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ACID ZINC ELECTROPLATING COMPOSITIONS AND METHOD

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

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

Another object of the invention is to provide a new and improved acid zinc electroplating bath.

Still a further object of the invention is to provide an acid zinc electroplating bath which is capable of electrodepositing a milky gray zinc plate with a high sheen.

Another object is to provide a new and improved acid zinc plating bath which is capable of electrodepositing a milky gray zinc plate with a high sheen over a wide range of current densities.

Another object is to provide a new and improved acid zinc plating bath which is capable of electrodepositing a milky gray zinc plate with a high sheen over a relatively wide pH range.

Another object is to provide a new and improved acid zinc plating bath which is capable of electrodepositing a milky gray zinc plate with a high sheen in still baths or with agitation and with no substantial change in appearance.

Still a further object is to provide a new and improved acid zinc plating bath which is capable of electrodepositing a milky gray zinc plate with a high sheen in piece baths or continuously with substantially no difference in appearance.

A further object is to provide a method of plating from an acid zinc bath which avoids black streaking and spongy deposits such as are usually obtained with such baths at low current densities.

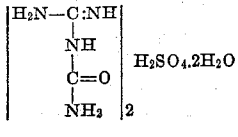
Still a further object of the invention is to produce ductile zinc coatings on wire, sheets and other articles to be plated.

Another object of the invention is to provide a new and improved acid electroplating bath which will tolerate substantial quantities of impurities, such as lead.

Still a further object of the invention is to provide an acid zinc plating bath which is capable of electrodepositing a ductile zinc plate that can be after-treated to produce a very bright finish while still maintaining its ductibility. Other objects will appear hereinafter.

These objects are accomplished in accordance with this invention by preparing and electrodepositing zinc from an acid zinc electroplating bath containing a zinc aldonate and guanyl urea sulfate, with or without the addition of fluoboric acid.

Guanyl urea sulfate has the following formula:



$H_2SO_4.2H_2O$

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The hydrated compound has a molecular weight of 338. The anhydrous compound has a molecular weight of 302. The solubility in water increases with temperature. The compound loses its water hydration at 100 degrees C. The pH of a saturated aqueous solution at room temperature (25 degrees C.) is 5 to 6.

The aldonate, for example, zinc gluconate, provides a complex organic ion and is employed in sufficient quantities to buffer the bath. It permits operations at a higher pH than is customary in acid zinc plating baths and also produces finer grained deposits. The aldonate ion may be added either in the form of the free gulconic acid or as a salt thereof which is soluble in the acid zinc bath and the cation of which does not adversely affect the bath. 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. The aldonate is preferably added in the form of a zinc aldonate previously prepared by the reaction of zinc oxide with aldonic acid. Other examples of acids and salts thereof which may be used are galactonic, arabonic, xylonic and mannonic. The aldonate in addition to its other functions, has a pronounced anti-burn effect and produces improved plating efficiency.

The guanyl urea sulfate is employed in an amount which is effective to prevent black streaking and spongy deposits at low current densities. The minimum amount is that quantity which will prevent darkening of a Hull cell plate.

The fluoboric acid, sometimes called acid fluoborate (HBF_4) is an optional ingredient which tends to whiten and smooth the resultant zinc deposit.

The invention will be further illustrated by the following example.

Example

An electrolyte was prepared by mixing the following ingredients:

240 grams $ZnSO_4 \cdot 7H_2O$
20 grams zinc gluconate
14.4 milligrams guanyl urea sulfate
3 cc. acid fluoborate
Water sufficient to make a liter of solution.

The zinc gluconate was prepared by heating a commercial 50% by weight gluconic acid solution to 120 degrees F. sufficiently long to melt any crystalline lactone which might be present, then adding 1 mole of lead-free zinc oxide for every 2 moles of zinc gluconic acid, heating to 170 degrees F. with agitation and holding for 10 minutes until solution was complete. The resulting product was cooled to 120 degrees F.

in the liquid phase and poured into large stoneware vessels and cooled until a waxy solid formed containing some supernatant liquor. The liquor which was mainly glucose and water was removed by filtration and the residue was placed in drying trays. At this point it was washed with ice water to dissolve traces of residual glucose. The product was then dried by heating at temperatures below 250 degrees F. until dry and hard, after which it was ground in a hammer mill. The resultant product was stable and non-sticky.

The bath was purified by electrolyzing it as described in Transactions of Electrochemical Society, vol. 80 (1941), pages 391, 392.

