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METHOD OF ELECTROPLATING ZINC AND ELECTROPLATING COMPOSITIONS

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7 Claims. (Cl. 204—55)

This invention relates to a new and improved method of electroplating zinc from an acid zinc bath and to a new and improved electrolyte therefor.

One of the objects of the invention is to provide a new and improved method for electroplating zinc from acid zinc plating baths.

Another object of the invention is to provide a new and improved method for electrodepositing zinc in finely crystalline (fine grain) form from an electroplating bath which operates over a relatively wide range of pH, zinc content, current density and temperature.

Still another object of the invention is to provide a new and improved method for imparting luster or brightness to zinc coatings without treeing and pitting by a process in which the bright coating is formed directly in an acid zinc sulfate plating bath.

Another object of the invention is to provide a new and improved method for the continuous plating of zinc from an acid zinc sulfate bath.

An additional object of the invention is to provide a new and improved method for the continuous plating of zinc from an acid sulfate bath in which zinc is electrodeposited on the sheet or other object to be plated using a high current density on one side of the sheet or other object and a low current density on the other side and then reversing the sides, if desired.

Another object of the invention is to provide a method of electroplating wherein bright, lustrous, fine grained, ductile zinc deposits having a pleasing silvery color are deposited over a wide range of current density.

Still a further object of the invention is to provide a method of producing bright zinc deposits directly in an acid zinc sulfate plating bath, simply and economically.

Another object of the invention is to provide new and useful electroplating compositions. Other objects will appear hereinafter.

In accomplishing these objects in accordance with the invention it has been found that new and improved results in the production of bright zinc deposits from an acid zinc sulfate electroplating bath are obtained by carrying out the electrodeposition of zinc from said bath in the presence of a peptone dissolved in said bath. The bath also preferably contains a substance referred to herein as a carrier which serves to produce a fine grained zinc deposit. The carrier preferably employed for the purpose of the invention is thiourea with or without zinc gluconate, sodium fluoride and/or aluminum sulfate.

The peptones preferably employed for the purpose of the invention are mixtures of proteoses and amino acids derived by the enzymatic digestion of materials of animal origin, e. g., gelatin, animal stomach linings, and the like. Peptones can be made, for example, by starting with gelatin made from animal hoofs and preparing a nutrient broth to which is added a peptone-forming enzyme which acts on the proteins to form peptones. A specific peptone especially suitable for the practice of the present invention is Peptone No. 421 which is a viscous brown liquid made by Wilson & Company.

The invention will be further illustrated but is not limited by the following example in which the quantities are stated in parts by weight unless otherwise indicated.

Example

An acid zinc plating bath is prepared by dissolving 1 pound to 3 pounds of $ZnSO_4.7H_2O$ in water and adding sufficient sulfuric acid to give a pH within the range of 1 to 5.5, preferably 3 to 4. The bath preferably has a zinc content of .75 pound zinc per gallon of solution. A carrier is prepared by dry mixing the following ingredients:

Ingredients:	Percent by weight
Zinc gluconate	4.71
Thiourea	23.53
Sodium fluoride (commercial)	18.82
Aluminum sulfate (hydrated)	52.94

The carrier is added to the above mentioned acid zinc sulfate solution in proportions preferably within the range of ⅛ to 2 ounces of carrier per gallon of solution. This corresponds to about 0.28 to 4.48 grams of thiourea per liter of electrolyte.

Peptone No. 421 (Wilson & Company) is added to the previously described solution containing the carrier, preferably in proportions within the range of 0.075 to 0.5 cc. per liter of solution.

Steel strips or sheets are plated in this bath by passing them continuously through the bath. The current density may vary from about 3 amperes per square foot to several thousand amperes per square foot but the bath is usually run at an average current density of 300 amperes per square foot. It will be recognized, of course, that the current density on the edges of steel sheets or strips may be higher, say around 1000 amperes per square foot, when the average current density is 300 amperes per square foot.

