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PRODUCTION OF BRIGHT ZINC OR BRIGHT CADMIUM DEPOSITS

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18 Claims. (Cl. 204—50)

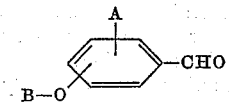
This invention relates to improvements in the electrodeposition of zinc and cadmium and is directed particularly to the use of novel organic addition agents employed in alkali cyanide plating baths for improving the luster and brightness of the deposits obtained.

Conventional alkali cyanide electroplating baths for use with zinc and cadmium usually contain various addition agents such as wetting agents, protective colloids and the like, as well as salts or compounds of the metal to be deposited.

In accordance with the present invention baths of this character further contain a brightening agent consisting of a formyl substituted phenyl ether of a hydroxy alcohol in which the phenyl group may be further substituted with a lower alkoxy radical. These agents when present in an amount of from about 0.1 to 10 grams per liter of the bath have been found to improve materially the luster or brightness of the deposit obtained.

The compounds of the present invention are characterized by their ability to produce bright electrolytic deposits of zinc and cadmium over a wide range of current densities. In this respect they extend the utility of the electrolytic baths in producing bright deposits under greatly varying conditions of operation.

The compositions which are preferred for use in accordance with the present invention are those which may be represented by the structural formula



in which A represents hydrogen or a lower alkoxy radical and B represents a hydroxyalkyl radical. The group B may contain either one or a plurality of hydroxyl groups. Typical examples of polyhydroxy alcohols, of which the formyl phenyl ethers comprise the compounds of this invention, are ethylene glycol, propylene glycol, glycerol, and the like. The ortho, meta, and para isomers of the compounds (i.e. referring to the position of the formyl group with respect to the ether group, B—O—, in the above formula) all serve to increase the brightness of the deposits obtained although the para compounds are generally preferred for zinc baths while the ortho compounds are generally preferred for the electrodeposition of cadmium.

The principal objects of the present invention are to increase the brightness and luster of the zinc and cadmium platings or deposits obtained from electrolytic baths and to provide new types of baths and procedures adapted for use in the electrolytic deposition of zinc and cadmium over a wide range of current densities.

A particular object of the invention is to provide alkali cyanide zinc and cadmium containing electrolytic baths wherein there is a brightening agent selected from the group consisting of formyl substituted phenyl ethers of polyhydroxy alcohols in which the phenyl group may be further substituted with a lower alkoxy radical.

A further object of the invention is to provide new methods for the electrolyic deposition of zinc and cadmium wherein the baths employed contain controlled amounts of these brightening agents.

These and other objects and features of the present invention will appear from the following description thereof wherein typical compositions and methods of procedure are described for the purpose of indicating the nature of the invention but without intending to limit the scope hereof.

It appears that formyl substituted phenyl alkyl ethers which contain at least one hydroxyl group attached to the alkyl moiety are highly effective as brightening agents when used in alkali cyanide baths employed for the electrodeposition of zinc or cadmium. The presence of a hydroxyl group as a substituent of the alkyl moiety appears to be important in assuring the formation of a bright deposit of the metal from an electrolytic bath under varying conditions of operation. Thus, for example, the zinc deposits obtained from electrolytic baths containing 3-(paraformylphenoxy)-1,2-propanediol are brighter than those obtained when anisic aldehyde is substituted therefor, even when smaller amounts of the 3-(para-formylphenoxy)-1,2-propanediol are employed. Moreover, bright deposits are obtained over a wide range of current densities.

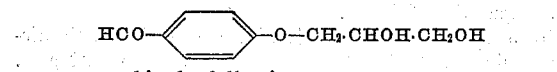
The brightening agents of the present invention may be prepared conveniently by reacting a hydroxy benzaldehyde or a lower alkoxy substituted hydroxybenzaldehyde with an alkyl halohydrin. Typical halohydrins which may be employed in such reactions are ethylene chlorhydrin, propylene chlorhydrin, epichlorhydrin, glycerol monochlorhydrin, etc. The reaction between the hydroxybenzaldehyde and the halohydrin is preferably carried out in the presence of an alkaline agent such as sodium hydroxide, potassium hydroxide, sodium carbonate, and the like. The resulting ether compound may be separated from the reaction mixture by solvent extraction or otherwise as desired, but it is not necessary that it be highly purified for use as a brightening agent. Thus, extraction products containing only about 50 to 75% of the ether compound may be used with great effectiveness.

