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ZINC PLATING

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This invention relates to the production of corrosion resistant zinc coatings on metals and more particularly to the production of zinc coatings by electroplating.

Zinc coatings offer excellent corrosion resistant protection for metallic articles, especially for iron or steel surfaces. Protective zinc coatings may be applied by hot dipping in molten zinc or by electroplating methods. Heretofore, it has been difficult to produce heavy zinc coatings of high ductility, with the result that when zinc coated articles are drawn or bent during manufacturing processes or when in use, the zinc coating tends to crack or chip, impairing the corrosion resistance of the coating. Thus, the "galvanizing" process wherein zinc is coated by dipping metal into molten zinc produces a bright, attractive surface but the coating is relatively brittle and tends to crack or chip off when plated articles are bent or hammered in manufacturing processes. A common method of electroplating zinc comprises the use of an electrolyte containing zinc cyanide, alkali metal cyanide and an alkalining agent such as caustic soda. This electroplating method as utilized heretofore results in zinc coatings of low ductility and furthermore, the coating is of a dull color and less attractive in appearance than the galvanized coating. Such dull electroplated coating must be brightened by burnishing or other mechanical treatment when a bright appearance is desired.

An object of the present invention is to provide a method for producing highly ductile electroplated zinc coating on iron, steel or other electrically conductive bases. A further object is to electrodeposit highly ductile zinc coatings which have a bright appearance. Other objects will be apparent from the following description of my invention.

The above objects may be attained in accordance with my invention by preparing an electrolyte solution containing zinc cyanide, alkali metal cyanide and an alkalining agent, e. g., sodium hydroxide, then purifying the electrolyte by methods hereinafter set forth and thereafter employing the purified solution as electrolyte for electroplating zinc while using a cathode current density sufficiently low to obtain a cathode current efficiency of at least 90%. The temperature of the electrolyte during the electroplating operation may be either at low temperature or at an elevated temperature, up to the boiling point of the solution. In some cases, as hereinafter more fully explained, it is preferable to operate at elevated temperature since this usually allows a higher cathode current density to be employed. When the electroplating process is operated in accordance with my invention at cathode current efficiencies of less than 100% but not lower than 90%, highly ductile deposits are formed which are dull in color or have yellow to brownish coating thereon. Such dull deposits may be transformed to bright plates without loss of ductility by a mild oxidizing treatment, as hereinafter explained. By operating at sufficiently low cathode current densities to attain a cathode current efficiency sufficiently high (i. e. close to 100%) that substantially no hydrogen is evolved at the cathode, bright, crystalline electrodeposits of extremely high ductility are directly obtained without further treatment.

In accordance with my invention, before the electroplating operation is carried out, the electrolyte, which consists of zinc cyanide and alkali metal cyanide and an alkalining agent, first must be purified by one of the hereinafter specified methods. Ordinarily, in zinc plating, the soluble anode is made of high purity zinc. However, I have found that even the best grades of zinc anodes available contain small amounts of impurities and these impurities may be imparted to the electrolyte during electrolysis if certain precautions are not followed. I have found that my herein described method of bath purification removes such impurities from the electrolyte and I have further discovered that once these impurities are removed, their occurrence in the electrolyte in soluble form is prevented by operating the bath to electroplate zinc in accordance with my herein described method.

One method of accomplishing purification of the bath consists in adding thereto a reducing agent. Among the reducing agents which I have found suitable for this purpose are: sodium bisulfite, sodium thiosulfate, phenyl hydrazine hydrosulfate and various water soluble aldehydes, e. g., formaldehyde. The amount of reducing agent required will depend upon the amount of impurities in the electrolyte and/or in the material used as soluble anode. In general, the amount of reducing agent required to purify the electrolyte will be from 0.25 to 0.5 ounce per gallon; if desired large amounts, e. g., up to 10 ounces per gallon may be used. The addition of the reducing agent appears to cause the impurities to precipitate in an insoluble form; the impurities usually settle to the bottom of the bath.