The carrier is not, or is only partially, destroyed by the passage of the current but in continuous plating operations it is necessary to add additional quantities of carrier in order to replace the quantities which are removed by dragout. Thus, if the bath contains 16 pounds of the carrier per 1000 gallons of solution, then 16 pounds of the carrier should be added for each 1000 gallons of solution lost by dragout. Since the quantity of the carrier is not extremely critical, it is usually possible to keep a satisfactory balance in the solution by making a daily addition of carrier equivalent to the loss by dragout. The bath can contain at least twice the normal concentration of carrier without suffering a bad plate.

The amount peptone added to the solution is controlled by the use of a Hull cell in which the temperature of the bath is maintained at 100° F. and the solution is kept moving on the surface of the plate during the plating operation by means of compressed air introduced below the bottom edge of the plate. The Hull cell when operated at 1 ampere for 10 minutes gives great contrast between the bright and dark zone because the bright zone in a properly balanced bath will be almost mirror bright. The quantity of brightener added to the bath is preferably such as to maintain a bright zone on the Hull cell that extends below 3 amperes per square foot. The presence of minute amounts of lead in the bath resist the extension of the bright zone downwardly and make it difficult to reach below 3 amperes per square foot. The bath is considered to be best when the lead content is below 1 part per million.

The Hull cell test also gives an indication of carrier requirements. If the quantity of carrier in the bath is low, it will shorten the bright range on the Hull cell plate and if the quantity of carrier is in excess of the optimum

amount, the bright zone on the Hull cell plate is darkened and divided into several zones and shows a graining at the high current density end. For the control of the operations in continuous plating, it is preferable to use at least one Hull cell test per day and make additions of the peptone sufficient to extend the bright range in the Hull cell below 3 amperes per square foot. Occasional checks are made by adding some of the carrier to the Hull cell and if an extension of the bright range is encountered, the indicated amount of carrier is added to the main bath.

In general, when larger amounts of the peptone are employed, it is desirable to use a greater amount of carrier in order to extend the bright range to the lower current densities and secure the desired result in the plating operation. For example, when using 0.075 cc. per liter of the peptone material, it is desirable to employ about 0.7 gram per liter of thiourea or a sufficient amount of the carrier composition previously described to furnish this quantity of thiourea. On the other hand, when employing 0.5 cc. of the peptone material per liter of plating solution, it is desirable to use about 1 to 1.25 gram of thiourea per liter of plating solution or a quantity of the previously described carrier composition sufficient to furnish this amount of thiourea.

The thiourea employed in the above described plating solution assists in producing a fine grained zinc plate. Without the thiourea, the desired brightening effect is not obtained with the peptone material. Apparently, the peptone material acts as an interference brightener.

The zinc gluconate has pronounced anti-burn effects and the combination of zinc gluconate and thiourea in itself has some brightening action but not to the extent of that obtained when the peptone material is also added to the bath.

The aluminum sulfate is preferably added to the bath in quantities from ¼ to 2 ounces per gallon and apparently serves to form a film of colloidal alumina in the vicinity of the anode and prevent excessive acid attack upon the zinc anode.

Sodium fluoride acts as a whitening and grain refining agent at the cathode and apparently causes more uniform solution of zinc at the anode while tending to prevent sludge formation.

Other optional ingredients which may be added to the bath are sugars, such as dextrose, molasses and the like, which apparently produce a refinement in the crystalline structure of the zinc and have some whitening effect. Other ingredients, such as sodium acetate, may be included in the bath but all of these auxiliary ingredients are optional.

The compositions employed in the practice of the invention are especially effective in the electrodeposition of zinc from acidic baths in which the zinc is principally present as zinc sulfate. The zinc sulfate baths can also contain additions of zinc chloride, preferably not more than 20 to 100 grams per liter.