While the compounds of this invention are useful as brighteners in both zinc and cadmium electroplating from alkali-cyanide baths, it is noteworthy that, in general those compounds in which the ether linkage of the polyhydroxy alcohol is attached to the benzene ring in the position para to the formyl group are relatively more effective in producing bright zinc deposits. Conversely, the corresponding compounds in which the ether linkage is ortho to the formyl group are relatively more effective in producing bright cadmium deposits. Thus, 3-(paraformylphenoxy)-1,2-propanediol possesses outstanding activity as a brightener for zinc but is relatively less effective for cadmium, whereas 3-(ortho-formylphenoxy)-1,2-propanediol is highly effective for cadmium. In general, the activity of the corresponding meta isomers are intermediate between the ortho and para compounds.

In order to illustrate typical procedure which may be employed in the practice of the present invention, the following examples are cited.

Example I

3-(para-formylphenoxy)-1,2-propanediol having the formula



was prepared in the following manner.

555 gms. epichlorohydrin was added in ½ hour to 800 gms. water plus 16 gms. conc. sulfuric acid with stir-

ring at reflux and the mixture refluxed for about 15 minutes until homogeneous. After cooling to about 35° C., 488 gms. p-hydroxybenzaldehyde was added followed by 280 gms. of 50% aqueous sodium hydroxide solution. The temperature rose spontaneously to about 50° and the mixture was then heated to 75° and maintained for 2 hours. A further addition of 216 gms. 50% sodium hydroxide was made and the mixture again maintained at 75° for 2 hours. Finally the temperature was gradually raised to reflux (110°) in ½ hour and the mixture refluxed for 1 hour. On cooling to about 25° C., the oil which had separated was extracted successively with 600 cc. and 300 cc. portions of isobutanol and the combined extracts washed with 600 gms. 10% sodium carbonate solution. The solvent was then removed to about 90° C. at 5 mm. of pressure leaving 835 gms. of an amber colored, viscous liquid which analyzed 83.5% as the desired ether. (Yield=83.5%.) This product was not further purified.

The product was evaluated in Hull cell tests for its activity as a surface brightening agent in producing bright metal deposits from conventional alkali zinc cyanide and cadmium cyanide plating baths.

For the zinc plating tests a solution was prepared containing the following composition: 4.2 oz. per gallon of zinc (as metal), 13.1 oz. per gallon of cyanide (as sodium cyanide), and 14.4 oz. per gallon of sodium hydroxide. Traces of contaminating metals were precipitated with a sulfide solution and the solution then "dummied" at low current density overnight to remove other metallic impurities. Tests were then carried out in the Hull cell at two temperatures (75° F. and 100° F.) and at three concentrations of the brightening agent (0.1, 1.0 and 10.0 gms. per liter). Agitation was employed and the zinc was plated out on a 2½ in. by 4 in. polished steel cathode. Three amperes of total current were used and the current density ranged from about 5 to 100 amperes per square foot.

When submitted to evaluation under the above described conditions, 3-(para-formylphenoxy)-1,2-propanediol prepared as described above, was found to be an especially effective agent for producing bright zinc deposits as compared to anisic aldehyde, which is a well known additive agent for bright zinc plating.

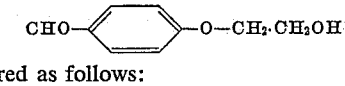
For cadmium plating, a conventional plating bath having the following composition: cadmium oxide—3.0 oz. per gallon and sodium cyanide 16.5 oz. per gallon; was prepared and "dummied" overnight to remove traces of metallic impurities. Tests were conducted in the Hull cell under the same conditions as described above for the zinc bath and it was found that 3-(para-formylphenoxy)-1,2-propanediol was an effective addition agent for producing bright deposits of cadmium.

Example II

3-(meta-formylphenoxy)-1,2-propanediol was prepared from meta-hydroxybenzaldehyde and epichlorhydrin according to the general procedure of Example I. The product was obtained as a dark amber, viscous liquid which analyzed 76.8% as the desired ether (Yield =58%). It was tested without further purification in the Hull cell according to the general procedure described in Example I, and was found to be an effective brightener for both zinc and cadmium plating.

Example III

Beta-(para-formylphenoxy)-ethanol having the formula



was prepared as follows:

70 gms. 50% sodium hydroxide was added with stirring at about 25° C in ¼ hour to a mixture of 122 gms. p-hydroxy-benzaldehyde, 123 gms. ethylene chlorhydrin and 100 gms. water. The temperature rose to about 45° C. The mixture was then heated to about 70–75° C. and maintained for 2 hours, after which a further addition of 50 gms. 50% sodium hydroxide was gradually made in 2 hours. Finally, the mixture was stirred at about 75° for 2 hours and then refluxed for 1 hour. 100 gms. water was added to dissolve separated salts and the mixture cooled to about 25° and extracted successively with 200 gms. and 100 gms. portions of isobutanol. After removing the solvent to 130° C. at about 15 mm. pressure, the product was distilled from 170–195° C. at about 5 mm. of pressure. There was obtained 151 gms. (87.5% yield) of a straw colored, viscous liquid which slowly solidified on standing and analyzed 96% as the desired ether.

