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ELECTRODEPOSITION

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This invention is directed to the electrodeposition of bright zinc and more particularly to novel brightener compositions for incorporation into cyanide baths useful in the electrodeposition of bright zinc.

It is an object of this invention to provide an improved process for electrodepositing bright zinc.

It is also an object of this invention to provide an improved aqueous bath for the electrodeposition of bright zinc.

It is still another object of this invention to provide novel brightener compositions for incorporation in improved aqueous cyanide baths for electrodepositing bright zinc.

Since about 1935, various additives have been added to aqueous cyanide zinc baths to produce "bright" zinc electrodeposits. Among the more widely used additives have been a group of aromatic aldehydes including anisaldehyde, piperonaldehyde, veratraldehyde, and 2,3-dimethoxybenzaldehyde. I have now discovered that when o-vanillin (3-methoxy-2-hydroxy-benzaldehyde) is used in conjunction with at least one of the aforelisted aldehydes as the brightener additive, the consequent bright zinc electrodeposit is superior to any heretofore known. The deposits are more lustrous and glossy. It was found that it was possible to obtain bright zinc over a wider current density range than heretofore possible. During the electrodeposition process, the deposit appears to have leveling characteristics superior to those from prior baths which have little or no leveling ability.

The electrodeposition of bright zinc from aqueous cyanide zinc solutions using my brightener composition is similar to the conventional processes using similar baths which do not contain o-vanillin in conjunction with one of the four noted aldehydes. Such baths and processes are described in "Modern Electroplating," edited by A. G. Gray, The Electrochemical Society, 1953, pages 460–482.

It is important that the baths be relatively free of impurities. Although my brightener composition is effective with all known bright cyanide aqueous solutions, for barrel plating I prefer to use baths and conditions as noted in Column A of Table I, and for rack plating I prefer to use baths and conditions set forth in Column B of Table I. Conventional wetting agents, such as trimethyl-C-decyl-α-betaine, in amounts between 0.1 g./l. (gram per liter) and 1 g./l. are useful for rack plating purposes to prevent pitting and to eliminate some tendency toward vertical striations. The use of polyvinylalcohol and/or gelatin with aldehydes is common in the known bright zinc baths and their use is also preferred with my brightener combination.

Table I

	Column A	Column B
zinc ---- g./l.	30–52	45–60
total NaCN ---- g./l.	82–143	82–143
sodium hydroxide ---- g./l.	75–105	90–135
ratio, NaNC(total)/Zn	2.0–3.3	1.8–3.3
temperature ---- °C.	20–50	20–38
cathode C.D. ---- a.s.d.[1]	0.2–1.6	1–6.6
anode C.D. ---- a.s.d.	1–2	1–2

[1] Amperes per square decimeter.

The amount of my brightener combination, consisting of o-vanillin together with at least one of the following aldehydes: anisaldehyde (p-methoxybenzaldehyde), piperonaldehyde (3,4-methylenedioxybenzaldehyde), veratraldehyde (3,4-dimethoxybenzaldehyde), and 2,3-dimethoxybenzaldehyde, to be added to the bath varies widely dependent on such factors as the composition of the plating bath, the plating conditions, the relative proportion of the o-vanillin to the other aldehyde(s) in the brightener composition, the kind and surface of the basis metal, and the brightening effect desired. Although brightening effect is noted with amounts as small as 0.05 g./l., it is preferred to use at least about 0.1 g./l. It is not contemplated that more than about 0.5 g./l. will be utilized since in excess of this concentration there is little increase in brightness with increased concentration of the brightener composition. In addition, in excess of about 0.5 g./l. the solubility of some of the aldehydes, such as anisaldehyde, released from the bisulfite adduct, may be substantially exceeded.

Due to the various factors noted above, the relative proportion of the o-vanillin to the other aldehyde(s) in the brightener composition may vary widely. However, it is generally preferred that the weight ratio of the o-vanillin to the other aldehyde(s) be at least about 1:10 and may be as much as 1:1. Good commercial results are obtained in the range of 1:4 to 1:1 and optimum results are obtained within different portions of this range dependent upon the particular brightener composition.

