

[54] ALKALINE BRIGHT ZINC PLATING	3,655,534	4/1972	Kampe.....	204/55 R
[75] Inventors: Joseph R. Duchene , Southfield, Mich.; Philip J. De Christopher , Chicago, Ill.	3,672,971	6/1972	Senge et al.....	204/55 R
	3,803,008	4/1974	Rosenberg et al.....	204/55 Y
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[52] **U.S. Cl.**..... **204/55 R; 204/DIG. 2**
 [51] **Int. Cl.**..... **C23b 5/10; C23b 5/46**
 [58] **Field of Search**..... **204/55 R, 55 Y, 43 Z, 44, 204/114**

[57] **ABSTRACT**

Non-cyanide, alkaline electroplating baths for bright zinc plating containing quarternized polymeric condensates of alkylene polyamines and 1,3-dihalo-2-propanol as grain refiners preferably in admixture with aldehyde type brighteners and mercapto substituted heterocyclic compounds capable of producing the bright, fine grained deposits over a broad current density range.

[56] **References Cited**

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30 Claims, No Drawings

ALKALINE BRIGHT ZINC PLATING

This invention relates to zinc electroplating and more particularly to alkaline bright zinc electroplating conducted in an aqueous bath free from cyanides.

Zinc electroplating has conventionally been conducted in a plating bath employing alkali metal cyanide salts such as sodium cyanide as a complexing agent to achieve the desired plating operation and to produce bright, smooth grained zinc deposits. However, because of the toxicity of cyanides and more recently because of the environmental considerations adversely affecting the economic employment of these cyanides other plating methods have been sought which avoid and do not require the use of these cyanide salts.

A wide variety of procedures and additives have been suggested for use in zinc plating for the purpose of avoiding cyanides. Most of these employ an alkaline plating bath system utilizing an alkali metal or sodium zincate combined with additives to achieve the desired bright zinc deposit with a smooth or fine grained, mirror-like surface. Foremost of these various additives which have been suggested and employed in these highly alkaline bath systems are materials generally classified as polyamines, and especially the relatively simple polyamines such as alkylene diamines for example ethylenediamine which reportedly serve as complexing agent replacements for the cyanide salts. These polyamines are usually employed with a variety of other additives conventionally employed in zinc plating, for example, grain refiners, brighteners and throwing agents.

While these alkaline systems employing the polyamine type additives do avoid the use of substantial amounts of cyanides, they generally have not been overly successful, however, and the zinc plating deposits typically produced have a number of deficiencies such as a dull or granular finish which render them of little commercial value. Such systems, moreover, typically also lack the desired capability of producing a suitable smooth, mirror-like plating deposit over a broad current density range and generally are especially ineffective at the lower current density ranges conventionally used in commercial plating. In addition, a substantial number of these systems for effective operation still require the presence of some cyanide, although at a reduced concentration, which in effect only minimizes but does not eliminate the problems associated with the use of cyanide salts.

Various other alkaline bath systems have been suggested which also utilize polyamines although generally of more complex nature, and usually in polymeric form and/or interacted with other compounds such as aldehydes and heterocyclic compounds, for example, a reaction product or a polymeric condensate of an alkylene polyamine and an epihalohydrin. While certain of these have been somewhat successful they generally suffer from one or more deficiencies in that the deposits obtained do not have the degree of brightness or luster desired or a smooth, fine-grained surface necessary for most commercial application. Moreover, certain of these systems generally are not capable of producing fine-grained, mirror-like deposits over a broad current density range and more specifically at the low current density range of from 0 to 20 to 40 amperes per square foot. This limitation or inability to achieve desirable plating over a broad current density range substantially restricts the usefulness of these systems and generally

limits their application to plating objects which are relatively uniform in shape and configuration thus precluding their use in plating objects which are irregular or in barrel plating where the plating must be conducted over a broad current density range.

It has now been discovered, however, that certain quarternized polymeric condensates of alkylene polyamines and 1,3-dihalo-2-propanol may be employed in a non-cyanide zinc electroplating bath, typically also with brighteners, to produce fine grained, bright deposits. It has been further found that when such polymeric condensates are employed with certain mercapto substituted heterocyclic compounds the desired bright, mirror-like deposit is achieved over a broad current density range including the critical low current densities.

