

CARRIER BRIGHTENERS FOR ACID ZINC ELECTROLYTES

5 The present invention broadly relates to an improved electrolyte and process for electrodepositing zinc, and more particularly, to an improved non-cyanide acid zinc electrolyte containing improved carrier brightening agents.

10 A variety of aqueous cyanide-free acidic zinc electroplating solutions and processes have heretofore been used or proposed for use. In many instances, such acid zinc electrolytes contain polyalkoxylated nonionic surfactants as carrier brighteners in further combination with primary and supplemental brightening
15 agents to achieve a zinc deposit of the desired characteristics. A continuing problem associated with the use of polyalkoxylated nonionic surfactants as carrier brighteners in prior art electrolytes has been the tendency of such electrolytes to reach a cloud
20 point at relatively low bath temperatures, such as 80° to 100°F (27 to 38°C). This problem is further aggravated when the acid zinc electrolyte contains relatively high concentrations of soluble constituents, particularly dissolved metal ions of the periodic table
25 of Group I and II metals or ammonium ions. The operation of the bath at relatively high current densities also contributes toward an increase in the temperature thereof further aggravating the tendency of such carrier brighteners to attain the cloud point.
30 When the cloud point of the nonionic carrier brightener surfactant is attained, the carrier brightener is rendered inoperative and no longer contributes to a brightening effect of the zinc electrodeposit nor does

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it function secondarily as a surfactant to emulsify oils and other organic contaminants in the electroplating bath.

The present invention overcomes or at least mitigates problems and disadvantages associated with prior art acid zinc electroplating baths by employing an improved anionic surfactant carrier brightener, having a substantially higher cloud point, which is compatible with other conventional primary and supplemental brighteners of the types conventionally employed achieving the same benefits as heretofore provided by nonionic carrier brighteners while at the same time substantially increasing the flexibility of operation of the bath to obtain zinc electrodeposits of the desired quality.

The benefits and advantages of the present invention in accordance with the composition aspects thereof are achieved by a cyanide-free aqueous acidic zinc electrolyte containing zinc ions, generally in conventional amounts, effectively to electrodeposit zinc on a conductive substrate, hydrogen ions present in an amount to provide a pH on the acid side, and a brightening amount of a bath-soluble anionic sulphated polyoxyalkylene surfactant derived from the sulphation of a compound resulting from the alkoxylation

of a mono- or polyhydroxy compound selected from hydroxy-containing alkyl, alkenyl, alkynyl and aryl compounds, and carboxylic derivatives thereof, as well as mixtures thereof.

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The aqueous acidic zinc electrolyte can additionally and, preferably, does contain various other additive agents of the types conventionally employed including buffering agents, primary or
10 supplemental brightening agents, bath soluble and compatible conductivity salts to increase the electrical conductivity of the electrolyte, and the like.

15 In accordance with the process aspects of the present invention a zinc plate is deposited on a conductive substrate employing the aforementioned aqueous acidic zinc electrolyte which is controlled at a temperature generally ranging from 60° up to 180°F
20 (16 to 82°C) and which is operated at an average cathode current density ranging from as low as 1 up to as high as 300 amperes per square foot (ASF) (0.11 to 33 amperes per square decimetre (ASD)) or higher depending upon the specific type and composition of the
25 electrolyte and the geometry and processing parameters employed in the plating operation.

Additional benefits and advantages of the present invention will become apparent upon a reading of the
30 following description of the preferred embodiments taken in conjunction with the specific examples provided.

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The aqueous acidic cyanide-free zinc electrolyte in accordance with the composition aspects of the present invention contains zinc ions present in an amount effective to electrodeposit zinc from the electrolyte. The zinc ion concentration may range from about 4 g/l up to saturation; which concentration is used in practice will depend upon the operating bath temperature of the electrolyte. For example, at electrolyte temperatures of about 100°F (38°C) and above, zinc ion concentrations of about 300 g/l and higher may be employed. Typically, in acid chloride-type electrolytes, the zinc ion concentration is conventionally controlled within a range of from 7 up to 50 g/l whereas in acid sulphate-type electrolytes, the zinc ion concentration is generally controlled within a range of from 30 up to 110 g/l.