Another method of purifying the bath in accordance with my invention consists in electrolyzing the solution, preferably using zinc anodes, with low anode current densities, preferably current densities not above about 15 amperes per square foot, until the impurities in the electrolyte have been removed from solution by precipitation on the anode. Ordinarily, the time required for this method of purification varies from 12 to 72 hours. If the solution is cold, the

anode current density should not be substantially higher than 15 amperes per square foot; at temperatures of 60° C. or higher, somewhat higher anode current densities may be employed, although I prefer not to exceed about 20 amperes per square foot. Another electrolytic method of purifying the bath in accordance with my invention consists in subjecting the electrolyte to the galvanic action produced by immersing zinc anodes in the bath in intimate contact with iron or steel cathodes. This may conveniently be done by placing the solution in a steel tank and hanging zinc anodes in the solution in contact with the sides of the tank. This galvanic action also may be produced by covering the bottom of a steel tank containing the electrolyte with a layer of granulated zinc. The time required for the purification may be shortened by heating the solution to 60° C. or higher. In these electrolytic methods, the impurities precipitate out on the anodes and fall to the bottom of the container.

A still further method of bath purification consists in precipitating a flocculent, colloidal precipitate in the solution, which precipitate apparently adsorbs the impurities. For example, I have obtained excellent purification by precipitating ferric hydroxide by slowly adding a ferric salt, as ferric sulfate to the alkaline bath, with stirring and then allowing the precipitate to settle. In this method, it is preferable to have substantially all of the iron in the ferric state.

If desired, the bath purification may be accomplished by combination of the above methods, for example, in addition to the purification by electrolysis or galvanic action, a reducing agent may be added to the electrolyte before plating.

The above described bath purification methods will remove soluble impurities from the bath to produce an electrolyte which will deposit highly ductile zinc by my herein described method. Under the conditions of plating in accordance with my invention, further impurities which exist in the anode or in electrolyte material thereafter added to the bath are precipitated during electrolysis, and hence the electroplating operation may be conducted for long periods of time without further bath purification. The bath when purified, may be allowed to stand for considerable periods between plating operations without purification and ordinarily no further purification is required when plating is resumed. The impurities removed or rendered insoluble by the bath purification appear to be soluble compounds of heavy metals such as cadmium and/or lead. The presence of extremely small amounts of such impurities appear to be deleterious in my process and such small amounts are effectively removed by the above described purification methods.

By way of illustration, one method of practicing my invention will be described. A solution is made up which contains from 6 to 12 ounces per gallon of zinc cyanide, 3 to 6 ounces per gallon of sodium zinc cyanide and 6 to 16 ounces per gallon of sodium hydroxide. This aqueous solution then is purified by one of the above described purification methods, for example by adding thereto a small amount of sodium bisulfite. The solution then is employed as electrolyte for electroplating zinc with soluble zinc anode at low temperature. The anode may be of the high purity zinc commonly used in zinc plating or it may be of zinc containing a small amount of alloyed mercury. A zinc-mercury anode is preferable to the pure zinc anode because the effect of the mercury in the former is to facilitate the separation of impurities which deposit on the anode during the electro-plating operation. The small amount of mercury in the zinc anode, e. g., 1 to 2%, apparently tends to amalgamate with the impurities deposited on the anode and thereby aids such impurities to settle to the bottom of the electrolyte container. During the electroplating operation, the cathode current density is maintained sufficienty low that a cathode current efficiency of at least 90% is obtained. For this purpose, cathode current densities of 10 to 60 amperes per square foot may be advantageously employed; with these cathode current densities cathodic zinc deposits are somewhat dull and usually are covered with a brownish or yellowish film. At lower cathode current densities, e. g., 1 to 8 amperes per square foot, a bright crystalline deposit is directly obtained. In either case, whether the deposit is dull or bright, it is highly ductile. The high ductility of the deposit may be demonstrated by bending or folding the electroplated article, which manipulation may be accomplished without cracking, breaking or other failure of the zinc coating. I have thus produced highly ductile deposits on sheet steel which showed no signs of failure on continuous fold and unfolding of the plated sheet until the base metal itself was cracked by this manipulation.

