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2,860,089

METHOD OF ELECTRO DEPOSITING ZINC

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This invention relates to the electrodeposition of zinc, and is more particularly directed to a new and improved plating bath and process for producing bright zinc deposits wherein a cyanide bath contains in solution polyvinyl alcohol and 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 ordinarily 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 zinc coating upon articles of varying shape having 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 common practice in producing 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 predetermined balance between the concentration 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, 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 chromate type or phosphate coatings to promote lacquer adhesion.

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 to the bath because of their instability when in the bath, and the like disadvantage applies to colloids such as gelatin. The use of polyvinyl alcohol is quite common, but much of this material is subject to the disadvantage of salting out of the bath thereby forming a scum on the bath surface, producing an undesirable yellow coloring of the zinc deposit and a zinc deposit which is nonuniform in composition.

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It is among the objects of my invention to provide an addition agent for zinc cyanide plating bath which is effective in producing a bright, smooth relatively pure zinc deposit upon an article treated in the bath. A further object of my invention is to provide cyanide zinc plating baths and a plating process employing the same which produce bright zinc deposits that are uniformly responsive to oxidizing bright dips, chromate type protective dips and phosphatizing dips.

The foregoing objects are accomplished briefly by the use of aqueous cyanide zinc plating baths containing certain low molecular weight polyvinyl alcohols and bath-soluble reaction products of epichlorhydrin with ammonia or primary amines either alone or for some purposes in combination with an aromatic aldehyde selected from the group consisting of oxyheterocyclic aldehydes, phenyl esters and methoxy benzaldehydes. Such reaction products may be known as polyepoxyamines and will be so designated hereinafter. Such polyepoxyamines and polyvinyl alcohol are usually stable in the plating bath and 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 and polyvinyl alcohol also greatly improves the covering power of cyanide zinc plating baths to the extent that recesses in the article being plated which cannot be covered with the metal under ordinary operating conditions are readily covered if such addition agents are present. The polyvinyl alcohols that are usually effective and yet free from the above mentioned salting out may be characterized by the molecular weight range which will produce an aqueous solution having a viscosity between 1 and 4 centipoises at 20° C. when said compounds are dissolved in water at a concentration of 4 percent by weight.

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. A temperature range of from 6 to 10 degrees centigrade is 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 reflex 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.

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In the above procedure 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 with the same amount of epichlorhydrin. In this case it is desirable to remove any excess of ethylene diamine which may be present by distillation prior to final polymerization.

I have discovered that a combination of these polyepoxyamines with a low molecular weight polyvinyl alcohol is synergistic in their effect in that the combination is far superior in effectiveness than could be expected by the additive effect of both additions.

Zinc cyanide plating baths containing my novel brighteners produce bright zinc deposits direct from the plating bath. Furthermore, the additive herein provided is relatively stable and will retain its effectiveness in the plating bath over long periods of operation. The zinc coating 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 1/4%), 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 surface 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. If desired for some applications, a metal brightening agent such as a compound of molybdenum or chromium or others disclosed in United States Patent No. 2,080,520 may be employed with my combination of polyepoxyamine and polyvinyl alcohol.

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 the degree of covering power required. A desirable range of effectiveness has been found to be between the limits of 0.04 to 0.4 gram of polyvinyl alcohol and 0.1 to 1.0 gram of polyepoxyamine per liter of plating bath, with the preferred range from 0.1 to 0.2 gram per liter and 0.2 to 0.4 gram per liter respectively.

While my novel brighteners are effective in any commercially operable cyanide zinc bath, best results are obtained with the approximate bath compositions and operating conditions illustrated by the following examples, which can be varied as required for special purposes in accordance with the known skill in the art. The plating bath is prepared by dissolving the constituents in water, after which the bath should be purified by using about one-half gram of sodium sulfide 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. The brighteners should be dissolved in five to ten parts of water before addition to the bath.

Example 1

	Grams per liter	
Zinc cyanide	60	70
Sodium cyanide	42	
Sodium hydroxide	80	
Polyepoxyamine	0.35	
Polyvinyl alcohol	0.15	75

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This bath was found to produce a bright deposit up to 60 amperes per square foot with an even balance of brightness between the low and high current densities.

Example 2

	Grams per liter
Zinc cyanide	80
Sodium cyanide	50
Sodium hydroxide	113
Polyepoxyamine	0.35
Polyvinyl alcohol	0.15

This bath is preferred where high efficiency plating is desired, at the expense of some of the throwing power.

Example 3

	Grams per liter
Zinc cyanide	60
Sodium cyanide	42
Sodium hydroxide	80
Polyepoxyamine	0.50
Polyvinyl alcohol	0.10

This bath emphasized the brightness in the range below 30 amperes per square foot for installations having limited available electric power.

Example 4

	Grams per liter
Zinc cyanide	60
Sodium cyanide	42
Sodium hydroxide	80
Polyepoxyamine	0.20
Polyvinyl alcohol	0.20

This formulation enhanced the brightness in the high current density range and is therefore suitable for installations having adequate electric power.

Example 5

	Grams per liter
Zinc cyanide	60
Sodium cyanide	42
Sodium hydroxide	80
Polyepoxyamine	0.35
Polyvinyl alcohol	0.15
Anise aldehyde	0.25

This bath produced brilliant deposits in the low current densities, and is recommended in barrel or very low current density plating. Some economy is sacrificed in lieu of added brightness of deposit.

Having thus described my invention so that those skilled in the art may practice the same, what I desire to obtain by Letters Patent is defined by the scope of the appended claims.

I claim:

1. An aqueous cyanide zinc electroplating bath containing a brightening addition agent therefor comprising 0.04 to 0.4 gram per liter of polyvinyl alcohol and from 0.1 to 1.0 gram per liter of a bath soluble polyepoxyamine resulting from the condensation reaction of epichlorhydrin with a primary amine.

2. In the process of electroplating zinc, the step of depositing zinc from an aqueous cyanide zinc bath containing an addition agent comprising 0.04 to 0.4 gram per liter of polyvinyl alcohol and from 0.1 to 1.0 gram per liter of a bath soluble polyepoxyamine resulting from the condensation reaction of epichlorhydrin with a primary amine.

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