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ZINC CYANIDE PLATING BATH

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The present invention is directed to an improved alkaline cyanide plating bath and the method of making the same. The invention is particularly directed to the use of a catalytic ingredient in alkaline cyanide plating baths for the electrolytic deposition of zinc and zinc alloys such as copper-zinc alloys.

It is an object of the present invention to provide an improved alkaline cyanide plating bath for the electrolytic deposition of zinc and zinc alloys in which a catalytic ingredient comprising a reaction product of hexamethylene tetramine and salicylic acid is used.

It is an object of the present invention to provide an improved plating bath and a method of making the same in which zinc and zinc alloys are deposited electrolytically from the bath, the bath containing an anode corroder and a smoothing and grain refining agent.

It is an object of the present invention to provide an improved alkaline cyanide plating bath and the method of making the same in which a catalytic ingredient is used, the catalytic ingredient being an anode corroder as well as a smoothing and grain refining agent.

It is an object of the present invention to provide an improved aqueous alkaline cyanide plating bath comprising a zinc or zinc alloy cyanide, an alkali metal hydroxide, an alkali metal cyanide, an alkali metal tartrate, and a reaction product of salicylic acid and hexamethylene tetramine.

These and other objects will be apparent from the specification that follows and from the appended claims.

The present invention provides an aqueous alkaline cyanide plating bath in which a reaction product of salicylic acid and hexamethylene tetramine (also called hexamine) is used as an anode corroder and a smoothing and grain refining agent for the electrolytic deposition of zinc and zinc alloys. In accordance with the present invention, the plating bath deposits a fine grained, smooth coating in which any sandpaper effect is eliminated or reduced substantially and in which the cathode performance is improved.

The amount of smoothing and grain refining agent generally used to obtain the above improvement may be in the range of about 0.1 to 7.0 ounces per gallon (or about 0.75 to 53 grams per liter) of the reaction product of salicylic acid and hexamine—although, for best results, it is preferred that at least about 0.4 ounce and up to as high as about 4 ounces per gallon or more, sometimes even as high as 6 ounces, of the above described smoothing agent be used.

Suitable plating bath formulations, including the general ranges and preferred ranges of the above described reaction product used as an anode corroder and a smoothing and grain refining agent, are set forth below in Table 1.

As it will hereinafter be described in detail, the above described smoothing and grain refining agent or reaction product is an alkaline solution made by reacting hexamine and salicylic acid at pH of 2½ to 5½ and thereafter further reacting the acidic reaction product with an alkali hydroxide to provide the final solution. Thus, the final solution contains amino derivatives (apparently ortho and para) of salicylic acid and hexamine as well as unreacted starting ingredients, etc., which act as buffers and the like to aid the catalytic activity of the amino derivatives.

As previously indicated, the above described amino derivatives apparently provide most of the catalytic activity and, thus, may be considered the catalytic ingredient. The amino derivatives, as the catalytic agent, are generally

present in an amount of about 0.9% to about 67% by weight of the total alkaline solution used as the smoothing and grain refining agent. Thus, the amino derivatives are generally present in the range about 0.0009 to 4.7 ounces per gallon (or about 0.6 to 35 grams per liter) of the plating bath. The preferred range for the amino derivatives, as previously indicated for the final alkaline solution, is about 0.1 to 1 ounce per gallon. As seen from the above discussion, it is possible, according to the present invention, to provide a concentrated solution of the above described amino derivatives and add other materials such as tartrates and alkali metal hydroxides to provide an alkaline solution for use as a smoothing and grain refining agent as well as an anode corroder. In any event however, the total amount of amino derivatives of salicylic acid must be within the above described amounts to have an effective plating bath additive.

TABLE 1

Bath

Ingredients	General Range (Oz. per gal.)	Preferred Range (Oz. per gal.)
Cyanide (Zn or, for depositing zinc alloy, Zn+Cu)	3 to 26	6 to 9
Alkali hydroxide (NaOH)	1 to 20	3 to 9
Alkali Cyanide (potassium cyanide)	4½ to 26	10 to 15
Reaction product of salicylic acid and hexamine	0.1 to 7.0	0.4 to 4
Alkali tartrate (potassium tartrate)	0.0 to 7.0	0.8 to 2.0

In accordance with the present invention, the cyanide (as indicated in Table 1) may be zinc cyanide or a combination of zinc and copper cyanide, the combination being used to deposit a zinc-copper alloy, the zinc cyanide salt preferably being a substantial portion say, about at least 10% of the metal cyanide content. While the alkali hydroxide may be potassium hydroxide, is preferred that sodium hydroxide be used as indicated in Table 1.