The dull deposits or those having a brownish film may be transformed into bright deposit by a mild oxidation treatment. The oxidizing treatment may be carried out by merely immersing the plated article in a dilute, acidic solution of an oxidizing agent, preferably at room temperature, until the desired brightening effect is obtained. Ordinarily, the brightening effect is obtained by immersion of less than one minute, e. g., 5 to 20 seconds. After the brightening treatment, it is preferable to wash the plated article before allowing it to dry. Examples of preferred oxidizing agents suitable for making these brightening solutions are nitric acid, hydrogen peroxide and chromic oxide. Examples of specific brightening solutions which I have found suitable follow:

Solution A

Aqueous solution containing ½ to 1% by weight of nitric acid.

Solution B

Aqueous solution containing:

	Percent by weight
Sulfuric acid	2 to 5
Hydrogen peroxide (100-volume)	2 to 5

Solution C

Aqueous solution containing:

	Ounces per gallon
Chromic acid	16 to 32
Sulfuric acid (conc.)	0.16 to 0.32

Solution D

Another solution which may be used for brightening the dull plate consists of an alkali metal cyanide solution containing a small amount of hydrogen peroxide, for example a solution containing 2 to 4 ounces per gallon of sodium cyanide, to which is added 2 to 5% by weight of 100-volume hydrogen peroxide solution.

Another mildly oxidizing operation which is effective in removing the brown film comprises

an anodic electrolytic treatment wherein the plated article is made in the anode in an alkaline electrolyte, preferably an alkaline electrolyte containing sodium cyanide, for a short time, e. g., 5 to 10 seconds.

The brown film often may also be removed by merely allowing the wet, electroplated article to stand in the air for a short time after its removal from the plating bath whereupon the oxidizing effect of the air upon the wet surface causes the plate to brighten.

My invention is further illustrated by the following examples:

EXAMPLE 1

Bath purification by electrolysis

Pieces of sheet steel 2" x 6" were plated in the following solution and operating condition:

Electrolyte:	Ounces per gallon
Zinc cyanide	10
Sodium cyanide	3
Caustic soda	10

Operating conditions:

Anodes—Electrolytic zinc	
Ratio of anode to Cathode	2 or 3 to 1
Cathode current density	15 to 40 amps. per sq. ft.
Anode current density	5 to 15 amps. per sq. ft.
Bath temperature	20° to 35° C.

The resulting electrodeposits were dark, grey-colored and unsightly and tarnished and finger-stained readily. These deposits were somewhat brittle and tended to crack and peel from the base metal when the plated sheets were bent.

The solution then was purified by electrolyzing it for 24 hours under the following operating conditions:

Cathode current density	10 amperes per square foot
Anode current density	5 amperes per square foot
Bath temperature	20° to 30° C.

As a result of the above electrolysis, the anode became covered with a dark colored, loosely adherent spongy film. Portions of the spongy mass also settled to the bottom of the bath. Portions of the spongy mass were removed from the bath and upon analysis, was found to contain considerable amounts of cadmium and traces of lead.

After the above described purification by electrolysis, the bath again was employed as electrolyte to electroplate zinc on various steel articles, under the folowing operating conditions:

Bath temperature	20° to 30° C.
Cathode current density	1 to 100 amperes per sq. ft.

At cathode current densities of 1–8 amperes per square foot, there was no hydrogen evolution at the cathode and a bright crystalline deposit was obtained, which were highly ductile. The high ductility was demonstrated by bending steel wire, coated with 0.001 to 0.003 inch of the electrodeposit, about their own diameter; no cracking or other failure of the deposit occurred during this manipulation.

At cathode current densities of 10 to 100 amperes per square foot, some hydrogen evolution occurred at the cathode and the deposit was covered with a brownish film but had substantially the same ductility as that of the plate produced at the lower current densities. Various articles plated at the cathode current densities of 10 to 15 amperes per square foot and having this brownish coloration were successfully brightened by subjecting them to any one of the following mildly oxidizing treatments:

(*a*) Immersing in a 1% aqueous nitric acid solution for 10 to 30 seconds, at room temperature.

(*b*) Immersing for 10 to 30 seconds at room temperature in an aqueous solution of:

	Percent by weight
Sulfuric acid	2 to 5
Hydrogen peroxide (100-volume)	2 to 5

(*c*) Immersing for 10 to 30 seconds at room temperature in an aqueous solution of:

	Ounces per gal.
Chromic acid	16 to 32
Sulfuric acid	0.16 to 0.32

(*d*) Immersing at room temperature in an aqueous solution of:

Sodium cyanide	2 to 4 ounces per gal.
Hydrogen peroxide (100-vol.)	2 to 5% by weight

(*e*) The plated article, wet with the electrolyte, was allowed to stand in the air immediately after its removal from the plating bath for 10 to 30 minutes.

