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2,791,554

METHOD OF ELECTRODEPOSITING ZINC

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This invention relates to the electrodeposition of zinc, and is more particularly directed to a new and improved bath composition and process for producing bright zinc deposits wherein the cyanide bath contains in solution bath-soluble reaction products of epichlorhydrin with ammonia or primary amines.

Zinc plated from cyanide baths is widely employed as a coating to protect steel base metals from corrosion and to provide corrosion resistant undercoats for organic and other protective finishes which are applied thereover. A zinc coating upon an article plated from a cyanide plating bath is dull gray or dark in color, relatively crystalline in structure, is poor in appearance, stains readily and accordingly such coating has a very limited field of application. It has long been common practice to obtain a coating of improved physical characteristics, particularly in appearance, by incorporating in the cyanide plating bath various organic and inorganic substances which are generally referred to as addition agents or brighteners.

Heretofore it has been the common practice in obtaining bright zinc deposits from cyanide plating baths to use as addition agents a combination of organic and inorganic compounds, and optimum results depended on maintaining a pre-determined balance between the concentrations of the organic and inorganic constituents. Accordingly the prior practice required relatively close control over a plurality of the constituents of the plating bath by chemical analysis, or other means if analytical methods were not feasible. In the commercial operation of plating baths employing such addition agents, numerous drawbacks were encountered by reason of such addition agents which were in addition to those brought about by any unbalanced relationship between the organic and inorganic substances. For example, one of the disadvantages of the combination of organic-inorganic addition agents is that the inorganic constituent is a soluble metal compound, the metal of which co-deposits with the zinc, greatly to the detriment of some of its physical properties, such as ductility and corrosion resistance. Such co-deposition causes stains and undesirable appearance of the coated surface upon the subsequent application of surface treatments which are commonly used to passivate the zinc surface or to produce thereon a tarnish or corrosion resistant film. The purer the zinc deposit upon the surface of the article the better it is for corrosion protection and for accepting subsequent surface treatments designed to produce passive or protective films such as the chromate type or phosphate coatings to promote lacquer adhesion.

It is among the objects of my invention to provide an addition agent for zinc cyanide plating bath compositions by means of which bright, smooth and relatively pure zinc deposits can be obtained therefrom. A further object of my invention is to provide zinc plating baths and a plating process employing the same which produce bright zinc deposits that are uniformly responsive to

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oxidizing bright dips, chromate type protective dips and phosphatizing dips.

These objects are accomplished briefly by the use of aqueous cyanide zinc baths that contain bath-soluble reaction products of epichlorhydrin with ammonia or with primary amines either alone or for some purposes in combination with an aromatic aldehyde selected from the group consisting of oxyheterocyclic aldehydes, phenyl ethers and methoxy benzaldehydes. Such reaction products may be known as polyepoxyamines and will be so designated hereafter.

While my novel brighteners are effective in any commercially operable zinc cyanide plating bath, best results are obtained with the approximate bath composition and operating conditions shown in Table 1, which can be varied as required for special purposes in accordance with the known skill in the art.

Table 1

Bath composition:	Grams per liter
Zinc cyanide.....	60
Sodium cyanide.....	42
Sodium hydroxide.....	80

Ratio of $\frac{\text{NaCN (free and combined)}}{\text{Zn}} = 2.7$

Operating conditions:

Temperature—about..... 80° F.
Cathode current density.... 20 amps. per sq. ft.
Anodes..... Zinc of suitable purity.

The plating bath is prepared by dissolving the constituents in water, after which the bath should be purified by adding about one-half gram of sodium sulphide per liter of bath dissolved in water, or the bath may be treated by stirring about two grams of zinc dust per liter of bath for a few hours, then settling and decanting or filtering.

I have found that addition agents used for cyanide zinc plating baths in accordance with the prior art are subject to certain disadvantages. For example, the use of aromatic aldehydes requires very frequent additions because of their instability in the bath, and the same disadvantage applies to colloids such as gelatin. The use of polyvinyl alcohol is quite common, but this material is subject to the disadvantages of salting out of the bath, forming an undesirable scum on the bath surface, producing an undesirable yellow color to the bright zinc deposit, and furthermore is not uniform in its composition.

The above disadvantages are entirely overcome with my new and novel bath-soluble polyepoxyamines. These polyepoxyamines are unusually stable in the plating bath, their solubility is more than sufficient to preclude their being salted out, they do not produce yellow deposits upon a plated article and they can be readily produced in batches that are uniform in effect when used in a plating bath. The addition of bath-soluble polyepoxyamines also greatly improves the covering power of cyanide zinc plating baths to the extent that recesses in the article which cannot be covered with the metal under ordinary operating conditions are readily covered if such addition agents are present.

The polyepoxyamines may be prepared by any one of a number of well known and established procedures. However, for both maximum effectiveness and bath stability, the preparation of the polyepoxyamine in accordance with the following procedure has been found most desirable.

Using a jacketed stainless steel reaction vessel, 10 gallons of water and 56 pounds of aqueous ammonia (29%) are combined and cooled to a temperature commensurate with the ability of the apparatus to convey away heat. I have found that a temperature of from 6 to 10

degrees is the most desirable. Five gallons of epichlorhydrin are then added to the vessel. Cold water circulated within the jacket serves to convey away the heat of reaction and to maintain the substances within the vessel within a desirable temperature range. An initial, very slow reaction or condensation takes place which leads to an intermediate product. This is later polymerized at a controlled rate. The evidence of such a slow reaction is continuous liberation of heat and a continuous drop in pH from about 12.5 to 8.0 as determined by a glass electrode.