The aldehydes generally and particularly those of interest in the present invention are only slowly soluble in aqueous cyanide zinc electroplating baths. The compounds per se are dissolved in such baths slowly with agitation. It has been found that the aldehyde-bisulfite adduct formed by the mixing and heating of the aldehyde with sodium bisulfite in at least a 1:1 molar ratio is a convenient method of solubilizing aldehydes and placing them in a more convenient form for handling. These aldehyde-bisulfite adducts are used in the known addition of such aldehydes as anisaldehyde to zinc electroplating baths. In similar manner, I have found that the combination of o-vanillin together with one or more of the other specified aldehydes also is most conveniently made in the form of the bisulfite adduct. The method of preparing the adduct is not critical; for a brightener combination containing one part of o-vanillin to one part of anisaldehyde, the adduct could be made by physically mixing one mole of o-vanillin, one mole of anisaldehyde, and at least two moles, but preferably an excess, of sodium bisulfite; or the o-vanillin-sodium bisulfite adduct and the anisaldehyde-bisulfite adduct could be prepared separately and the two adducts then combined to form my brightener combination. My preferred brightener compositions contain the o-vanillin-bisulfite adduct and one of the other four specified aldehyde-bisulfite adducts in a weight ratio of 1:4 to 1:1.

I have found that the use of between about 0.1 g./l. to about 1.0 g./l. of an animal gelatin or glue and between about 0.02 g./l. and 0.1 g./l. of a polyvinylalcohol are optimumly advantageous in the bath.

I have prepared novel and preferred compositions incorporating the various additives necessary for bright zinc plating in both solid and liquid formulations. The preferred solid formulations are shown in Table II, and the preferred liquid formulations are shown in Table III.

Table II

	Range, percent	Optimum Concentration, percent
aldehyde-bisulfite adduct	40–50	45
animal gelatin	10–15	12.5
polyvinylalcohol	5–10	6.5
sodium sulfate (anhydrous)	Balance	36

The solid compositions of Table II are added to zinc baths in amounts sufficient so that the total weight of composition added is between 0.25 g. and 2.5 g. to each liter of bath and preferably between 0.6 g. and 1.2 g.

Table III

	Range, g./l.	Optimum Concentration, g./l.
total aldehyde	45–60	55.2
animal gelatin	125–175	150
polyvinylalcohol	2–5	3.82
sodium metabisulfite ($Na_2S_2O_5$)	45–60	55.5

In the liquid compositions shown in Table III, the aldehydebisulfite adduct was formed during the preparation of the liquid composition. The liquid composition is added to the zinc plating bath in amounts between 1 ml./l. of bath and 10 ml./l., and preferably 2.5 ml./l. of bath to 5 ml./l., which is equivalent to 0.14 to 0.2 g./l. of the mixed aldehydes.

For the purpose of giving those skilled in the art a better understanding of the invention, illustrative examples are given. In Examples 1 through 4 an aqueous bath containing 60 g./l. of zinc cyanide, 42 g./l. of sodium cyanide, and 80 g./l. of sodium hydroxide was used. Electroplating was carried out at 25° C. in conventional Hull cells and in other tests which simulate barrel plating conditions.

Example 1.—The optimum concentration of the composition from Table II containing 22.5% of anisaldehyde-bisulfite and 22.5% of o-vanillin-bisulfite was used in a range of from 0.6 to 1.2 g./l. of solution.

Example 2.—The optimum concentration of the composition from Table II containing 22.5% of piperonaldehyde-bisulfite and 22.5% of o-vanillin-bisulfite was used in a range of from 0.6 to 1.2 g./l. of solution.

Example 3.—The optimum concentration of the composition from Table II containing 22.5% of veratraldehyde-bisulfite and 22.5% of o-vanillin-bisulfite was used in a range of from 0.6 to 1.2 g./l. of solution.

Example 4.—The optimum concentration of the composition from Table II containing 22.5% of 2,3-dimethoxybenzaldehyde-bisulfite and 22.5% of o-vanillin-bisulfite was used in a range of from 0.6 to 1.2 g./l. of solution. The zinc electrodeposited in Examples 1–4 was bright with good luster and gloss. Similar experiments were run utilizing instead of the noted amounts of the two additives 45% of the bisulfite adduct of each of the four noted additives, and a fifth experiment was run using 45% of the o-vanillin-bisulfite adduct. In all cases, the deposits of Examples 1–4 were superior to those where only one of the aldehydes was used. In addition, the bath characteristics in relation to leveling and the useful current density range were superior. The deposits with the discovered combinations of additives were also much less yellowish in color, which is a desirable characteristic when the use of a subsequent nitric acid or proprietary bright dip is not desired.