(*f*) Reversing the current in the plating bath, to make the plated article the anode and then electrolyzing for 5 to 10 seconds.

EXAMPLE 2

A number of solutions were made up having the following ingredients in the concentration limits noted:

	Ounces per gallon
Zinc cyanide	6 to 16
Sodium cyanide	2 to 8
Sodium hydroxide	6 to 16

These solutions were used to carry out the operations described in Example 1, and substantially the same results were obtained. In each case, deposits from unpurified baths were dark-colored and more or less brittle, while after purification by electrolysis, the baths plated highly ductile deposits.

EXAMPLE 3

Effect of reducing agents

The following solution was prepared:

	Ounces per gal.
Zinc cyanide	10
Sodium cyanide	5
Sodium hydroxide	10

This solution was purified by adding thereto 0.25 to 3 ounces per gallon of sodium bisulfite and allowing precipitated material to settle. The solution then was employed as a zinc plating bath, under the following operating conditions:

Anode—Electrolytic zinc	
Ratio of anode to cathode area	2 to 1
Cathode current density	1 to 40 amps. per sq. ft.
Bath temperature	20 to 30° C.

The same results were obtained as under Example 1, that is,

(a) Shiny white deposits having high ductility at cathode current densities of 1 to 8 amperes per square foot.

(b) Brownish yellow deposits which could be brightened by dipping in acidic oxidizing solutions at cathode current densities of 10 to 40 amperes per square foot.

EXAMPLE 4

Purification by galvanic action

A solution similar to that of Example 3 was prepared in a steel tank. Zinc anodes then were hung in the solution in direct contact with the steel tank. As a result, the steel tank became cathodic and the impurities present deposited on the tank. After standing for 48 hours under these conditions, the solution was employed as a zinc plating bath at cathode current densities of 1 to 40 amperes per square foot and gave results substantially the same as those obtained from the purified baths in Examples 1 and 3.

EXAMPLE 5

Zinc plating solutions were made up containing varying concentrations of zinc cyanide, sodium cyanide and caustic soda. Each bath was purified before use by the addition of 0.5 ounces per gallon of sodium bisulfite. Pieces of sheet steel two inches by three inches, used as cathodes, were plated in these baths, some at 60° C. bath temperature and others 80° C. bath temperature. During each electroplating operation, the electroplating circuit included a copper coulometer for the purpose of determining the cathode current efficiency. Varying cathode current densities were used and the maximum cathode current density at which a cathode current efficiency of 95% or higher could be obtained was determined at each temperature. With each electrolyte, operating at cathode current efficiencies of 90% or higher, highly ductile deposits of zinc were obtained. The ductility of these deposits was demonstrated by folding the plated sheet upon itself and unfolding; no cracking or other failure of the zinc plate was caused by this manipulation. The above mentioned maximum cathode current densities are shown in the following table:

Concentrations of electrolyte ingredients			Maximum cathode C. D. for cathode current efficiency of at least 95 percent	
$Zn(CN)^2$ Ounces per gallon	NaCN Ounces per gallon	NaOH Ounces per gallon	At 60° C. bath temperature A/SF	At 80° C. bath temperature A/SF
4	3	6	65	100
4	3	10	78	120
8	3	4	80	90
8	3	8	Over 130	Over 200
8	5	8	80	150
8	9	8	40	100
12	3	12	250	500
12	3	16	Over 300	Over 500

EXAMPLE 6

A number of solutions containing zinc cyanide, sodium cyanide and caustic soda were made up and to each was added 0.5 ounce per gallon of sodium bisulfite. These solutions were used as electrolytes to zinc plate sheet steel pieces three by six inches. The plating conditions were the same as described in Example 5, except that the maximum current density was used which would produce bright plate, with substantially no hydrogen evolution at the cathode. Under these conditions, bright, lustrous deposits of highly ductile zinc were produced. The maximum current densities, at temperatures of 70° and 90° C. are given in the following table:

Concentrations of electrolyte ingredients			Maximum cathode current densities	
$Zn(CN)^2$ Ounces per gallon	NaCN Ounces per gallon	NaOH Ounces per gallon	At 70° C. bath temperature Amps./Sq. Ft.	At 90° C. bath temperature Amps./Sq. Ft.
4	3	4	8	32
4	3	8	20	40
8	4	8	24	48
12	6	12	40	80

EXAMPLE 7

The following solution was prepared and by analysis was found to contain:

	Ounces per gallon
Zinc cyanide	9.45
Sodium cyanide (total)	13.8
Caustic soda	7.0

The solution was electrolyzed with electrolytic zinc anodes for a period of approximately 48 hours under the following conditions:

Bath temperature	80° C.
Cathode current density	60 to 100 amperes per square foot
Anode current density	10 to 20 amperes per square foot

Heavy zinc deposits, 0.003 inch to 0.008 inch thick, were produced, which were very ductile and did not separate from the steel on bending. Beautiful shiny white deposits were obtained at cathode current densities of 18 to 100 amperes per square foot on cold rolled sheet steel cathodes, two to three inches in size.

EXAMPLE 8

The following solution was prepared in a steel tank:

	Ounces per gallon
Zinc cyanide	10
Sodium cyanide	4
Caustic soda	12

Because of the heat of solution of the caustic soda, the temperature of the solution when made up was about 60° C. Pure zinc anodes (electrolytic grade) immediately were hung into the solution in direct contact with the sides of the steel tank. As a result, considerable hydrogen was evolved on the surface of the steel tank which became cathode in contact with the zinc anodes. After 48 hours the surface of the steel tank was visibly coated, chiefly with precipitated impurities. Upon subsequent electrolysis of the solution at temperatures above 60° C. and at cathode current densities at which cathode current efficiencies of 90 to 100% were obtained, heavy zinc deposits having very high ductility were readily produced on the cathode.

EXAMPLE 9

Samples of steel wire were electroplated from two plating baths, each containing about eight ounces per gallon of zinc cyanide, about four ounces per gallon of sodium cyanide and about eight ounces per gallon of sodium hydroxide. One bath was purified prior to the electroplating operation by the addition of about 0.5 ounce per gallon of sodium bisulfite. The other bath was used without purification treatment. The purified bath was operated at cathode current densities at

which (a) in one operation, the cathode current efficiency was about 95% and (b) in another operation there was substantially no hydrogen evolution at the cathode. The ductility of the coatings obtained was tested by bending the plated wires. The data and results obtained are tabulated below:

Bath	Run	Cathode C. D.	Bath temp.	Description of electrodeposit
		Amp./sq. ft.	*°C.*	
A—purified bath.	A-1	40	90	Bright, crystalline; and about 0.03 inch thick; coating did not crack when wire was bent about itself.
	A-2	200	80	Dull grey color; about 0.001 inch thick; coating did not crack when wire was bent about itself.
B — Unpurified bath.	B-1	30	30	Dull grey color, darker than A-2, about 0.001 inch thick; coating cracked and peeled, exposing base metal when wire was bent about itself.
	B-2	30	30	Coating about 0.003 inch thick; darker than B-1; very brittle coating, cracking badly and peeling to expose base when wire was bent at an angle of less than 45°.

In order to obtain a highly ductile coating of zinc plate in accordance with my invention, the purified electrolyte, is operated at a cathode current density sufficiently low to result in a cathode current efficiency of at least about 90%. The maximum current density which may be used will vary depending upon the bath temperature and the concentration of the ingredients. Under the above stated conditions, the respective concentrations of zinc cyanide, alkali metal cyanide and alkalining agent may be varied greatly in practicing my invention. However, it is preferable to have some of the concentrations of alkali metal cyanide and alkalining agent, expressed in equivalents of sodium cyanide and caustic soda, respectively, equal to at least about 0.8 times the concentration of the zinc cyanide. Also the alkali metal cyanide and alkalining agent each should be present in appreciable amounts; I prefer to use an amount of alkali metal cyanide equivalent to a sodium cyanide concentration equal to at least 0.25 times the zinc cyanide concentration and an alkalining agent concentration equivalent to a caustic soda concentration equal to at least 0.2 times the zinc cyanide concentration.