Accordingly, an objective of this invention is to provide an alkaline, bright zinc plating bath which does not require or utilize cyanide salts. Another object is to provide such a bath employing a quarternized polymeric condensate of an alkylene polyamine and a 1,3-dihalo-2-propanol capable of producing a smooth, fine-grained deposit. A further object is to employ such polymeric condensate with brightening agents to achieve bright, mirror-like deposits. A still further object is to provide such a bath with the addition of certain mercapto substituted heterocyclic compounds capable of producing the bright, fine-grained zinc deposit over a broad current density range. Still another object is to provide a method of zinc electroplating employing such improved bath and capable of effectively operating in a commercially desirable manner completely free of any cyanides. These and objects of this invention will be apparent from the following further detailed description thereof.

The electroplating of zinc in an aqueous alkaline bath is effected in accordance with this invention by adding a quarternized polymeric condensate of an alkylene polyamine and a 1,3-dihalo-2-propanol to such bath so as to obtain smooth, fine-grained deposits. In general, these polymeric condensates are produced by reacting the alkylene polyamine and dihalopropanol in a condensation reaction to produce a substantially uncross-linked, aqueous soluble polymeric condensate. In accordance with this invention the polymeric condensate is employed as a quarternary salt which involves a further reaction of the polymeric condensate with a suitable quarternizing agent.

The dihalopropanols which may be interacted with the alkylene polyamines include 1,3-dibromo-2-propanol; 1,3-diiodo-2-propanol or 1,3-dichloro-2-propanol with the 1,3-dichloro-2-propanol being particularly preferred in most instances.

The alkylene polyamines which may be reacted with the dihalopropanol have at least one tertiary amino group such as dimethylaminopropylamine (N,N-dimethylpropylenediamine), diethylaminopropylamine (N,N-diethylpropylenediamine), N-aminopropylmorpholine, dimethylaminoethylamine, diethylaminoethylamine, N-aminopropyldiethanolamine, or N-methyliminobispropylamine.

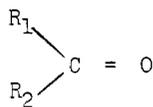
Other alkylene polyamines containing at least one tertiary amino group and at least one secondary amino group may also be employed such as N,N-dimethyl-N'-methylpropylenediamine; N,N-dimethyl-N'-methyl ethylenediamine; or N,N-diethyl-N'-ethylethylenediamine.

Of the various alkylene polyamines which may be condensed with the dihalopropanol either alone or in admixture, the lower alkylene polyamines, where the alkylene bridge contains from 2 to 5 carbon atoms and where the tertiary amino group is substituted with alkyl groups of from 1 to about 5 carbon atoms, are preferred particularly when the dihalopropanol is 1,3-dichloro-2-propanol with a particularly preferred alkylene polyamine being dimethylaminopropylamine.

In preparing the desired polymeric condensates for use in accordance with this invention, the alkylene polyamine should be condensed with the dihalopropanol in a mol ratio of from about 0.5 to 1.75 mols of the amine per one mol of the dihalopropanol. Usually a more limited range is preferred, however, and when employing the preferred 1,3-dichloro-2-propanol the mol ratio of the polyamine to 1,3-dichloro-2-propanol advantages ranges from about 0.8 to about 1.5 mols of polyamine to one mol of dichloropropanol. Usually the condensation is effected according to conventional procedures over a period of about 1 to 3 hours with the temperature being maintained between 15° to 40°C.

As indicated, the polymeric condensate employed in accordance with this invention to effect the grain refinement of the deposit is utilized as a quarternary salt. This quarternization may be effected according to conventional procedures and suitable quarternized agents for the polymeric condensates are the lower alkyl halides such as methyl-chloride, -bromide, or -iodide, ethyl-chloride, -bromide or -iodide, or alpha chloroglycerol, diloweralkyl sulfates such as dimethyl-, diethyl-, dipropyl- or dibutyl-sulfates; lower alkyl esters of aryl sulfonates such as methyl toluene sulfonate and methyl benzene sulfonate; alkylhalo esters such as ethyl-chloroacetate; alkylene halohydrins such as ethylenechlorohydrin or alkylene oxides such as ethylene oxide and propylene oxide.