When evaluated in Hull cell tests as described in Example I the product was found to be an effective brightener for both zinc and cadmium electroplating.

Example IV

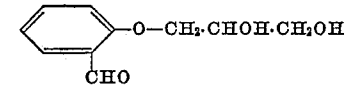
Beta-(meta-formylphenoxy)-ethanol was prepared according to the general procedure of Example III from m-hydroxybenzaldehyde and ethylene chlorhydrin. The product was obtained as a straw colored liquid distilling from 145–165° C. at about 3 mm. of pressure and analyzing 97.5% as the desired ether (yield=82.5%). When evaluated in Hull cell tests it was found to be an effective "brightener" for both zinc and cadmium electroplating.

Example V

Beta-(ortho-formylphenoxy)-ethanol was prepared according to the general procedure of Example III from salicylaldehyde and ethylene chlorhydrin except that the product was not distilled after removing the solvent. It was obtained as a dark amber, viscous liquid and analyzing 89% as the desired ether (yield=75%). It was evaluated in Hull cell tests and was found to be an effective brightener for cadmium plating.

Example VI

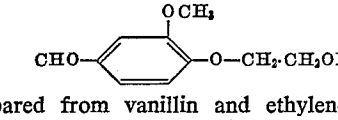
3-(ortho-formylphenoxy)-1,2-propanediol having the formula



was prepared from salicylaldehyde and epichlorhydrin according to the general procedure of Example I. It was obtained as an amber, viscous liquid analyzing 84% as the desired ether (yield=66%). When tested in the Hull cell, it was found to be an especialy effective brightener for cadmium plating.

Example VII

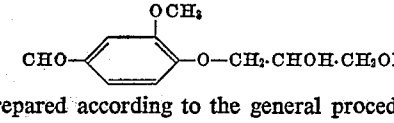
Beta-(para-formyl - ortho-methoxyphenoxy) - ethanol having the formula



was prepared from vanillin and ethylene chlorhydrin according to the general procedure of Example III, except that in this case the crude product was obtained as a solid, which was filtered and washed with water. It melted at 97–97.5° C. and analyzed 94% as the desired ether (yield=63%). When evaluated in Hull cell tests it proved to be an effective brightener for both zinc and cadmium electroplating.

Example VIII

3-(para-formyl-ortho-methoxyphenoxy)-1,2 - propanediol having the formula



was prepared according to the general procedure of Ex-

ample I from vanillin and epichlorhydrin. The product was obtained as a dark amber, viscous liquid analyzing 85.7% as the desired ether (yield=66.5%). When evaluated in the Hull cell it was found to be an especially effective brightener for zinc plating and an effective brightener for cadmium plating.

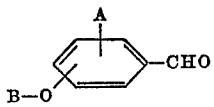
While the brightening agents of the present invention may be separated from the reaction mixture in which they are produced, and purified if desired, it has been found that the products obtained by extraction of the desired ether by means of a solvent, such as butanol for example, are sufficiently pure for effective use in the plating of zinc or cadmium. Thus, as indicated above, reaction products containing approximately 50% or more of the desired ether had been found to be effective.

If desired, mixture of the ethers described above may be employed as brightening agents. Furthermore, the brightening agents of the present invention may be used in combination with other known or acceptable brightening agents such as anisic aldehyde, although in general, the use of such other brightening agents is not necessary or desirable.

While typical formyl substituted phenyl ethers of polyhydroxy alcohols and typical baths containing the same have been cited above and various methods of using the electrolytic baths have been described, it should be understood that the invention is not limited to the specific compositions of the brightening agents or of the baths employed and is not limited with respect to the methods in which the electrolytic process is carried out. In view thereof, it should be understood that the foregoing examples have been cited for the purpose of indicating typical compositions and procedures which may be employed and are not intended to limit the scope of the invention.

I claim:

1. An aqueous alkali cyanide bath for use in electroplating, said bath containing metal ions selected from the group consisting of zinc and cadmium, together with a formyl substituted phenyl ether having the general formula



wherein A is selected from the group consisting of hydrogen, and lower alkoxy radicals and B is a hydroxy alkyl radical, said compound being present in sufficient amount to yield a metallic electrodeposit of improved brightness.

2. The bath of the character described in claim 1 wherein the amount of the formyl substituted phenyl ether present is equal to from about 0.1 to 10 grams per liter of the bath.

3. An aqueous alkali cyanide bath for use in the electrodeposition of zinc containing zinc ions and as a brightening agent a para formyl substituted phenyl ether of a polyhydroxy alcohol, said brightening agent being present in sufficient amount to yield a metallic electrodeposit of improved brightness.