In general, as the total concentration of electrolyte ingredients is increased, the maximum current density at which the highly ductile deposits may be obtained is likewise increased, for a given operating temperature. However, I have found that the increase in this maximum current density depends on the relative proportions of the ingredients, as well as the total concentration. For example, for a given zinc cyanide concentration, in order to attain the highest possible current density at which highly ductile zinc may be plated at a given temperature, the alkali metal cyanide concentration, expressed in sodium cyanide equivalent, must lie in the range 0.25 to 0.8 times the zinc cyanide concentration and the sum of the concentration of alkali metal cyanide and alkalining agent, expressed in equivalents of sodium cyanide and caustic soda, respectively, should be at least equal to the zinc cyanide concentration. Preferably, the concentration of the alkalining agent, expressed as caustic soda equivalent, should be equal to or greater than the zinc cyanide concentration. Examples of preferred electrolyte compositions follow:

Bath	$Zn(CN)_2$	NaCN	NaOH
	Oz./gal.	*Oz./gal.*	*Oz./gal.*
A	4	3	4
B	8	4	8
C	12	6	12

It is to be understood that baths having different concentration ratios may be used but in such cases correspondingly lower cathode current densities usually must be employed. For example, if the sodium cyanide concentration is either greatly increased or greatly decreased beyond that shown in the above table in any one of the baths illustrated, the maximum allowable cathode current density will be correspondingly less. Also if the proportion of caustic soda is greatly decreased from that shown, the maximum cathode current density will be less but if desired, higher concentrations of caustic than those given above may be used without decreasing the maximum cathode current density figure.

I have found that by carefully proportioning the electrolyte ingredients, I may produce highly ductile zinc deposits at cathode current efficiencies of 90% or better while employing unusually high cathode current densities, e. g., 40 to 100 amperes per square foot with a cold bath and 100 to 500 amperes per square foot or even higher if the bath is heated, e. g. to 60° C. or higher. In order to obtain a highly ductile deposit and utilize such high cathode current densities, the zinc cyanide content of electrolyte preferably is not less than about 8 ounces per gallon, the ratio of sodium cyanide concentration to zinc cyanide concentration must lie between 0.25 and 0.6 and the concentration of alkalining agent must be equivalent to at least 6 ounces per gallon of sodium hydroxide. By operating at high bath temperatures, e. g., 80° C. or higher, the same results may be obtained with a wider range of concentration of the electrolyte ingredients. However, even at these higher temperatures, in order to utilize a cathode current density of 100 amperes per square foot or higher, the zinc cyanide content ordinarily should not be less than 4 ounces per gallon, the alkalining agent should be equivalent to a caustic soda concentration at least equal to that of the zinc cyanide and the ratio of the alkali metal cyanide concentration to the zinc cyanide concentration should be substantially as specified above.

I have discovered that if the conditions of the electrolysis are so conducted that the cathode current density is sufficiently low that there is substantially no hydrogen evolution at the cathode, the highly ductile deposit which is formed on the cathode has a bright and lustrous appearance. To attain this result, it is necessary to operate with a cathode current efficiency close to 100%, e. g. 97 to 100% efficiency. This bright, lustrous, ductile deposit is unique in that it is highly resistant to tarnish and does not readily finger stain when handled. Further, these bright deposits in general are somewhat more ductile than the above described slightly dull but highly

ductile deposits produced by operating at around 90 to 95% cathode efficiency. Practically any alkaline zinc plating bath containing zinc cyanide, sodium cyanide and caustic soda or its equivalent may be used to produce such bright, lustrous, ductile deposits provided that the conditions are such that substantially no hydrogen is evolved at the cathode. In order to produce the extremely high current efficiency necessary to produce the bright deposit, the cathode current density must be correspondingly lower than is required to electroplate at lower cathode current efficiencies. Thus a solution containing four ounces per gallon of zinc cyanide may have to be operated at cathode current densities as low as 1 to 5 amperes per square foot in order to produce the bright deposits. In order to utilize a reasonably high current density and thereby decrease the time required for plating a given deposit, I prefer to operate at temperatures of 60 to 80° C. or higher, preferably at the boiling point of the solution. At such temperatures, a bath containing four ounces per gallon of zinc cyanide and suitable amounts of alkali metal cyanides and alkalining agents may be operated at 10 to 50 amperes per square foot current density to produce the bright, ductile plate. At higher zinc cyanide concentrations and with suitable proportions of alkali metal cyanide and alkalining agent and by operating at bath temperatures of around 90° C., I have been able to produce these lustrous, ductile deposits at cathode current densities as high as 80 amperes per square foot.