As to the alkali cyanide, it is highly preferred that potassium cyanide be used although sodium cyanide can be used. As indicated above the alkali cyanide is preferably used in amounts as low as 5 or 10 oz. per gal. up to about 15 oz. per gal.

Returning to the reaction product of salicylic acid and hexamine which has been found to be an outstanding anode corroder as well as an excellent smoothing and grain refining agent, the reaction product is preferably made by reacting the hexamine and salicylic acid at about 155° up to as high as 170° F. to 175° F. in an aqueous solution. However, generally about 125° to 190° F. may be employed as the reaction temperature range to obtain a useful product. Also a pH of about 2½ to 5½ and preferably about 4.2 to 4.8 must be used with the above temperature range to obtain a commercially useful product.

The reaction time should be at least 4 hours, and, better, at least 8 hours. In general, the time of reaction may be varied between 8 to 72 hours, the best catalytic ingredient solution being usually obtained with a reaction time of about 20 to 40 hours.

During the reaction, the amount of each of the ingredients used is important. Generally, the reaction is made by reacting about one mole of hexamine with about 1 to 4 moles of salicyclic acid to provide sufficient amino derivatives although it is preferred that about 2½ up to as high as about 3¼ to 3½ moles of salicyclic acid be used under the above reaction conditions just described.

After the reaction has completed and all the salicylic acid has been dissolved and the gassing has ceased, an alkali metal hydroxide such as sodium hydroxide and

preferably potassium hydroxide should be added for further reaction which brings the pH of the solution up to about 8.5 to 12. Again, while a pH of 12 may be employed for further reaction with the KOH, a pH of 9½ or 10½ up to 11½ is highly preferred with the best results being obtained with a narrow pH range of about 9.8 to 10.5 or slightly higher, up to about 11.6. It has been found that when the pH is about 12, the reaction product is different and is generally not acceptable as an additive for a plating bath containing copper. Likewise, a pH of 8 or less does not provide a satisfactory material, its stability not being enough to justify its use as a catalytic ingredient in plating baths.

As to the amount of potassium hydroxide or other alkaline metal hydroxide added, it is preferred that around 2½ to 3½ moles of potassium hydroxide be used, although generally about 2¼ to 4 moles may be employed in accordance with the present invention. Along with the above amount of KOH or other alkali metal hydroxide, it is preferred that the reaction be continued at about 70° to 190° F. for at least 4 hours and preferably about 8 to 72 hours.

Thus, on the basis of 1200 lbs. of salicylic acid used as one of the starting ingredients, generally 300 to 450 lbs. of hexamine may be used, although the preferred amount is about 380 to 420 lbs. Likewise, the preferred amount of potassium hydroxide is about 380 to 420 lbs. The best results are obtained using about 400 lbs. of KOH, although generally about 300 to 500 lbs. may be used with the 1200 lbs. of salicyclic acid to obtain a reaction product that is useful commercially.

Also, in the above process, it is highly desirable to let the acidic reaction solution stand about 8 to 72 hours and preferably 16 to 32 hours before further reacting the solution with the potassium hydroxide.

While adding the potassium hydroxide in accordance with the present invention, it is also preferred that about 1 to 3 moles of an alkaline metal salt of tartaric acid be used, the preferred additive being potassium tartrate although sodium tartrate and potassium bitartrate may also be used. On the basis of starting with 1200 parts by weight of salicyclic acid and 400 to 500 parts of hexamine, generally as low as about 400 to 600 parts up to as high as 1600 to 2000 parts by weight of potassium tartrate may be added although for best results about 1000 to 1500 parts should be used.

During the performance of the process steps just described, it is preferred that the potassium hydroxide and tartrate be added as a premixed solution of about 300 to 500 lbs. of potassium hydroxide and 600 to 1500 lbs. of water along with about 800 to 1000 up to 1200 lbs. of cream of tartar or potassium tartrate.

While not desiring to be strictly held to a particular theory, it is probable that formation of one or more of the derivatives of salicylic acid (including the para-amino derivatives) provide the solution with its anode corroding activity and its grain refining and smoothing ability. Apparently, as previously indicated, derivatives (ortho and para) are formed in which the following groups are attached to the benzene ring of the salicylic acid: amino, carbonyl followed by an amino group; —NHR and $—NR_2$ where R is preferably methyl or even ethyl or where R is methylol. Apparently a minor portion of the mixture is p-amino salicylic acid and it is preferred that only a small portion be the p-amino salicylic acid since it appears that more than 10% of p-amino salicylic acid in the mixture of derivatives provides too active a solution. Thus, the above described reaction condition and process steps should be closely followed to obtain a desirable mixture of derivatives.