After the initial reaction has been completed which takes approximately a period of three hours, polymerization is promoted by gradual elevation of the temperature to about 101 degrees centigrade or the reflux temperature. After maintaining the high temperature for about three additional hours, the desired degree of polymerization is reached and the resulting polyepoxyamine is suitable for addition to zinc cyanide plating baths. The product made in accordance with this procedure possesses a relatively low degree of polymerization which is most effective in the zinc plating bath within the range of current densities from about 5 to 125 amperes per square foot.

Another procedure for preparing polyepoxyamines suitable for use as an additive for zinc plating baths consists in adding epichlorhydrin slowly to the diluted ammonia at higher temperatures. Using the same type of reaction vessel, 10 gallons of water and 56 pounds of aqueous ammonia (29%) are combined and heated to about 60 degrees centigrade. Epichlorhydrin in the amount of 5 gallons is then slowly added to the vessel with the continued agitation of the mixture therein while maintaining a constant temperature by means of the circulation of cold water in the jacket until all of the epichlorhydrin has been added. The speed at which the epichlorhydrin is added is determined by ability of the circulating water through the jacket of the container to convey away the reaction heat. After the initial exothermic reaction is complete as evidenced by no further tendency toward temperature rise for a period of from 30 to 60 minutes, hot water under pressure is circulated through the jacket to slowly elevate the temperature to 101 degrees centigrade or reflux temperature as in the first procedure. The resultant product shows a higher degree of polymerization than the first product and is particularly effective in the zinc plating bath in the lower current density ranges of from 2 to 40 amperes per square foot.

In each of the above procedures for preparing a polyepoxyamine in lieu of aqueous ammonia a solution of 32 pounds of ethylene diamine in 15 gallons of water may be used. The same amount of epichlorhydrin is used. In this case it is desirable to remove any excess of ethylene diamine which may be present by distillation prior to final polymerization.

The amount or concentration of my novel addition agents will depend upon various conditions such as bath composition, degree of brightness of deposit desired and degree of covering power. A desirable range of effectiveness has been found through the use of from 0.25 to 4.0 grams per liter of cyanide zinc plating bath. The preferred range of concentration is from 0.5 to 2 grams per liter of cyanide zinc plating bath.

Zinc cyanide plating baths containing my novel brighteners produce bright zinc deposits direct from the plating baths. The zinc is relatively pure as it contains no co-deposited brightener metal and its normal ductility has not been materially impaired. If under some conditions of operation a light yellow film occurs over the bright zinc surface, such film can be removed by dipping in any of the commercially used bright dips such as dilute nitric acid (approximately ¼%), dilute acidified hydrogen peroxide, etc., all of which are well known in the art, without staining the bright zinc surface.

Bright zinc deposits from my novel bath composition

can be subjected to any of the many chromate type dips for producing passive surfaces or protective coatings with uniform and satisfactory results. Likewise such bright zinc deposits will take a uniform phosphatizing treatment by any of the widely used commercial processes for producing undercoats on zinc for organic finishes and the like.

My novel brighteners greatly improve the plating characteristics of the zinc cyanide bath in which they are used by increasing both its covering power and throwing power, and by providing a broad range of current densities over which bright deposits can be plated. While my novel brighteners are self-sufficient in producing bright, smooth, relatively pure zinc electrodeposits from zinc cyanide plating baths containing them in solution, there are certain conditions encountered, for example, in barrel plating, where the use of an aromatic aldehyde such as anisic aldehyde or heliotropin, in conjunction with my novel brighteners produces superior results mainly from the standpoint of coverage on low current density areas with improvement in brightness thereon. Accordingly, under such conditions I find it advantageous to add about ¼ to 1 gram of such aromatic aldehyde per liter of zinc cyanide bath containing my novel brightener. Experiments have proven that the action of my novel brighteners with such compounds is synergistic as identical results can not be obtained by the use of either alone. Similarly, if desired for some applications, a metal brightening agent such as a compound of molybdenum or chromium or others given in United States Patent No. 2,080,520, may be employed with my polyepoxyamines.

Having thus described my invention so that those skilled in the art may understand and practice the same, what I desire by Letters Patent is embodied in the appended claims.

I claim:

1. An aqueous zinc cyanide electroplating bath containing a bath soluble polyepoxyamine resulting from the condensation reaction of epichlorhydrin with a primary amine in sufficient amount to provide a bright zinc deposit.

2. An aqueous zinc cyanide electroplating bath containing from 0.25 to 4.0 grams per liter of a bath-soluble polyepoxyamine resulting from the condensation reaction of epichlorhydrin with a primary amine.

3. In the process for electrodepositing zinc, the step comprising depositing zinc from an aqueous zinc cyanide bath containing in solution from 0.25 to 4.0 grams per liter of bath of a bath soluble polyepoxyamine resulting from the condensation reaction of epichlorhydrin with a primary amine.

4. In the process for electrodepositing zinc, the step comprising depositing zinc from an aqueous zinc cyanide bath containing in solution from 0.25 to 4.0 grams per liter of a bath soluble polyepoxyamine resulting from the condensation reaction of epichlorhydrin with a primary amine and an oxyheterocyclic aldehyde.

5. In the process for electrodepositing zinc, the step comprising depositing zinc from an aqueous zinc cyanide bath containing in solution from 0.25 to 4.0 grams per liter of a bath soluble polyepoxyamine resulting from the condensation reaction of epichlorhydrin with a primary amine and a phenyl ether.

6. In the process for electrodepositing zinc, the step comprising depositing zinc from an aqueous zinc cyanide bath containing in solution from 0.25 to 4.0 grams per liter of a bath soluble polyepoxyamine resulting from the condensation reaction of epichlorhydrin with a primary amine and a methoxy benzaldehyde.

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