4. An aqueous alkali cyanide bath for use in the electrodeposition of zinc containing zinc ions and as a brightening agent a para formyl substituted phenyl ether of a polyhydroxy alcohol in which the phenyl group is further substituted with a lower alkoxy radical, said brightening agent being present in sufficient amount to yield a metallic electrodeposit of improved brightness.

5. An aqueous alkali cyanide bath for use in the electrodeposition of cadmium containing cadmium ions and as a brightening agent an ortho formyl substituted phenyl ether of a polyhydroxy alcohol, said brightening agent being present in sufficient amount to yield a metallic electrodeposit of improved brightness.

6. An aqueous alkali cyanide bath for use in the electrodeposition of cadmium containing cadmium ions and as a brightening agent an ortho formyl substituted phenyl ether of a polyhydroxy alcohol in which the phenyl group is further substituted with a lower alkoxy radical, said brightening agent being present in sufficient amount to yield a metallic electrodeposit of improved brightness.

7. An aqueous alkali cyanide bath for use in electrodeposition of metal selected from the group consisting of zinc and cadmium, said bath containing metal ions selected from the group consisting of zinc and cadmium and as a brightening agent from about 0.1 to 10 grams per liter of the bath of 3-formylphenoxy-1,2-propanediol.

8. An aqueous alkali cyanide bath for use in electrodeposition of zinc, said bath containing zinc ions and a brightening agent consisting of from about 0.1 to 10 grams per liter of 3-(para-formyphenoxy)-1,2-propanediol.

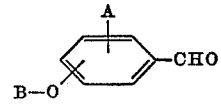
9. An aqueous alkali cyanide bath for use in electrodeposition of cadmium, said bath containing cadmium ions and a brightening agent consisting of from about 0.1 to 10 grams per liter of 3-(ortho-formylphenoxy)-1,2-propanediol.

10. An aqueous alkali cyanide bath for use in electrodeposition of metal selected from the group consisting of zinc and cadmium, said bath containing metal ions selected from the group consisting of zinc and cadmium and as a brightening agent from about 0.1 to 10 grams per liter of the bath of beta-formylphenoxy-ethanol.

11. An aqueous alkali cyanide bath for use in electrodeposition of metal selected from the group consisting of zinc and cadmium, said bath containing metal ions selected from the group consisting of zinc and cadmium and as a brightening agent from about 0.1 to 10 grams per liter of the bath of beta-formylmethoxyphenyl-ethanol.

12. An aqeuous alkali cyanide bath for use in electrodeposition of metal selected from the group consisting of zinc and cadmium, said bath containing metal ions selected from the group consisting of zinc and cadmium and as a brightening agent from about 0.1 to 10 grams per liter of the bath of 3-formylmethoxyphenyl-1,2-propanediol.

13. A process for producing a lustrous deposit of a metal selected from the group consisting of zinc and cadmium which comprises electrolyzing an aqueous alkali cyanide bath containing a compound of the metal to be deposited together with a brightening agent selected from the group consisting of formyl substituted phenyl ethers of polyhydroxy alcohols which have the general formula



wherein A is selected from the group consisting of hydrogen, and lower alkoxy radicals, and B is a hydroxyalkyl radical, said brightening agent being present in sufficient amount to yield a metallic electrodeposit of improved brightness.

14. A process as described in claim 13 wherein the amount of the formyl substituted phenyl ether present is equal to from about 0.1 to 10 grams per liter of the bath.

15. A process for producing a lustrous deposit of zinc which comprises electrolyzing a zinc ion containing aqueous alkali cyanide bath having therein from about 0.1 to 10 grams per liter of a para formyl substituted phenyl ether of a polyhydroxy alcohol.

16. A process for producing a lustrous deposit of zinc which comprises electrolyzing a zinc ion containing aqueous alkali cyanide bath having therein from about 0.1 to 10 grams per liter of a para formyl substituted phenyl ether of a polyhydroxy alcohol in which the phenyl group is further substituted with a lower alkoxy radical.

17. A process for producing a lustrous deposit of cadmium which comprises electrolyzing a cadmium ion

containing aqueous alkali cyanide bath having therein from about 0.1 to 10 grams per liter of an ortho formyl substituted phenyl ether of a polyhydroxy alcohol.

18. A process for producing a lustrous deposit of cadmium which comprises electrolyzing a cadmium ion containing aqueous alkali cyanide bath having therein from about 0.1 to 10 grams per liter of an ortho formyl substituted phenyl ether of a polyhydroxy alcohol in which the phenyl group is further substituted with a lower alkoxy radical.

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