Generally the amount of water used when the hexamine and salicylic acid are first reacted is about 30 to 90 moles, and preferably 40 to 60 moles, although, as little as 20 moles or even as high as 90 to 95 moles or more can be used per mole of hexamine.

In another variation of the process of making the reaction product, the acidic reaction product of salicylic acid and hexamine is reacted with a limited amount of potassium hydroxide, about 150 to 250 lbs. based on 1200 lbs. of salicylic acid. Also, unexpectedly, a small amount of hexamine added before the KOH is added and reacted with the acidic reaction product provides an improved catalytic solution. This solution (made by reacting the acidic product with hexamine and the then KOH) is an improved anode corroder, an excellent smoothing and grain refining agent, and efficiency at the cathode is also improved.

When adding the limited amount of additional hexamine (.05 to 0.3 mole based on one mole of hexamine starting material), about 5 to 25 moles and preferably 10 to 18 moles of water is used to make a premixed solution of the additional hexamine and the limited amount of caustic, namely the 1 to 1.9 moles of KOH or other alkali metal hydroxide.

As before discussed, to help stabilize the resultant solution and to increase its grain refining activity, generally about ½ to 3⅓ moles and preferably about 1½ to 2½ moles of potassium tartrate or other alkali metal tartrate is also added to the solution.

The solution made with the double use of hexamine provides a product improvement over the process in which salicylic acid and hexamine are reacted at temperatures of 125°–190° F. at a pH of 2½ to 5½ for about 16 to 32 hours. At the end of this time, according to the second process just described, the solution is further reacted with only about 1.2 to 1.9 of a mole of KOH in contrast to the former reaction in which 2 to 4 moles of KOH are used.

It has been found, surprisingly, that the relatively pure para-amino salicylic acid does not work well as an anode corroder and a smoothing and grain refining agent; evidently its catalytic action is too great and violent to make a good addition to a plating bath. However, when it is diluted with unreacted hexamine and some of the para-amino or other amino derivatives of salicylic acid formed by the above described reactions, the reaction solution is an excellent anode corroder and a fine smoothing and grain refining agent.

While the amounts of an anode corroder and a smoothing and grain refining agent have been expressed in ounces per gallon, they may also be expressed in grams per liter. Thus, the reaction product of salicylic acid and hexamethylene tetramine is preferably present in amounts of about 3 to 30 grams per liter.

The following examples are used to illustrate the present invention and not to limit it in any way.

EXAMPLE 1

A reaction product of salicylic acid and hexamine was made by mixing 1200 lbs. of salicylic acid and 400 lbs. of hexamethylene tetramine (hexamine) in an aqueous solution of 300 gallons or about 2490 lbs. of water. The salicylic acid and hexamine were heated at a temperature of about 160° F. for a period of 24 hours to produce a para-amino derivative of salicylic acid. The temperature of the reaction was held within 3° of 160° F. at a pH of 4.3 to 4.5.

The batch was vigorously stirred for the first 15 minutes and thereafter the reaction allowed to proceed for 24 hours with intermittent stirring. The reaction mixture was allowed to stand for 24 hours, the 24-hour period including about 8 hours that the solution took to cool to room temperature.

Thereafter, 400 lbs. of potassium hydroxide was added to the solution with stirring to bring the pH up to 11½ and the reaction continued for 8 hours at 120° F.

The resultant solution was found to be an excellent anode corroder and a good smoothing and grain refining agent for zinc and zinc-alloy cyanide plating baths.

EXAMPLE 2

A zinc cyanide plating bath was made using the following ingredients.

Ingredients:	Ounces per gallon
Zinc cyanide	9
Sodium hydroxide	8
Potassium cyanide	6
Potassium tartrate	0.1
Reaction product of salicylic acid and hexamine prepared as described in Example 1	1.0

Steel sheets were plated in the above described bath using a bath temperature of 100° F. and using a current density of 30 amperes per sq. ft. on the anodes. The resultant coating was smooth, evenly distributed throughout the low and high current density ranges, fine grained and no sandpaper effect was visible. The anodes were smooth and no loose particles were found to be present.

Steel plates were also plated in a control bath containing all the ingredients of the bath just described except for the reaction product of salicylic acid and hexamine. The resultant deposit was uneven, coarse grained in spots, dull in most areas and generally poor.