Example 5.—The liquid composition of Table III utilizing 11.4 g./l. of o-vanillin and 43.8 g./l. of anisaldehyde was added to the zinc plating bath in a range of from 2.5 to 5.0 ml./l.

Example 6.—The liquid composition of Table III utilizing 11.4 g./l. of o-vanillin and 43.8 g./l. of piperonaldehyde was added to the zinc plating bath in a range of from 2.5 to 5.0 ml./l.

Example 7.—The liquid composition of Table III utilizing 11.4 g./l. of o-vanillin and 43.8 g./l. of veratraldehyde was added to the zinc plating bath in a range of from 2.5 to 5.0 ml./l.

Example 8.—The liquid composition of Table III utilizing 11.4 g./l. of o-vanillin and 43.8 g./l. of 2,3-dimethoxybenzaldehyde was added to the zinc plating bath in a range of from 2.5 to 5.0 ml./l.

In Examples 9–11 an aqueous bath containing 60 g./l. of zinc cyanide, 17 g./l. of sodium cyanide, and 80 g./l. of sodium hydroxide was used.

Example 9.—The optimum concentration of the composition from Table II containing 22.5% of anisaldehyde-bisulfite and 22.5% of o-vanillin-bisulfite was used in a range of from 0.6 to 1.2 g./l. of solution.

Example 10.—The optimum concentration of the composition from Table II containing 22.5% of piperonaldehyde-bisulfite and 22.5% of o-vanillin-bisulfite was used in a range of from 0.6 to 1.2 g./l. of solution.

Example 11.—The optimum concentration of the composition of Table II containing 22.5% of veratraldehyde-bisulfite and 22.5% of o-vanillin-bisulfite was used in a range of from 0.6 to 1.2 g./l. of solution.

In Examples 12 and 13 the same zinc bath composition was used as for Examples 5–7 inclusive.

Example 12.—A concentration of the composition from Table II containing 33.8% of anisaldehyde-bisulfite and 11.2% of o-vanillin-bisulfite was used in a range of from 0.6 to 1.2 g./l. of solution.

Example 13.—A concentration of the composition from Table II containing 30% of anisaldehyde-bisulfite and 15% of o-vanillin-bisulfite was used in a range of from 0.6 to 1.2 g./l. of solution.

In Examples 9–13 inclusive utilizing a zinc bath having a NaCN to Zn ratio of 2.0 all the advantages realized in Examples 1–8 (NaCN to Zn ratio of 2.74) inclusive were realized. In addition, for the baths having a NaCN to Zn ratio of 2.0 there seemed a lesser tendency toward vertical striations obtained in rack plating, thus permitting operation with little or no cationic surface active agent.

In Examples 14 and 15 the same zinc bath composition was used as for Examples 9–13.

Example 14.—The liquid composition of Table III utilizing 20 g./l. of o-vanillin and 35.2 g./l. of anisaldehyde was added to the zinc plating bath in a range of from 2.5 to 5.0 ml./l.

Example 15.—The liquid composition of Table III utilizing 5.2 g./l. of o-vanillin and 50 g./l. of anisaldehyde was added to the zinc plating bath in a range of from 2.5 to 5.0 ml./l.

In Examples 16 and 17 the same zinc bath composition was used as for Examples 1–8.

Example 16.—The liquid composition of Table III utilizing 20 g./l. of o-vanillin and 35.2 g./l. of anisaldehyde was added to the zinc plating bath in a range of from 2.5 to 5.0 ml./l.

Example 17.—The liquid composition of Table III utilizing 5.2 g./l. o-vanillin and 50 g./l. of anisaldehyde was added to the zinc plating bath in a range of from 2.5 to 5.0 ml./l.

In Examples 14–17, there were realized all the advantages enumerated for Examples 1–13. Again it was noted in Examples 14 and 15 that the lower NaCN to zinc ratio of 2.0 reduced the tendency toward deposit striation in rack plating.