In addition to the effects of temperature and electrolyte concentration, the maximum current density which may be used in practicing my invention may also depend more or less on the size and shape of the electrodes and the spacing between anode and cathode. For example, theoretical considerations indicate that a spherical cathode, concentric with a hollow sphere anode would allow higher cathode current densities to be employed with a given solution and temperature, to attain a given cathode current efficiency than any other cathode-anode arrangement. In general, large cathodes require smaller cathode current densities than small ones and deeply recessed cathodes require smaller current densities than flat pieces.

While, for the purpose of illustration, I have described electrolytes containing sodium cyanide, other alkali metal cyanides, e. g., potassium cyanide may be used equally well. Likewise, I have found that other strong alkalies, e. g., potassium hydroxide, may be used in place of caustic soda as alkalining agent.

I claim:—

1. A process for electroplating zinc comprising preparing an aqueous solution containing zinc cyanide, alkali metal cyanide and an alkalining agent, treating said solution to substantially completely precipitate soluble heavy metal impurities therefrom and thereafter employing the purified solution as electrolyte to electroplate articles of electrically conductive material at a cathode current density sufficiently low to obtain a cathode current efficiency not lower than about 90%.

2. A process for electroplating zinc comprising preparing an aqueous solution containing zinc cyanide, alkali metal cyanide and an alkalining agent, treating said solution to substantially completely remove soluble heavy metal impurities therefrom and thereafter employing the purified solution as electrolyte to electroplate articles of electrically conductive material at a cathode current density sufficiently low to prevent substantial hydrogen evolution at the cathode.

3. A process comprising adding to a zinc plating bath which contains zinc cyanide, alkali metal cyanide and an alkalining agent a soluble reducing agent in a concentration not less than that required to substantially completely precipitate heavy metal impurities from said bath and thereafter electrodepositing zinc from said bath at a cathode current density which is sufficiently low to obtain a cathode current efficiency not lower than about 90%.

4. A process for electroplating zinc comprising preparing an aqueous solution containing zinc cyanide, alkali metal cyanide and an alkali metal hydroxide, treating said solution to precipitate soluble impurities therefrom by adding to said solution sodium bisulfite in a concentration not less than about 0.25 ounce per gallon and thereafter employing the purified solution as electrolyte to electroplate articles of electrically conductive material at a cathode current density sufficiently low to obtain a cathode current efficiency not lower than about 90%.

5. A process for electroplating zinc comprising preparing an aqueous solution containing zinc cyanide, alkali metal cyanide and an alkali metal hydroxide, treating said solution to substantially completely precipitate soluble heavy metal impurities therefrom by subjecting said solution to electrolysis with an anode current density of not more than about 20 amperes per square foot when the solution temperature is not lower than 60° C. and not more than about 15 amperes per square foot when the solution temperature is below 60° C. and thereafter employing the purified solution as electrolyte to electroplate articles of electrically conductive material at a cathode current density sufficiently low to obtain a cathode current efficiency not lower than about 90%.

6. A process for electroplating zinc comprising preparing an aqueous solution containing zinc cyanide, alkali metal cyanide and an alkalining agent, the alkali metal cyanide concentration of said solution, expressed in equivalents of sodium cyanide, being 0.25 to 0.8 times the zinc cyanide concentration and the sum of the concentrations of the alkali metal cyanide and the alkalining agent being not less than the zinc cyanide concentration, treating said solution to substantially completely precipitate soluble heavy metal impurities therefrom and thereafter employing the purified solution as electrolyte to electroplate articles of electrically conductive material at a cathode current density sufficiently low to obtain a cathode current efficiency not lower than about 90%.