EXAMPLE 3

A zinc-copper alloy plating bath was made up using the same ingredients as described in Table 1 except that the cyanide of zinc was replaced in part by copper cyanide, there being 6 parts of zinc cyanide and three parts of copper cyanide present in the bath of Example 3, making a total of 9 ounces per gallon of metal cyanide. The plating procedure employed was similar to that of Example 2, the bath temperature being 80° F. and the amperage per sq. ft. on the anodes being 40. The resultant coating was semi bright, fine grained, smooth and no sandpaper effect was visible. The reaction product of salicylic acid and hexamine was an excellent anode corroder and, as indicated, a fine smoothing and grain refining agent.

EXAMPLE 4

A bath was made up using 8 ounces per gallon of zinc cyanide, 5 ounces per gallon of sodium hydroxide, 5 ounces per gallon of potassium cyanide and 5 ounces per gallon of potassium bitartrate, and 8 ounces per gallon of a reaction product of salicylic acid and hexamine. The reaction product was made as described in Example 1 except 450 lbs. of hexamine was used and the reaction temperature was 170° F. The resultant coating, when deposited from the bath with a current density of 40 ASF and a temperature of 150° F. was not satisfactory, the surface being streaked and dull in spots. Apparently there was too much catalytic action to form a good zinc coating.

Zinc was deposited from a bath made from the same ingredients as above described (Example 4) and using the same amounts thereof except that 2 ounces per gallon of the reaction product of salicylic acid and hexamine was used. Again the current density was 40 ASF and the bath temperature was 90° F. In contrast to the bath containing 8 ounces per gallon of the reaction product; the bath with 2 ounces per gallon of the catalytic agent produced a commercially satisfactory coating, the coating being smooth and fine grained.

In the above examples, the temperatures of the zinc and zinc-alloy plating bath may be generally from about 68° to 178° F. in order to provide good coatings. The current density may be varied all the way from slightly above 0 to as high as about 50 amperes per sq. ft. on the anodes.

In the above working examples, equivalent ingredients, as described in the previous part of the specification, may be used in whole or part for the ingredients actually used to provide similar results. For instance, sodium hydroxide can be substituted for potassium hydroxide in the baths shown in Examples 2, 3 and 4. Also, sodium

tartrate can be substituted for potassium tartrate. In addition, the reaction product made (as previously described) from a reaction temperature range from about 125° F. to 190° F. and at a pH of about 2½ to 5½ and then reacted with alkali metal hydroxide can be used in place of the particular reaction product of salicylic acid and hexamethylene tetramine used in the above examples to provide similar results.

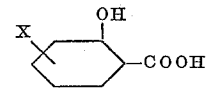
Also, the reaction product of salicylic acid and hexamine made with the double use of hexamine and a limited amount of alkali metal hydroxide can be used as a part or all of the reaction product of salicylic acid and hexamine employed in the examples to provide nearly similar results, the above reaction product being a good anode corroder and producing even a denser plate with improved cathode efficiency.

It is to be understood that other modifications of this invention may be made without departing from the spirit and scope thereof.

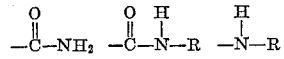
What is claimed is,

1. An aqueous alkaline cyanide plating bath comprising about 3 to 26 ounces per gallon of a cyanide of a metal comprising zinc cyanide, about 1 to 20 ounces per gallon of an alkali metal hydroxide, about 4½ to 26 ounces per gallon of an alkali metal cyanide, up to about 7.0 ounces per gallon of an alkali metal tartrate, and about 0.1 to 7.0 ounces per gallon of a reaction product of salicylic acid and hexamethylene tetramine.

2. An aqueous alkaline cyanide plating bath comprising about 3 to 26 ounces per gallon of a cyanide of a metal comprising zinc cyanide, about 1 to 20 ounces per gallon of an alkali metal hydroxide, about 4½ to 26 ounces per gallon of an alkali metal cyanide, up to about 7.0 ounces per gallon of an alkali metal tartrate, and about 0.1 to 7.0 ounces per gallon of a reaction product of salicylic acid and hexamine, the reaction being at a temperature of about 125° to 190° F. at a pH of about 2½ to 5½ for at least about 4 hours, and the product thereafter reacted with an alkali metal hydroxide and the final solution having a pH of about 8½ to 12, said reaction product of salicylic acid and hexamine having the following general formula:

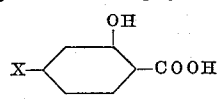


where X is a member of the group consisting of $-NH_2$,

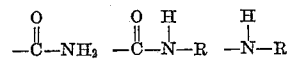


and $-NR_2$, where R is a member of the group consisting of alkyl and alkylol.