The acid zinc electrolyte may be formulated in accordance with conventional practice by introducing a zinc salt such as a chloride, sulphate, or sulphamate in an aqueous solution along with a noncomplexing acid such as hydrochloric acid, sulphuric acid or sulphamic acid. Mixtures of zinc salts, for example, zinc chloride and zinc sulphate, can be employed if desired providing a mixed-chloride type bath. Acid zinc plating baths can also be based on zinc fluoroborate.

The electrolyte further contains hydrogen ions to provide a pH on the acid side with a pH ranging from about 0 up to about 6 being typical and a pH of from 4 up to 5.7 being preferred. The electrolyte can also contain additional additives or agents of the

types conventionally employed including buffering agents and bath modifiers such as boric acid, acetic acid, benzoic acid, salicylic acid, ammonium chloride or the like. Acid chloride-type electrolytes conventionally include inert salts to increase the electrical conductivity of the electrolyte and are usually employed in amounts of about 20 up to about 450 g/l. Such inert salts conventionally comprise magnesium and alkali metal chlorides in which the term "alkali metal" is employed in its broad sense to also include ammonium chloride as well as the specific alkali metals such as sodium, potassium and lithium. Typically, the conductivity salts comprise sodium chloride or potassium chloride.

In accordance with the present invention, the acid zinc electrolyte incorporates, as an essential ingredient, a carrier brightener present in a brightening amount comprising a bath-soluble low-foaming anionic sulphate polyoxyalkylene surfactant produceable by the sulphation of a compound resulting from the alkoxylation of a mono- or polyhydroxy compound selected from hydroxy-containing alkyl, alkenyl, alkynyl and aryl compounds, and carboxylic derivatives thereof, as well as mixtures thereof.

The molecular weight of the carrier brightener or

mixtures thereof is generally controlled to render the compound soluble in the electrolyte in the concentration desired. Classes of compounds encompassed within the foregoing definition include

5 _____ sulphated alkoxyated acetylenic diols, sulphated ethoxylated and/or propoxylated alpha- and beta-naphthols, sulphated ethoxylated and/or propoxylated sorbitol and gluconates, sulphated alkoxyated fatty alcohols, and the like. Particularly
10 satisfactory compounds comprise the mono or di-sulphated derivatives of the reaction of ethylene oxide with the acetylenic glycol 2,4,7,9-tetra-methyl-5-decyne-4,7-diol employing from about 10 to about 30 mols ethylene oxide. It will be appreciated that the
15 carrier brightener may contain one sulphate group on the molecule or may contain more than one sulphate group depending on the degree of sulphation and the number of reactive hydroxyl groups on the molecule.

20 Carrier brighteners of the present invention may be derived by the sulphation of commercially available non-sulphated nonionic surfactants such as Surfynol 465 containing 10 mols of ethylene oxide and Surfynol 485 containing 30 mols of ethylene oxide available from Air
25 Products; the sulphation of beta-naphthol-13 EO available from Heterene Chemical; the sulphation of Carbowax 3350 available from Union Carbide Corporation; the sulphation of IL-1554 and IL-1562 available from Imperial Chemical Industries. The words SURFYNOL and
30 CARBOWAX are Trade Marks. The carrier brightener may further be characterized as being of relatively low-foaming properties to avoid excessive foam formation during operation of the electrolyte particularly in the

presence of air agitation or severe mechanical agitation including circulation of the electrolyte by pumps.

5 It is further contemplated that polyethoxylated phenols can be employed having the terminal hydroxyl group sulphated. Compounds of the foregoing type which are commercially available include Alipal CO-436, Alipal CD-128, Alipal CO-433 available from GAF and
 10 Polystep B-20 available from Stepan. The words ALIPAL and POLYSTEP are Trade Marks. Such sulphated polyethoxylated phenols are generally less desirable because of their higher foaming characteristics but can be employed in baths which are subjected to minimal
 15 agitation to avoid excessive foaming. Other commercially available products are sulphated ethoxylated fatty alcohols, such as Lutensit AS 2230 from BASF. The word LUTENSIT is a Trade Mark.

20 The carrier brightening agent may be employed in the electrolyte in an amount ranging from 0.5 up to 20 g/l with concentrations of from 2.5 to 10 g/l being preferred. The specific concentration of the carrier brightener will vary in consideration of the
 25 concentration and presence of other bath constituents, the processing parameters of the electrolyte and the type of zinc plate desired.