While the polymeric condensates in accordance with this invention produce a grain refined or smooth deposit, such deposit is not usually of the brightness or luster desired in most instances and accordingly, a preferred embodiment of this invention is to employ brightening agents together with the polymeric condensate so as to produce both smooth grained and bright deposits. These brighteners include those materials conventionally employed in zinc plating and typically contain a carbonyl group of aldehyde functionality which generally may be represented by the formula



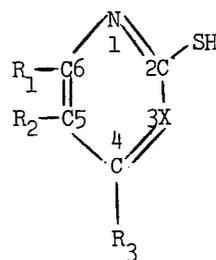
wherein R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl of 1 to about 10 carbon atoms, aryl and heterocyclic oxygen and sulfur containing radicals and include, for example, m-hydroxy benzaldehyde, p-hydroxy benzaldehyde, piperonal, o-hydroxy benzaldehyde (salicylaldehyde), vanillin, veratraldehyde, benzaldehyde, β -methoxy propionaldehyde, furfural, glyceraldehyde and anisaldehyde, thiophene-2-aldehyde.

Of the various aldehyde materials which may be employed, the aryl aldehydes and particularly the benzaldehydes such as anisic aldehyde (p-

methoxybenzaldehyde) or vanillin (p-hydroxy-methoxybenzaldehyde) or various combinations thereof are preferred. These aldehydes brighteners may be employed in the bath of this invention as addition products with such materials as sodium bisulfite to increase their alkaline solubility if desired.

Employment of these brightening agents in most instances substantially improves the luster or brightness of the deposit. However, this frequently only occurs at the higher current density ranges generally above about 40 or more usually above about 20 amperes per square foot up to about 100 to 200 amperes per square foot. In accordance with this invention, certain mercapto substituted heterocyclic compounds may be and are preferably employed in combination with the polymeric condensate and brightener so as to achieve the bright, fine-grained deposit over a broad current density range and particularly at the lower current density ranges conventionally employed in most commercial plating operations and generally below about 40 or more usually about 20 down to 0 amperes per square foot.

These mercapto substituted heterocyclic compounds employable with the polymeric condensates and brighteners in accordance with this invention may generally be described as ortho mercapto substituted pyridines or pyrimidines, that is where the mercapto substituent is positioned on the 2 ring carbon atom. These mercapto substituted pyridines or pyrimidines may be represented by the following general formula:



or the tautomers thereof wherein X is selected from the group consisting of N R_{C-R4} wherein R_4 is selected from the group consisting of hydrogen, hydroxy, mercapto and acyl and wherein R_1 , R_2 and R_3 are each independently selected from the group consisting of hydrogen, hydroxy, mercapto, acyl, amino, alkyl, carboxy and carbamoyl.

Examples of mercapto substituted heterocyclic compounds which may be employed either individually or in admixture according to this invention includes pyridines, that is where X of the formula is $C-R_4$ and pyrimidines, that is, where the X is nitrogen. These compounds may be substituted as indicated in the formula and where any of the various R substituents is alkyl or acyl such substituents can contain from 1 to about 5 and more preferably from 1 to 3 carbon atoms such as methyl, ethyl, or propyl or where acyl such groups as formyl, acetyl or propionyl. Typical examples of these compounds include pyridines such as

- 2-mercaptopyridine;
- 2-mercapto-3-acetylpyridine;
- 2-mercapto-3-hydroxypyridine;
- 2,3-dimercaptopyridine;
- 2,3-dimercapto-6-acetylpyridine;

2-mercapto-4-hydroxypyridine;
 2,4-dimercaptopyridine;
 2-mercapto-4,5-dihydroxypyridine;
 2-mercapto-4-aminopyridine;
 2,6-dimercapto-3-acetylpyridine;
 2-mercapto-5-methylpyridine;
 2-mercapto-5-aminopyridine;
 2-mercapto-5-hydroxypyridine;
 2-mercapto-6-hydroxypyridine;
 2-mercapto-6-carbamoylpyridine;
 2,6-dimercapto-3-carboxypyridine; or
 2-mercapto-5,6-diethylpyridine; and
 pyrimidines such as 2-mercaptopyrimidine;
 2,6-dimercaptopyrimidine;
 2-mercapto-4-aminopyrimidine;
 2-mercapto-4,6-dihydroxypyrimidine;
 2-mercapto-4-ethylpyrimidine;
 2-mercapto-4-hydroxy-6-methylpyrimidine;
 2-mercapto-6-acetylpyrimidine;
 2-mercapto-4-hydroxy-5,6-diethylpyrimidine;
 2,4-dimercaptopyrimidine; or
 2-mercapto-6-hydroxypyrimidine