As is well known in the prior art, other tests where the zinc metal concentration was varied keeping the NaCN to Zn ratio within the preferred limits, showed only an effect in increasing or decreasing the limiting current density with increasing or decreasing zinc metal concentration.

Similar experiments were run utilizing instead of the noted combination of the two aldehydes only one aldehyde in an amount equal to the total o-vanillin-aldehyde combination. In turn, each of the five aldehydes was utilized separately. In all cases, the results were inferior to those obtained in Examples 5–17 in the same respects as those discussed hereinbefore regarding the superiority of Examples 1–4.

In addition to the advantages of process and deposit obtained utilizing the o-vanillin-aldehyde combination noted hereinbefore, I find that my "as plated bright zinc" may be brought to a superlative luster and appearance resembling bright chromium, heretofore unattainable, by treatment with a nitric acid or one of the bright zinc proprietary dips.

Another advantage is based on the finding that o-vanillin imparts a strong yellow color to the electro-plating solution which is a basis for a simple analytical technique based on colorimetric measurements. The o-vanillin-containing brighteners have also been found to be long lasting and unusually stable at the conventional zinc plating temperatures. They are also stable at plating temperatures up to as high as about 50° C., whereas the usual brighteners suffer more rapid breakdown at temperatures above about 35° or 40° C. Zinc is usually electro-deposited directly on various iron and steel alloys, although it may be electrodeposited on other basis metals as well.

As many embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention includes all such modifications and variations as come within the scope of the appended claims.

I claim:

1. A process for electroplating bright, lustrous zinc comprising electrodepositing zinc from an aqueous alkali cyanide bath containing zinc ions and containing at least 0.05 g./l. of total aldehyde, said total aldehyde consisting essentially of o-vanillin and at least one compound selected from the class consisting of anisaldehyde, piperonaldehyde, veratraldehyde, and 2,3-dimethoxybenzaldehyde, the weight ratio of said o-vanillin to said compound being between 1:10 and 1:1.

2. A process for electroplating bright, lustrous zinc comprising electrodepositing zinc from an aqueous alkali cyanide bath containing zinc ions and containing between 0.05 g./l. and 0.5 g./l. of total aldehyde, said total aldehyde consisting essentially of o-vanillin and at least one compound selected from the class consisting of anisaldehyde, piperonaldehyde, veratraldehyde, and 2,3-dimethoxybenzaldehyde, the weight ratio of said o-vanillin to said compound being between 1:10 and 1:1.

3. A process for electroplating bright, lustrous zinc comprising electrodepositing zinc from an aqueous alkali cyanide bath containing zinc ions and containing between 0.1 g./l. and 0.5 g./l. of total aldehyde, said aldehyde consisting essentially of o-vanillin and at least one compound selected from the class consisting of anisaldehyde, piperonaldehyde, veratraldehyde, and 2,3-dimethoxybenzaldehyde, the weight ratio of said o-vanillin to said compound being between 1:4 and 1:1.

4. An aqueous alkali cyanide bath containing zinc ions for the electrodeposition of bright and lustrous zinc and containing as the brightening additives at least about 0.05 g./l. of total aldehyde, said total aldehyde consisting essentially of o-vanillin and at least one compound selected from the class consisting of anisaldehyde, piperonaldehyde, veratraldehyde, and 2,3-dimethoxybenzaldehyde, the ratio weight of said o-vanillin to said compound being between 1:10 and 1:1.

5. An aqueous alkali cyanide bath containing zinc ions for the electrodeposition of bright and lustrous zinc and containing as the brightening additives between 0.1 g./l. and 0.5 g./l. of total aldehyde, said total aldehyde consisting essentially of o-vanillin and at least one compound selected from the class consisting of anisaldehyde, piperonaldehyde, veratraldehyde, and 2,3-dimethoxybenzaldehyde, the weight ratio of said o-vanillin to said compound being between 1:4 and 1:1.