A particularly preferred acid zinc electrolyte in
 30 accordance with the present invention comprises an acid-chloride-type electrolyte containing from 15 to 53 g/l zinc ions, hydrogen ions to provide a pH of 4 to 5.7, conductivity salts such as



5 sodium chloride and potassium chloride present in an amount of about 100 to about 210 g/l, a buffering agent such as boric acid present in an amount of about 15 to about 38 g/l, a carrier brightener present in an amount of about 1 to about 5 g/l selected from sulphated 2,4,7,9-tetra-methyl-5-decyne-4,7-diol ethoxylated with 30 mols ethylene oxide, sulphated ethoxylated/propoxylated sorbitol (M.W. 6500), sulphated ethoxylated (15 mols ethylene oxide) beta-naphthol, 10 ~~_____~~ sulphated polyethoxylated lauryl alcohol (about 20 mols ethylene oxide), sulphated polyethoxylated phenol (about 20 mols ethylene oxide), and mixtures thereof, and, optionally, but preferably, primary and/or supplemental brightening 15 agents eg of the types conventionally employed in acid zinc electrolytes in conventional amounts.

The presence of the carrier brightener provides a primary function in the electrolyte of producing grain 20 refined deposits and allowing the primary brightener to function, secondarily, to effect an emulsification of organic soils, such as oils, which may escape past the cleaner, on the substrates being electroplated. In prior art electrolytes employing nonionic surfactant 25 carrier brighteners, the progressive accidental introduction of organic grease and oils on the parts has occasioned an increase in the sensitivity of the electrolyte to attaining a cloud point at only moderate increases in temperature above room temperature thereby 30 rendering the bath inoperative or less effective in achieving zinc deposits of the desired property and appearance. In addition, high electrolyte content had to be avoided even though it offered operational

advantages such as increased throwing power in deep recess areas. In contrast, the anionic sulphated carrier brighteners of the present invention, provide for a substantial latitude in the operating temperature and electrolyte content enabling its use at relatively high operating temperatures such as as high as 180°F (82°C) or even higher without encountering the cloud-point phenomenon. In this way the operating temperature limit becomes the brightening ability of the primary brightener, not the solubility limit of the carrier brightener. Additionally, the sulphated anionic surfactant carrier brighteners of the present invention further enable their use under conditions when the bath is highly loaded with other ingredients, particularly metals of the Group I and II of the periodic table and also enable operation over a relatively broad range of pH. In contrast, acid zinc baths of the sulphate type generally cannot be operated employing prior art nonionic surfactant carrier brighteners at pHs substantially below about 4.

As previously mentioned, the electrolyte further contains as an optional but preferred constituent, primary and/or supplemental brightening agents to further enhance the crystal structure of the zinc electrodeposit and to provide for a broader operating average current density range. Such primary and/or supplemental brightening agents of the types well-known in the art include those disclosed in United States Patents No. 4,170,526, 4,207,150, 4,176,017, 4,070,256 and 4,252,619. A particularly satisfactory class of such supplemental brightening agents is set forth in Table 1 of the aforementioned United States Patent No.

4,252,619. The primary or supplemental brightening agents can generally be employed in amounts up to about 10 g/l with amounts as low as about 0.001 g/l being effective. Generally, concentrations of from
5 0.01 up to 5 g/l are preferred.

In accordance with the process aspects of the present invention, the aqueous acid zinc electrolyte is employed for electrodepositing zinc on a conductive
10 substrate and the electrolyte is controlled at a temperature ranging from room temperature (60°F 16°C) up to 180°F (82°C) with temperatures of from 65° to 90°F (18 to 32°C) being typical. The electrodeposition of zinc is performed at an average cathode current
15 density generally ranging from 1 to as high as 300 ASF (0.11 to 33 ASD) depending upon the particular plating technique employed, the type and configuration of the article being plated, the specific composition of the electrolyte employed and the concentration of active
20 constituents therein. For acid chloride-type electrolytes, operation at an average cathode current density of from 1 to 80 ASF (0.11 to 8.8 ASD) is preferred while for acid sulphate-type electrolytes, average cathode current densities of from 20 up to 300
25 ASF (2.2 to 33 ASD) are preferred.

In order further to illustrate the improved aqueous cyanide-free zinc electrolyte of the present invention and the process for electrodepositing zinc on
30 a conductive substrate, the following specific examples are provided. It will be appreciated that the examples

are provided for illustrative purposes and are not intended to be limiting of the present invention as herein described and as set forth in the claims.