As indicated, the mercapto pyridines or pyrimidines represented by the above formula may also in many instances exist in tautomeric or isomeric form. For example, one of the preferred compounds according to this invention is 2-thiouracil and such compound can exist as 2-mercapto-4-hydroxypyrimidine or 2-thio-4-oxopyrimidine or as an intermediate tautomer as 2-thioxo-4-hydroxypyrimidine and 2,4-dithiouracil can exist as 2,4-dimercaptopyrimidine or 2,4-dithiopyrimidine. All of these tautomeric compounds are accordingly embraced within the compounds which may be used in accordance with this invention as represented by the above formula.

Of the various compounds which may be employed according to the invention the preferred compounds are pyridines or pyrimidines of the formula where the mercapto group is substituted in the 2 ring position and generally also with a hydroxy group in one of the 4 or 6 position. Within this preferred class of compounds the pyrimidines are especially preferred and examples of compounds having particular utility in the bath of this invention are 2-thiouracil and 2-mercapto-4,6-dihydroxypyrimidines.

The electroplating bath of this invention may be prepared and operated in accordance with the general procedures conventionally employed for alkaline bright zinc plating. Typically the bath is prepared as an aqueous solution and rendered alkaline by the addition of a suitable alkaline material such as alkali metal hydroxide or carbonate for example sodium or potassium hydroxide. The quantity of alkaline material added should be capable of dissolving the zinc compound employed as the source of the zinc ion in the bath and generally should be in excess of that required to create the desired alkali metal zincate such as sodium zincate as well as to maintain the pH of the solution alkaline and generally above 7 and preferably above 14.

The source of the zinc ion in the bath can be varied and generally any of the zinc compounds conventionally employed in alkaline bright zinc baths may be utilized. Typically such compounds include zinc salts or oxides such as zinc sulfate, zinc acetate or zinc oxide with the zinc sulfate generally being preferred. The amount of zinc in the bath can be varied depending upon the desired results and operating condition but

generally is maintained within the range of from about 3 to about 15 grams per liter.

The quantity of the quarternized polymeric condensate utilized in the bath will in general be a function of the particular brightener and mercapto substituted compound employed as well as the particular polymeric condensate utilized. Typically, however, when employing polymeric condensates of such alkylene polyamines as dimethylaminopropylamine and 1,3-dichloro-2-propanol, the quantity of the condensate in the bath should range from about 0.25 to about 5 grams per liter with a more limited range of from about 0.3 to about 0.75 grams per liter being preferred especially when used in combination with the preferred mercapto compounds.

The quantity of the mercapto substituted compound employed in the bath in similar fashion is also interrelated to the specific polymeric condensate and aldehyde brightener employed as well as the particular mercapto substituted compound or combination of compounds utilized. Generally, however, the mercapto compound is maintained in the bath within the range of from about 0.01 to about 0.2 grams per liter with a more limited range being preferred of from about 0.025 to about 0.075 grams per liter particularly when employing such preferred mercapto compounds such as 2-thiouracil or 2-mercapto-4,6-dihydroxypyrimidine.

The brighteners used in combination with the quarternized polymeric condensate typically will be present in the bath within the ranges conventionally utilized for alkaline zinc plating baths. Typically this will range from about 0.1 to about 5 grams per liter with a more limited range from about 0.2 to about 0.5 grams per liter being more advantageously employed particularly when employing the preferred benzaldehyde-type brighteners.

The electroplating of zinc conducted in accordance with the method of this invention is effected in conventional fashion basically by passing a direct current from a zinc anode through the aqueous alkaline, non-cyanide bath of this invention containing essentially the polymeric condensate, brightener and mercapto substituted compound to the desired cathode article which is to be electroplated with the zinc. This method may be conducted at temperatures from about 60° to about 100°F. The current densities employed may range from above 0 to about 200 amperes per square foot with a more limited range of from about 0.5 to about 90 amperes per square foot being satisfactory for most plating operations.

The plating bath of this invention may contain further additives of the type conventionally employed in alkaline zinc electroplating baths and includes such materials as polyvinyl alcohols, gelatine, polyether alcohols, polyesters, glue and peptone. Of these various materials polyvinyl alcohol or its various derivatives are especially preferred and appear to greatly enhance the mirror-like deposits of the platings produced in accordance with this invention. When so employed, these polyvinyl alcohols should be utilized in the bath within a range of from about 0.02 to about 0.2 grams per liter.