Steel sheets, wire and other articles were plated out of this bath to produce zinc deposits having a milky gray appearance with high sheen over a wide range of current density from 5 amperes per square foot to 1000 amperes per square foot, over temperature ranges from room temperature to 135 degrees F., and over a pH range from 3 to 5.6, with or without agitation.

Similar baths were employed in other tests with the addition of up to 14 parts per million of lead without changing the nature or appearance of the deposit.

Wire was plated out of this bath in amounts up to 2 ounces of zinc per square foot of wire surface and the deposit exhibited no cracking on bending.

A bright plate was readily produced by dipping a plated product into a second bath consisting of ½% nitric acid in water. Other types of bright dipping baths gave excellent results. The bright plate obtained in this manner retained its original ductility as contrasted with bright plates formed directly in another type of acid bath which tended to be brittle in the heavier deposits.

The quantities of zinc gluconate in the foregoing bath were varied within a range of 5 grams per liter per 80 grams per liter without essentially altering the results. As previously indicated the minimum quantity of the zinc gluconate or other aldonate can be measured by its buffering effect, that is, by the pH drop caused by the addition of a given amount of acid. If no aldonate is present the pH drop will not be affected. If the aldonate is present the pH drop will be retarded or reduced. The optimum amount of zinc gluconate or other aldonate can readily be determined by one skilled in the art by simple testing procedures. Obviously, there is no particular advantage in employing an excessive amount where a smaller amount will produce the effective result.

The quantity of guanyl urea sulfate was varied over a range from 13.1 milligrams to 50 grams of guanyl urea sulfate per liter of electrolyte with good results. As previously indicated, the least amount or minimum employed for the purpose of the invention is that amount which will prevent darkening of a Hull cell plate at low current density areas.

Although the preferred operating pH range is from 3 to 5.5, it is possible to operate within a pH range of from 2.4 to 6.0. Below a pH of about 2.4 the acid bath has a stripping action and this determines the minimum pH. Where it is desired to adjust the pH of the bath any acid ordinarily employed for this purpose may be used, preferably sulfuric acid. In carrying out the invention the pH was allowed to drift upward from 3 to 5.6 without substantially changing the appearance of the deposit. Thus it is possible in the practice of the invention to operate over a relatively wide pH range as contrasted with the pH ranges hitherto employed in proprietary acid zinc sulfate electrolytes. In one such proprietary bath the pH must be maintained around 3.0 because at a pH of 3.3 to 3.7 the zinc plate has the appearance of a spongy dark background with white spots and at higher pH's the plate becomes even darker.

The effective addition agents for the purpose of the present invention can be combined into a composition that may be employed as an additive for proprietary baths. A composition of this type may consist of, for example, 19.9 parts by weight of zinc gluconate, .1 part by weight guanyl urea sulfate, with or without minor amounts of fluoboric acid.

If the aldonate and guanyl urea sulfate, with or without the fluoboric acid, are added to a proprietary bath it is preferable to keep the pH around 3.0 until the essential chemicals of the proprietary bath have been exhausted.

The fluoboric acid is preferably employed in a range of zero to 10 cc. per liter of electrolyte.

The invention is not limited to the range of current densities mentioned in the foregoing example. The upper limit of the current density can be determined in any given case and will be that amount which can be employed with the agitation available without burning the plate. By providing proper agitation in commercial operations up to 5000 amperes per square foot can be employed. In the past it has been customary to prepare acid zinc plating baths containing other zinc salts together with glucose or other reducing sugars and various types of organic colloids which have been alleged to have beneficial effects 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 temperature of the electroplating bath during the electrodeposition of zinc may vary within limits which will be understood by those skilled in the art. As previously indicated excellent results have been obtained at temperatures within the range from room temperatures of say 65 degrees F. to higher temperatures of say 135 degrees F. 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.

It is believed that the results obtained by the combined use of the aldonate and guanyl urea sulfate in the zinc electroplating bath as previously described in an acid zinc electroplating bath have never before been equalled as to uniformity and ductility of the deposit over such a wide range of variation in current density, temperature, pH and agitation. The optimum results are not obtained with either the zinc aldonate alone or the guanyl urea sulfate alone in an acid zinc bath. The aldonate, for example, zinc gluconate, not only has the functions previously mentioned, but also is capable, apparently, of sequestering iron so that the bath can be operated over a longer period of time without difficulties due to the presence of iron sulfate and likewise is capable of holding zinc sulfate in solution at a pH of 6. This latter function permits operations at a higher pH and as already mentioned makes it possible to allow the pH to drift upward. As a result it is no longer necessary to control the pH of a bath within a narrow range. The guanyl urea sulfate in some unexplained manner prevents black streaking and spongy deposits at low current densities and contributes to the uniformity of the deposit over a relatively wide range of pH values in still baths or at high speed agitation even in the presence of amounts of impurities such as lead which would cause streaking or ridging in the usual acid bath. The electrolytes provided in accordance with the invention also have exceptional throwing power for acid zinc electrolytes.