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EXAMPLE 1

An aqueous acid zinc electrolyte of the chloride-type is prepared containing 60 g/l zinc chloride, 200 g/l potassium chloride, 25 g/l boric acid, 1 g/l of a sulphated carrier brightener comprising sulphated 2,4,7,9-tetra-methyl-5-decyne-4-diol ethoxylated with 30 mols of ethylene oxide and hydrogen ions to provide a pH of 5.1. The electrolyte is provided with air agitation and is controlled at a temperature of about 85°F (29°C).

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A cleaned, bare steel test panel is electroplated in the zinc electrolyte at an average cathode current density of 40 ASF (4.4 ASD) and the test panel is observed to have a semi-bright zinc plate with good coverage in the low current density areas. Heating the electrolyte to an elevated temperature approaching its boiling point evidenced no problem of the cloud-point phenomenon.

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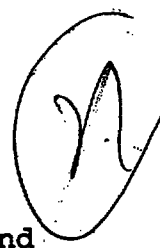
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EXAMPLE 2

An electrolyte is prepared as in Example 1 further containing 1.6 g/l sodium benzoate, 40 mg/l benzalacetone and hydrogen ions to provide a pH of 5.1.

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A cleaned, bare steel test panel is plated in the electrolyte at a temperature of 85°F (29°C) at an



average cathode current density of 40 ASF (4.4 ASD) and the plated panel is observed to have a fully bright zinc deposit over the entire surface thereof. Heating the electrolyte to an elevated temperature did not result in any cloud-point problem.

EXAMPLE 3

An aqueous acidic zinc electrolyte of the chloride-type is prepared containing 50 g/l zinc chloride, 100 g/l ammonium chloride, 10 g/l of a carrier brightener comprising a sulphated ethoxylated beta-naphthol of an average molecular weight of about 900; 15 mg/l of isopropyl nicotinate benzyl chloride quaternary and hydrogen ions to provide a pH of about 5.5.

Cleaned steel parts positioned in a rotating plating barrel are plated in the electrolyte maintained at a temperature of 80°F (27°C) at an average cathode current density of 10 ASF (1.1 ASD) and the parts are observed to have a fully bright zinc deposit. Heating the electrolyte evidenced no cloud-point problem.

EXAMPLE 4

An aqueous acidic zinc electrolyte of the chloride type is prepared containing 85 g/l zinc chloride, 125 g/l sodium chloride, 30 g/l boric acid, 2 g/l sodium benzoate, 6 mg/l butyl nicotinate dimethyl sulphate, 4.8 g/l of a carrier brightener comprising sulphated ethoxylated/propoxylated sorbitol (M.W. 6500) and hydrogen ions to provide a pH of 5.2.



Cleaned steel parts on a supporting rack are plated in the electrolyte maintained at a temperature of 80°F (27°C) at an average current density of 35 ASF (3.85 ASD) in the presence of air agitation. The parts after plating are observed to have a fully bright zinc deposit thereon. Heating the electrolyte to an elevated temperature did not evidence any cloud-point problem.

10 EXAMPLE 6

An aqueous acidic zinc electrolyte of the acid sulphate-type is prepared containing 250 g/l zinc sulphate, sulphuric acid in an amount sufficient to provide a pH of 1.5 and 0.3 g/l of a carrier brightener comprising sulphated polypropylene glycol of an average molecular weight of about 750.

Cleaned steel strip is immersed and transferred through the electrolyte at a speed of about 300 feet per minute (1.5 m/s) effecting mechanical agitation of the electrolyte and is plated at an average current density of about 120 ASF (13.2 ASD) with the temperature of the electrolyte controlled at about 120°F (49°C). The resultant strip is examined and observed to have a smooth, semi-bright zinc deposit thereover of a commercially acceptable quality. Heating the electrolyte to an elevated temperature up to the boiling point did not encounter any cloud-point problem.

While it will be apparent that the preferred embodiments of the invention disclosed are well

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calculated to fulfill the objects above stated, it will be appreciated that the invention is susceptible to modification, variation and change without departing from the proper scope or fair meaning of the claims.