The invention provides a new and improved method for electrodepositing zinc in finely crystalline form from an electroplating bath which operates over a relatively wide range of pH, zinc content, current density and temperature. The invention also provides a new and improved method for imparting luster or brightness to zinc coatings without treeing and pitting and by a process in which the bright coating is formed directly in an acid zinc plating bath without secondary treatments. The invention is especially suitable for continuous plating of steel strips or sheets from an acid zinc sulfate bath in which zinc is electro-deposited on the sheet or other object to be plated using a high current density on one side of the sheet or other object and a low current density on the other side and then reversing the sides. The quantities of the additives required in order to produce bright, lustrous, fine grained, ductile zinc deposits having a pleasing silvery color over a relatively wide range of current densities are extremely small.

The term "acid zinc sulfate plating bath" is used herein to describe acidic plating baths in which the zinc is present principally as zinc sulfate but can also be present in minor amounts in one or more other forms.

The invention is hereby claimed as follows:

1. An aqueous acid zinc sulfate plating bath comprising an acid zinc sulfate eectrolyte, a quantity of thiourea sufficient to produce a fine grained ductile zinc deposit when zinc is electrodeposited from said electrolyte and a quantity of a peptone sufficient to enhance the brightness of said deposit.

2. An aqueous acid zinc sulfate plating bath comprising an acid zinc sulfate electrolyte, about 0.28 gram to about 4.48 grams of thiourea per liter of said electrolyte and about .075 to about 0.5 cc. of a peptone per liter of said electrolyte.

3. In a process for the electrodeposiiton of zinc, the step which comprises electrodepositing zinc from an acid zinc sulfate plating both containing a sufficient quantity of thiourea to refine the grain size of the electrodeposited zinc and a sufficient quantity of a peptone to enhance the brightness of the electrodeposited zinc.

4. In a process for the electrodeposition of zinc, the step which comprises electrodepositing zinc from an acid zinc sulfate plating bath containing thiourea, a peptone and zinc gluconate, the quantity of thiourea being sufficient to refine the grain size of the electrodeposited zinc and the quantity of the peptone being sufficient to enhance the brightness of the electrodeposited zinc.

5. In a process for the electrodeposition of zinc, the step which comprises electrodepositing zinc from an acid zinc sulfate plating bath containing thiourea, a peptone, zinc gluconate and aluminum sulfate, the quantity of thiourea being sufficient to refine the grain size of the electrodeposited zinc and the quantity of the peptone being sufficient to enhance the brightness of the electrodeposited zinc.

6. In a process for the electrodeposition of zinc, the step which comprises electrodepositing zinc from an acid zinc sulfate plating bath containing thiourea, a peptone, zinc gluconate, aluminum and sodium fluoride, the quantity of thiourea being sufficient to refine the grain size of the electrodeposited zinc and the quantity of the peptone being sufficient to enhance the brightness of the electrodeposited zinc.

7. A process for continuously electrodepositing zinc which comprises electrodepositing zinc from an acid zinc sulfate plating bath containing about .075 to 0.5 cc. of a peptone per liter of said bath and about 0.28 gram to 4.48 grams of thiourea per liter of said bath, the quantity of thiourea being low when the quantity of peptone is low, and the quantity of thiourea being high when the quantity of peptone is high, and replenishing at intervals the quantities of said materials which are removed from said bath by dragout.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,799,635 July 16, 1957

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

Column 1, line 37, for "acid sulfate" read -- acid zinc sulfate --; column 4, line 21, for "electrodeposiiton" read -- electrodeposition --; line 23, for "both" read -- bath --; line 45, after "aluminum" insert -- sulfate --; same column 4, line 69, list of references cited, under "OTHER REFERENCES", for

"Diggin: Metal Industry, June 25, 1943, p. 385."

read

-- Diggin: Metal Industry, June 25, 1943, p. 407. --.

Signed and sealed this 21st day of January 1958.

(SEAL)
Attest:

KARL H. AXLINE
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