3. An aqueous alkaline cyanide plating bath comprising about 3 to 26 ounces per gallon of a cyanide of a metal comprising zinc cyanide, about 1 to 20 ounces per gallon of an alkali metal hydroxide, about 4½ to 26 ounces per gallon of an alkali metal cyanide, about 0.01 to 7.0 ounces per gallon of an alkali metal tartrate, and about 0.1 to 7 ounces per gallon of a solution containing about 0.0009 to 4.7 ounces per gallon of a derivative of salicylic acid having the following general formula:



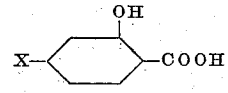
where X is a member of the group consisting of $-NH_2$,



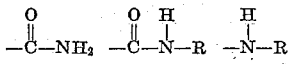
and $-NR_2$, where R is a member of the group consisting of alkyl and alkylol.

4. An aqueous alkaline cyanide plating bath comprising about 3 to 26 ounces per gallon of a cyanide of a metal of the group consisting of zinc and a zinc alloy, about 1 to 20 ounces per gallon of an alkali metal hydroxide,

about 4½ to 26 ounces per gallon of an alkali metal cyanide, and about 0.11 to 14 ounces per gallon of a solution having a pH of about 9 to 12, the solution comprising an alkali metal tartrate, an alkali metal hydroxide and a derivative of salicylic acid which is a reaction product of salicylic acid and hexamine at a pH of about 4.1 to 4.6 and a temperature of about 155 to 170° F. for about 8 to 72 hours to provide a reaction mixture and the mixture further reacted with an alkali metal hydroxide at about 70° to 190° F. for at least about 4 hours, said reaction products of salicylic acid and hexamine having the following general formula:

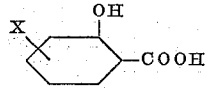


where X is a member of the group consisting of —NH_2,

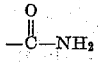


and —NR_2, where R is a member of the group consisting of alkyl and alkylol.

5. An aqueous alkaline cyanide plating bath comprising about 3 to 26 ounces per gallon of zinc cyanide, about 1 to 20 ounces per gallon of an alkali metal hyroxide, about 4½ to 26 ounces per gallon of an alkali metal cyanide, about 0 to 7.0 ounces per gallon of an alkali metal tartrate, and about 0.1 to 7.0 ounces per gallon of a reaction product of salicylic acid and hexamine, said reaction product of salicylic acid and hexamine having the following general formula:

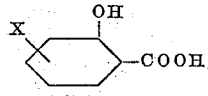


where X is a member of the group consisting of —NH_2,

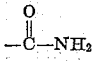


—C—N—R, —N—R, and —NR_2, where R is a member of the group consisting of alkyl and alkylol.

6. An aqueous alkaline cyanide plating bath comprising about 3 to 26 ounces per gallon of copper cyanide and zinc cyanide, about 1 to 20 ounces per gallon of an alkali metal hydroxide, about 4½ to 26 ounces per gallon of an alkali metal cyanide, about 0 to 7.0 ounces per gallon of an alkali metal tartrate, and about 0.1 to 7.0 ounces per gallon of a reaction product of salicylic acid and hexamine, said reaction product of salicylic acid and hexamine having the following general formula:



where X is a member of the group consisting of —NH_2,



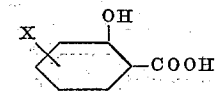
—C—N—R, —N—R, and —NR_2, where R is a member of the group consisting of alkyl and alkylol.

7. An aqueous bath for the electrolytic deposition of zinc and zinc alloys comprising about 3 to 26 ounces per gallon of a cyanide of a metal of the group consisting of zinc and zinc alloys, about 1 to 20 ounces per gallon of sodium hydroxide, about 1½ to 26 ounces of potassium cyanide, about 0 to 7.0 ounces per gallon of alkali tartrate and about 0.1 to 7.0 ounces per gallon of a solution comprising a reaction product of salicylic acid and hexamethylene tetramine, the solution including a mixture of amino derivatives of salicylic acid and at least some para-amino salicylic acid.