The invention is hereby claimed as follows:

1. An acid zinc plating bath comprising zinc in a soluble form dissolved in an acidic aqueous liquid containing a zinc aldonate and guanyl urea sulfate dissolved in said bath.

2. An acid zinc plating bath comprising zinc in a soluble form dissolved in an acidic aqueous liquid containing zinc gluconate and guanyl urea sulfate.

3. An acid zinc plating bath comprising essentially 50 to 150 grams per liter of zinc dissolved as zinc sulfate in water containing zinc gluconate and guanyl urea sulfate.

4. An acid zinc plating bath comprising essentially 50 to 150 grams per liter of zinc dissolved as zinc sulfate in water containing zinc gluconate and guanyl urea sulfate, the quantity of zinc gluconate corresponding to at least 5 grams per liter of bath and the quantity of guanyl urea sulfate corresponding to at least 13.1 milligrams per liter of bath.

5. An acid zinc plating bath comprising essentially 50 to 150 grams per liter of zinc dissolved as zinc sulfate in water containing zinc gluconate and guanyl urea sulfate, the quantity of zinc gluconate being sufficient to exert a buffering action on said bath and the quantity of guanyl urea sulfate being sufficient to prevent darkening in the lower current ranges of a Hull cell plate.

6. An acid zinc plating bath comprising essentially zinc in a soluble form dissolved in water containing zinc gluconate and guanyl urea sulfate and having a pH within the range of 2.4 to 6.0.

7. An acid zinc plating bath comprising essentially a solution in water of 50 to 150 grams per liter of zinc in a soluble form dissolved as zinc sulfate, 5 to 80 grams per liter of zinc gluconate, about 13 milligrams to 50 grams per liter of guanyl urea sulfate and zero to 10 cc. per liter of fluoboric acid adjusted to a pH within the range of about 2.4 to about 6.0.

8. An acid zinc plating bath comprising essentially a solution in water of 50 to 150 grams per liter of zinc in a soluble form dissolved as zinc sulfate, 5 to 80 grams per liter of zinc gluconate, about 13 milligrams to 50 grams per liter of guanyl urea sulfate and zero to 10 cc. per liter of fluoboric acid adjusted to a pH within the range of about 3 to about 5.6.

9. A method of zinc plating which comprises electrodepositing zinc from an acid bath containing zinc in a soluble form, a zinc aldonate and guanyl urea sulfate.

10. A method of zinc plating which comprises electrodepositing zinc from an acid bath containing zinc in a soluble form, zinc gluconate and guanyl urea sulfate.

11. A method of producing a ductile milky gray deposit with a high sheen which comprises electrodepositing zinc from an acid bath comprising essentially zinc sulfate, zinc gluconate and guanyl urea sulfate at a pH within the range of 2.4 to 6.0 in a current density range of from 5 amperes to 1000 amperes per square foot, the quantity of zinc gluconate being effective to exert a buffering action on the bath and the quantity of guanyl urea sulfate being effective to prevent black streaking.

12. A method of producing a ductile milky gray deposit with a high sheen which comprises electrodepositing zinc from an acid bath comprising essentially zinc sulfate, zinc gluconate and guanyl urea sulfate at a pH within the range of 2.4 to 6.0 in a current density range of from 5 amperes to 1000 amperes per square foot, the quantity of zinc gluconate corresponding to at least 5 grams per liter of bath and the quantity of guanyl urea sulfate corresponding to at least about 13 milligrams per liter of bath.

13. A method of producing a ductile milky gray deposit with a high sheen which comprises electrodepositing zinc from an acid bath comprising essentially zinc sulfate, zinc gluconate and guanyl urea sulfate at a pH within the range of 2.4 to 6.0 in a current density range of from 5 amperes to 1000 amperes per square foot, the quantity of zinc gluconate corresponding to 5 to 80 grams per liter of bath and the quantity of guanyl urea sulfate corresponding to about 13 milligrams to 50 grams per liter of bath.

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