CLAIMS

1. An aqueous acidic zinc electrolyte containing zinc ions in an amount effective to electrodeposit zinc, hydrogen ions to provide a pH on the acid side, and a brightening amount of a bath soluble anionic sulphated polyoxyalkylene surfactant, produceable by the sulphation of a compound resulting from the alkoxylation of a mono- or polyhydroxy compound selected from hydroxy-containing alkyl, alkenyl, alkynyl and aryl compounds, and carboxylic derivatives thereof, as well as mixtures thereof.

2. An electrolyte as claimed in Claim 1 in which the sulphated polyoxyalkylene surfactant is present in an amount of from 0.5 to 20 g/l.

3. An electrolyte as claimed in Claim 1 in which the sulphated polyoxyalkylene surfactant is present in an amount of from 2.5 to 10 g/l.

4. An electrolyte as claimed in Claim 1, 2 or 3 in which the hydrogen ions are present to provide a pH of from 0 to 6.

5. An electrolyte as claimed in Claim 1, 2 or 3, in which the hydrogen ions are present to provide a

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pH of from 4 to 5.7.

5 6. An electrolyte as claimed in any one of
Claims 1 to 5, in which the zinc ions are present in an
amount of from 4 g/l up to saturation.

10 7. An electrolyte as claimed in any one of
Claims 1 to 5 which is an acid-chloride type in which
zinc ions are present in an amount of from 7 to 50 g/l.

15 8. An electrolyte as claimed in any one of
Claims 1 to 5, which is of the acid-sulphate type and
in which zinc ions are present in an amount of from 30
to 110 g/l.

20 9. An electrolyte as claimed in any one of
Claims 1 to 8, the electrolyte including primary and/or
supplemental brightening agents present in an amount up
to 10 g/l.

25 10. An electrolyte as claimed in Claim 8 in
which the primary and/or supplemental brightening
agents are present in an amount of at least 0.001 g/l.

30 11. An electrolyte as claimed in any one of
Claims 1 to 8, further including primary and/or
supplemental brightening agents present in an amount of
from 0.01 to 5 g/l.

35 12. An electrolyte as claimed in any one of
Claims 1 to 11, the electrolyte including conductivity
salts present in an amount up to 450 g/l.

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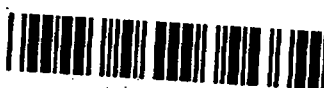
13. An aqueous acid chloride type zinc electrolyte in which zinc ions are present in an amount of from 15 to 53 g/l, hydrogen ions are present to provide a pH of from 4 to 5.7, the electrolyte further containing conductivity salts present in an amount of from 100 to 210 g/l a buffering agent present in an amount of from 15 to 38 g/l, and a sulphated polyoxyalkylene surfactant present in an amount of from 1 to 5 g/l comprising a compound selected from sulphated 2,4,7,9-tetra-methyl-5-decyne-4,7-diol ethoxylated with 30 mols ethylene oxide, sulphated ethoxylated/propoxylated sorbitol (M.W. 6500), sulphated ethoxylated (15 mols ethylene oxide) beta-naphthol, _____ sulphated polyethoxylated lauryl alcohol (about 20 mols ethylene oxide), sulphated polyethoxylated phenol (about 20 mols ethylene oxide), and mixtures thereof.

14. A process for electrodepositing zinc on a conductive substrate which process comprises the steps of contacting a substrate with an aqueous acidic zinc electrolyte as defined in any one of Claims 1 to 13 and electrodepositing zinc on the substrate to a desired thickness.

15. A process as claimed in Claim 14, which includes the further step of controlling the temperature of the electrolyte within a range of from 60° to 180°F (16° to 82°C).

16. A process as claimed in Claim 14, which includes the step of controlling the temperature of the

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electrolyte within a range of from 65° to 90°F (18° to 32°C).

5 17. A process as claimed in Claim 14, 15 or 16, the process including the step of controlling the average cathode current density during the step of electrodepositing zinc on the substrate within a range of from 1 to 300 ASF (0.11 to 33 ASD).

10 18. A process as claimed in Claim 14, 15 or 16, in which the electrolyte is of the acid chloride-type, the process including the step of controlling the average cathode current density during the step of electrodepositing zinc on the substrate within a range
15 of from 1 to 80 ASF (0.11 to 8.8 ASD).

19. A process as claimed in Claim 14, 15 or 16, in which the electrolyte is of the acid sulphate-type, the process including the step of controlling the
20 average cathode current density during the step of electrodepositing zinc on the substrate within a range of from 20 to 300 ASF (2.2 to 33 ASD).

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