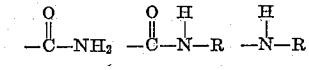
8. An aqueous bath for the deposition of zinc and zinc alloys comprising about 3 to 26 ounces per gallon of a cyanide of a metal of the group consisting of zinc and zinc alloys, of about 1 to 20 ounces per gallon of sodium

hydroxide, about 4½ to 26 ounces of potassium cyanide, about 0.5 to 50 grams per liter of potassium tartrate, and about .75 to 53 grams per liter of a solution comprising a reaction product of salicylic acid and hexamine, the solution including p-amino salicylic acid, unreacted hexamine and unreacted salicylic acid.

9. An aqueous alkaline cyanide plating bath adapted for electrolytically plating zinc and zinc alloys comprising at least about 3 ounces per gallon of a metal cyanide comprising zinc cyanide, at least about 3 ounces per gallon of sodium hydroxide, at least about 4½ ounces per gallon of potassium cyanide, about .8 to 3 ounces per gallon of alkali tartrate and about 0.4 to 4 ounces per gallon of a reaction product of salicylic acid and hexamethylene tetramine, said reaction product having the following general formula:



where X is a member of the group consisting of —NH_2,



and —NR_2, where R is a member of the group consisting of alkyl and alkylol.

10. An aqueous alkaline cyanide plating bath adapted for plating zinc and zinc alloys comprising about 6 to 9 ounces per gallon of a metal cyanide in which the metal includes at least some zinc, about 3 to 9 ounces per gallon of sodium hydroxide, about 10 to 15 ounces per gallon of potassium cyanide, and at least about 0.1 ounce per gallon of an aqueous solution having a pH of about 9 to 12 and containing potassium tartrate and a reaction product of salicylic acid and hexamethylene tetramine, the reaction product including p-amino salicylic acid and o-amino salicylic acid, and unreacted hexamethylene tetramine.

11. A method of making an alkaline cyanide plating bath adapted for electrodeposition of zinc and zinc alloys comprising (1) making a catalytic ingredient solution including the steps of (*a*) reaction about 1 to 4 moles of salicylic acid with about one mole of hexamine at a temperature of about 125° to 190° F. and a pH of 2½ to 5½ until substantially all the salicylic acid is dissolved and gassing has stopped to provide a reaction mixture and (*b*) thereafter reacting the mixture with an alkali metal hydroxide to provide the catalytic ingredient solution, and (2) mixing about 0.1 to 7.0 ounces per gallon of said solution with about 3 to 26 ounces per gallon of a cyanide of a metal comprising zinc cyanide, about 1 to 20 ounces per gallon of an alkali metal hydroxide, and up to 7.0 ounces per gallon of an alkali metal tartrate to provide a plating bath.

12. A method of electrodepositing zinc and zinc alloys comprising the steps of (1) making an alkaline cyanide plating bath adapted for electrodeposition of zinc and zinc alloys by (*a*) making a smoothing and grain refining agent solution including the steps of reacting about 1 to 4 moles of salicylic acid with about one mole of hexamethylene tetramine at a temperature of about 125° to 190° F. and a pH of 2½ to 5½ until substantially all the salicylic acid is dissolved and gassing has stopped to provide a reaction mixture and (*b*) thereafter reacting said mixture with an alkali metal hydroxide to provide the smoothing and grain refining solution, (2) mixing about 0.1 to 7.0 ounces per gallon of said solution with about 3 to 26 ounces per gallon of a cyanide of a metal comprising zinc cyanide, about 1 to 20 ounces per gallon of an alkali metal hydroxide and up to 7 ounces per gallon of an alkali metal tartrate to form a plating bath, and (3) electrolyzing said bath with a current density of up to about 80 amperes per square foot at a temperature of about 68° to 178° F.

13. A method of electrodepositing a metal including

at least some zinc, the method comprising electrolyzing an aqueous alkaline cyanide solution containing a metal cyanide comprising zinc cyanide and about 0.1 to 7.0 ounces per gallon of a reaction product of salicylic acid and hexamine.

14. An aqueous alkaline cyanide plating bath comprising about 3 to 26 ounces per gallon of a cyanide of a metal comprising zinc cyanide, about 1 to 20 ounces per gallon or an alkali metal hydroxide, about 4½ to 26 ounces per gallon of an alkali metal cyanide, up to about 7.0 ounces per gallon of an alkali metal tartrate, and about

0.1 to 7.0 ounces per gallon of a reaction product of salicylic acid and hexamine, the reaction being at a temperature of about 125° to 190° F. at a pH of about 2½ to 5½ for at least about 4 hours, and the product thereafter reacted with an alkali metal hydroxide and the final solution having a pH of about 8½ to 12.

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