6. The bath of claim 5 in which the total aldehyde consists essentially of o-vanillin and anisaldehyde.

7. The bath of claim 5 in which the total aldehyde consists essentially of o-vanillin and piperonaldehyde.

8. The bath of claim 5 in which the total aldehyde consists essentially of o-vanillin and veratraldehyde.

9. The bath of claim 5 in which the total aldehyde consists essentially of o-vanillin and 2,3-dimethoxybenzaldehyde.

10. An aqueous alkali cyanide bath containing zinc ions for the electrodeposition of bright and lustrous zinc and containing as the brightening additive o-vanillin and at least one compound selected from the class consisting of anisaldehyde, piperonaldehyde, veratraldehyde, and 2,3-dimethoxybenzaldehyde, the weight ratio of the o-vanillin to the other aldehyde being between 1:10 and 1:1; said brightener additives being added to said bath in the form of their bisulfite adducts and in an amount sufficient so that the bath contains between 0.1 g./l. and 0.5 g./l. of total aldehyde.

11. The bath of claim 10 in which the weight ratio of o-vanillin to the other aldehyde is between 1:4 and 1:1.

12. The bath of claim 10 in which the brightener additives are added in a composition which also contains animal gelatin and polyvinylalcohol.

13. A composition of matter for making up and for maintaining aqueous alkali cyanide zinc electroplating baths consisting essentially of an aldehyde-bisulfite adduct, said aldehyde-bisulfite adduct comprising (1) o-vanillin and (2) at least one aldehyde selected from the class consisting of anisaldehyde, piperonaldehyde, veratraldehyde, and 2,3-dimethoxybenzaldehyde, and (3) sodium bisulfite, the said sodium bisulfite being present in an amount equal to at least a 1:1 molar ratio with the total aldehyde, and the weight ratio of o-vanillin to the other aldehyde being between 1:10 and 1:1.

14. A composition of matter for making up and for maintaining aqueous alkali cyanide zinc electroplating baths consisting essentially of 40%–50% aldehyde-bisulfite adduct, 10%–15% animal gelatin, 5%–10% polyvinylalcohol, and the balance sodium sulfate; said aldehyde-bisulfite adduct comprising (1) o-vanillin and (2) at least one aldehyde selected from the class consisting of anisaldehyde, piperonaldehyde, veratraldehyde, and 2,3-dimethoxybenzaldehyde, the weight ratio of the o-vanillin to the other aldehyde being between 1:10 and 1:1, and (3) sodium bisulfite, the said sodium bisulfite being present in an amount equal to at least a 1:1 molar ratio with the total aldehyde.

15. The composition of claim 14 in which the weight ratio of o-vanillin to the other aldehyde is between 1:4 and 1:1.

16. An aqueous composition of matter for making up and for maintaining aqueous alkali cyanide zinc electroplating baths consisting essentially of 45 g./l. to 60 g./l. of total aldehyde, and 45 g./l. to 60 g./l. of sodium metabisulfite; the total aldehyde consisting of o-vanillin and at least one aldehyde selected from the class consisting of anisaldehyde, piperonaldehyde, veratraldehyde, and 2,3-dimethoxybenzaldehyde, the weight ratio of o-vanillin to said other aldehyde being between 1:10 and 1:1.

17. An aqueous composition of matter for making up and for maintaining aqueous alkali cyanide zinc electroplating baths consisting essentially of 45 g./l. to 60 g./l. of total aldehyde, 125 g./l. to 175 g./l. of animal gelatin, 2 g./l. to 5 g./l. of polyvinylalcohol, and 45 g./l. to 60 g./l. of sodium metabisulfite; the total aldehyde consisting of o-vanillin and at least one aldehyde selected from the class consisting of anisaldehyde, piperonaldehyde, veratraldehyde, and 2,3-dimethoxybenzaldehyde, the weight ratio of o-vanillin to said other aldehyde being between 1:10 and 1:1.

18. An aqueous composition of matter for making up and for maintaining aqueous alkali cyanide zinc electroplating baths consisting essentially of 45 g./l. to 60 g./l. of total aldehyde, 125 g./l. to 175 g./l. of animal gelatin,

2 g./l. to 5 g./l. of polyvinylalcohol, and 45 g./l. to 60 g./l. of sodium metabisulfite; the total aldehyde consisting of o-vanillin and at least one aldehyde selected from the class consisting of anisaldehyde, piperonaldehyde, veratraldehyde, and 2,3-dimethoxybenzaldehyde, the weight ratio of o-vanillin to said other aldehyde being between 1:4 and 1:1.

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