The following examples are offered to illustrate the plating bath and electroplating methods of this invention.

6. The electroplating bath of claim 3 wherein the heterocyclic compound is 2,4-dimercaptopyrimidine.

7. The electroplating bath of claim 3 wherein the heterocyclic compound is 2-mercapto-4-amino-6-hydroxypyrimidine.

8. The electroplating bath of claim 3 wherein the heterocyclic compound is 5-carboxy-2-mercaptopyridine.

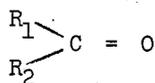
9. The electroplating bath of claim 3 wherein the heterocyclic compound is 3-hydroxy-2-mercaptopyridine.

10. The electroplating bath of claim 3 wherein the heterocyclic is 2-mercapto-4,6-dihydroxypyrimidine.

11. The electroplating bath of claim 3 wherein the heterocyclic compound is 2-thiouracil and the aldehyde is a mixture of anisic aldehyde and vanillin.

12. The electroplating bath of claim 3 wherein the heterocyclic compound is 2-mercapto-4,6-dihydroxypyrimidine and the aldehyde is a mixture of anisic aldehyde and vanillin.

13. The electroplating bath of claim 2 wherein the brightener is an aldehyde having the formula



wherein R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl, aryl and heterocyclic oxygen and sulfur containing radicals.

14. The electroplating bath of claim 13 wherein the aldehyde brightener is a benzaldehyde.

15. The electroplating bath of claim 13 wherein the aldehyde is vanillin.

16. The electroplating bath of claim 13 wherein the aldehyde is anisic aldehyde.

17. The electroplating bath of claim 13 wherein the aldehyde is p-hydroxy-benzaldehyde.

18. The electroplating bath of claim 1 wherein the bath contains from about 0.01 to about 0.2 grams per liter of a heterocyclic compound selected from the group consisting of a 2-mercapto substituted pyridine or pyrimidine.

19. The electroplating bath of claim 18 wherein the

polymeric condensate and heterocyclic compound are present in the bath with the ranges of from about 0.3 to about 0.75 and from about 0.025 to about 0.075 grams per liter, respectively.

20. The electroplating bath of claim 1 wherein the source of the zinc ions is a water soluble zinc salt.

21. The electroplating bath of claim 20 wherein the zinc salt is zinc sulfate.

22. The electroplating bath of claim 1 wherein in the polymeric condensate the dihalopropanol is 1,3-dichloro-2-propanol.

23. The electroplating bath of claim 1 wherein in the polymeric condensate the alkylene polyamine has a tertiary amino group substituted with alkyl groups of from 1 to 5 carbon atoms and the alkylene bridge contains from about 2 to about 5 carbon atoms.

24. The electroplating bath of claim 1 wherein in the polymeric condensate the alkylene polyamine is dimethylaminopropylamine.

25. The electroplating bath of claim 1 wherein in the polymeric condensate the alkylene polyamine is dimethylaminopropylamine and the dihalopropanol is 1,3-dichloro-2-propanol and the mol ratio of the polyamine to the 1,3-dichloro-2-propanol ranges from about 0.8:1 to about 1.5:1, respectively and the condensate is substantially uncrosslinked.

26. The electroplating bath of claim 1 wherein the polymeric condensate is present in the bath within the range of from about 0.3 to about 0.75 grams per liter.

27. The electroplating bath of claim 1 wherein the bath contains a polyvinyl alcohol within the range of from about 0.02 to about 0.2 grams per liter.

28. The electroplating bath of claim 1 wherein the pH is above 14.

29. In a process for the electroplating of zinc the improvement comprising effecting the electroplating with the alkaline bath of claim 1 free from any cyanide.

30. The process of claim 29 wherein the plating is conducted at a temperature of from about 60° to about 100°F and at a current density of up to 200 amperes per square foot.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,886,054 Dated May 27, 1975

Inventor(s) Joseph R. Duchene and Phillip J. DeChristopher

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 46

"R_{c-r}4" should be deleted and "and C-R₄" inserted in its place.

Column 8, line 39

"5.0" should be deleted and "0.5" inserted in its place.

Signed and Sealed this

fifth Day of *August* 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks