced image bright deposits when electrolyzed at normal current densities common to the art, such as 25 to 300 amperes per square foot.

Image bright deposits were obtained out of this bath at ordinary temperatures of 75 degrees F. without agitation.

Example II

To a zinc sulfate bath containing 1920 grams of zinc sulfate and 8000 cc. of water there was then added varying amounts of zinc gluconate, these amounts being respectively 40 grams, 120 grams, 200 grams, 480 grams and 800 grams. By a series of experiments it was determined that the optimum pH was around 2.5 to 3.5. Hull cells were made from these baths at a current density of 1 ampere per square foot for 10 minutes at 74 degrees F. The Hull cell plates showed that the addition of the zinc gluconate had a pronounced antiburn effect above 15 grams per liter especially in the highest current density range of the Hull cell tests, i. e., above about 50 amperes per square foot.

To the previously described purified zinc sulfate bath containing 1920 grams of zinc sulfate dissolved in water to produce eight liters of solution there was then added 5, 15, 25, 40, 65 and 80 cc. per gallon of a 25% by weight solution of isopropyl naphthalene sulfonic acid sodium salt. Hull cell plates were made with each of these baths in a manner similar to that previously described and again it was observed that image brightness was not produced. An effect on the grain structure of the deposit was noted above 15 cc. per gallon, apparently due to a decrease in crystal size.

Two acid zinc plating baths were then prepared by (1) adding 1920 grams of zinc sulfate

and 320 grams of zinc gluconate to 8000 cc. of water, and (2) adding 480 grams of zinc gluconate to the same quantities of zinc sulfate and water, and adjusting the pH to 2.47. These baths were electrolyzed 17 hours at 1 ampere per square foot for purification. To these baths there was then added varying amounts of isopropryl naphthalene sulfonic acid sodium salt, namely, 5 cc. per gallon, 15 cc. gallon, 25 cc. per gallon, 40 cc. per gallon, 65 cc. per gallon and 80 cc. per gallon of a 25% by weight solution of 95% isopropyl naphthalene sulfonic acid sodium salt. The Hull cell plates made from these baths at 74 degrees F. all showed image brightness in some areas and hence indicated that this image brightness was due to the combined effect of the gluconate and the isopropyl naphthalene sulfonic acid sodium salt. All of these Hull cell plates showed brightness in the lowest current density range. The optimum effect over the widest range of current densities was obtained with 25 cc. per gallon of the isopropyl naphthalene sodium sulfonate solution in the second bath which contained 60 grams per liter of the zinc gluconate.

Example III

An acid zinc electroplating bath was prepared by dissolving zinc sulfate in water in proportions such that the quantity of zinc in soluble form was within the range of 50 to 150 grams per liter, then adding to this electrolyte 30 cc. per gallon of a composition prepared by mixing together:

(a) 80 cc. of 20% Aerosol OS (made by dissolving 125 grams of Aerosol OS in 500 cc. of water) and 3.8 grams of cadmium sulfate made up to a gallon with water; and
(b) 20 cc. of 50% gluconic acid and 1 cc. of ammonium bisulfite made up to a gallon with water.

This bath produced bright zinc plates at temperatures of 75 degrees F. to 95 degrees F.

Example IV

In the bath described in Examples I and III lactic acid in chemically equivalent proportions was used instead of the gluconic acid or gluconate. Good results were obtained with this bath in piece plating at a temperature of 90 degrees F. and 120 amperes per square foot. This bath was not so sensitive to impurities as the gluconic acid bath but it did not produce a bright plate directly out of the bath even with the Aerosol OS present. A bright plate was produced, however, by dipping this plated product into a second bath consisting of ½% of nitric acid in water.

The current used in the various tests described in the examples was direct current. It will be understood that the invention can be employed with other types of current and abnormal wave forms, including pulsating direct current such as may be derived by superimposing alternating current on direct current or by the use of various types of rectifier arrangements. For example, a ratio of 5 volts A. C. to 8.4 volts D. C. has been used satisfactorily. Where a superimposed current is employed the optimum results can ordinarily be obtained with less agitation.

Although the invention has been specifically described with respect to isopropyl naphthalene sulfonic acid sodium salt, it will be understood that other water soluble alkylated naphthalene sulfonic acids and salts thereof can be employed in the practice of the invention, including the butyl, isobutyl, amyl and isoamyl derivatives and the ammonium, potassium and other water soluble alkali metal and alkaline earth metal salts of the various alkylated naphthalene sulfonic acids. Inorganic salts such as are sometimes present in the commercially available alkylated naphthalene sulfonic acid salts have no adverse effect on the results. Thus, the isopropyl naphthalene sulfonic acid sodium salt is commercially available in a form which is 95% pure and contains 5% inorganic salts. The optimum results have been obtained with about 1.5 to 2.5 grams of the alkylated naphthalene sulfonic acid derivative per liter of electrolyte. These alkylated naphthalene sulfonic acid derivatives also lower the surface tension of the resultant electrolyte, and this can be used as a measure of the quantity of the alkylated naphthalene sulfonic acid derivative which is to be added to the solution. Thus, in a particular test the surface tension was 30 dynes per square centimeter. It does not appear, however, that the surface tension in itself is a factor in producing the results because numerous other materials which have an effect in lowering the surface tension have no effect whatsoever in producing an image bright plate.

The brightness of the coating may be varied by controlling the conditions of plating in the manner previously described. The thickness of the coating, the nature of the surface of the article plated and the type of article are all factors to be considered. Thus, a very thin coat of zinc deposited on a dull surface will not have the brightness of a thicker coat.

The gluconic acid employed in the practice of the invention exists in several forms and the invention contemplates the use of one or more of these forms, or mixtures thereof, including mixtures of the lactone forms. Commercial gluconic acid is available as a 50% aqueous solution of approximately 99% gluconic acid and 1% glucose. The presence of the glucose is undesirable because it tends to build up in the bath to cause gumminess or stickiness. The zinc gluconate described in the examples is substantially free of glucose. This may be prepared by heating a commercial 50% by weight gluconic acid solution to 120 degrees F. sufficiently long to melt any crystalline lactone that might be present, then adding one mole of lead-free zinc oxide for every two moles of gluconic acid, heating to 170 degrees F. with agitation and holding for 10 minutes until solution is complete. The resultant product is cooled to 120 degrees F. in the liquid phase and poured into large stoneware vessels and cooled until a waxy solid forms containing some supernatant liquor. The liquor which is mainly glucose and water is removed by filtration and the residue is placed in drying trays. At this point it may be washed with ice water to dissolve traces of residual glucose. The product is then dried by heating at temperatures below 250 degrees F. until dry and hard, after which it is ground in a hammermill or other suitable means. The resultant product is stable and non-sticky. The quantities of this material employed with optimum results has been within the range of 25 to 80 grams per liter of electrolyte, or the chemically equivalent proportions of gluconic acid or other bath soluble gluconate, or other aldonic acid or bath soluble aldonate.

The oxidizing treatment referred to in connection with Example IV hereof may be effected with other oxidizing acids besides nitric acid, as,

for example, chromic acid and various combinations of chromic acid with other chemicals such as are sometimes used to brighten zinc plates made by the alkaline cyanide process.

The invention produces unusual results in the plating of zinc from acid baths. By the practice of the invention plates have been produced which have been comparable to bright chromium plates. So far as is known, these results have not heretofore been attained in this art. Additionally, the invention provides improved performance of acid plating baths, excellent zinc deposits, operation at high current densities and other advantages which will be apparent to those skilled in the art.

Throughout the specification and claims where the addition agents are referred to broadly as "a gluconate" and "an alkylated naphthalene sulfonate" it will be understood that these expressions comprehend the addition of the free gluconic acid and free alkylated naphthalene sulfonic acid as well as soluble salts thereof to the acid zinc electroplating bath.

The reaction products of zinc oxide and aldonic acids are disclosed and claimed as compositions of matter in my co-pending application, Serial No. 180,500, filed August 19, 1950.

The invention is hereby claimed as follows:

1. An acid zinc plating bath comprising zinc sulfate dissolved in an acidic aqueous liquid containing a member from the group consisting of aldonic acids and aldonates in a quantity at least effective to produce antiburn effects in said bath.

2. An acid zinc plating bath comprising zinc sulfate dissolved in an acidic aqueous liquid containing zinc gluconate and an alkylated naphthalene sulfonate dissolved in said bath.

3. An acid zinc plating bath comprising 50 to 150 grams per liter of zinc sulfate dissolved in an acidic aqueous liquid containing a gluconate and an alkylated naphthalene sulfonate dissolved in said bath in quantities effective to produce a bright plate directly out of the bath.

4. An acid zinc plating bath comprising zinc sulfate dissolved in an acidic aqueous liquid containing a gluconate and an alkylated naphthalene sulfonate dissolved in said bath, said bath having a pH between 1.0 and 5.5.

5. An acid zinc plating bath comprising zinc sulfate dissolved in an acidic aqueous liquid containing a gluconate and an alkylated naphthalene sulfonate dissolved in said bath, said bath having a pH between 2.5 and 4.0.

6. An acid zinc plating bath comprising essentially zinc sulfate dissolved in an acidic aqueous liquid containing zinc gluconate and isopropyl naphthalene sodium salt dissolved in said bath.

7. An acid zinc electrolyte resulting from mixing together zinc sulfate, a water soluble salt of an alkylated naphthalene sulfonic acid, zinc gluconate and water, said electrolyte containing 50 to 150 grams of dissolved zinc per liter of solution.

8. An acid zinc plating bath comprising zinc sulfate dissolved in an acidic aqueous liquid and containing lactic acid and an alkylated naphthalene sulfonate dissolved in said bath, the quantities of lactic acid and alkylated naphthalene sulfonate being effective to produce a bright zinc plate when the latter is dipped in a ½% nitric acid solution.

9. A method of zinc plating which comprises electrodepositing zinc from an acid bath containing zinc sulfate and a member from the group consisting of aldonic acids and aldonates in a quantity at least effective to inhibit burning of the zinc plate.

10. A method as claimed in claim 9 in which the electrodeposition is carried out with agitation at a temperature below 100 degrees F.

11. A method as claimed in claim 9 in which the electrodeposition is carried out at current densities in excess of 30 amperes per square foot.

12. A method of producing a bright zinc plate which comprises electrodepositing zinc from an acid zinc sulfate plating bath containing lactic acid and an alkylated naphthalene sulfonate in a quantity effective to produce a bright plate when the plated article is subjected to a secondary treatment with an oxidizing acid, and thereafter, subjecting said plated article to said secondary treatment.

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