7. A process for electroplating zinc comprising preparing an aqueous solution containing not less than about 8 ounces per gallon of zinc cyanide, not less than 3 ounces of sodium cyanide and not less than 6 ounces per gallon of sodium hydroxide, the sodium cyanide concentration being not more than 0.6 times the zinc cyanide concentration, treating said solution to precipitate soluble impurities therefrom by adding to said solution sodium bisulfite in a concentration not less than about 0.25 ounce per gallon in a concentration of 0.25 to 1.0 ounce per gallon and therafter employing the purified solution as electrolyte to electroplate articles of electrically conductive material at a cathode current density sufficiently low to prevent substantial hydrogen evolution at the cathode.

8. A process for electroplating zinc compris-

ing preparing an aqueous solution containing zinc cyanide, alkali metal cyanide and an alkalining agent, treating said solution to substantially completely precipitate soluble heavy metal impurities therefrom and thereafter employing the purified solution as electrolyte to electroplate articles of electrically conductive material at a cathode current density sufficiently low to obtain a cathode current efficiency not lower than about 90% and thereafter subjecting the electroplated articles to a mild oxidation treatment.

9. A process comprising adding to a zinc plating bath which contains zinc cyanide, alkali metal cyanide and an alkali metal hydroxide, a soluble reducing agent in an amount not less than that required to substantially completely remove heavy metal impurities from said bath, thereafter electrodepositing zinc from said bath at a current density sufficiently low to obtain a cathode current efficiency not lower than about 90% and treating the resulting electrodeposit with a dilute acidic solution of an oxidizing agent.

10. A process for electroplating zinc comprising an aqueous solution containing zinc cyanide, sodium cyanide and sodium hydroxide, the sodium cyanide concentration of said solution being 0.25 to 0.8 times the zinc cyanide concentration and the sum of the concentrations of the sodium cyanide and sodium hydroxide being not less than the zinc cyanide concentration, treating said solution to precipitate soluble impurities therefrom by adding to said solution sodium bisulfite in a concentration not less than about 0.25 ounce per gallon and thereafter employing the purified solution as electrolyte to electroplate articles of electrically conductive material at a temperature not lower than 60° C. with a cathode current density sufficiently low to obtain a cathode current efficiency not lower than about 90% and thereafter treating the electroplated articles with a dilute solution of hydrogen peroxide.

11. The process comprising treating a zinc plating bath containing zinc cyanide, alkali metal cyanide and an alkalining agent to substantially completely precipitate soluble heavy metal impurities therefrom, thereafter electrodepositing zinc from said bath and subjecting the resulting electrodeposit to a bright dipping operation.

12. The process comprising treating a zinc plating bath containing zinc cyanide, alkali metal cyanide and an alkalining agent to substantially completely precipitate soluble heavy metal impurities therefrom, thereafter electrodepositing zinc from said bath and treating the resulting electrodeposit with a dilute nitric acid solution.

13. The process comprising adding to a zinc plating bath which contains zinc cyanide, alkali metal cyanide and an alkali metal hydroxide a soluble reducing agent in a concentration not less than that required to substantially completely precipitate soluble heavy metal impurities in said bath, thereafter electrodepositing zinc from said bath and treating the resulting electrodeposit with a dilute acidic solution of an oxidizing agent.

14. The process comprising adding to a zinc plating bath which contains zinc cyanide, alkali metal cyanide and an alkali metal hydroxide a soluble bisulfite in a concentration not less than that required to substantially completely precipitate soluble heavy metal impurities in said bath, thereafter electrodepositing zinc from said bath and treating the resulting electrodeposit with a dilute nitric acid solution.

15. A process for electroplating zinc comprising preparing an aqueous solution containing zinc cyanide, alkali metal cyanide and an alkalining agent, treating said solution to substantially completely precipitate soluble heavy metal impurities therefrom and thereafter employing the purified solution as electrolyte to electroplate articles of electrically conductive material at a temperature not lower than 60° C. with a cathode current density sufficiently low to obtain a cathode current efficiency not lower than about 90%.

16. A process for electroplating zinc comprising preparing an aqueous solution containing not less than about 8 ounces per gallon of zinc cyanide, a concentration of alkali metal cyanide equivalent to not less than 3 ounces per gallon of sodium cyanide and a concentration of alkalining agent equivalent to not less than about 6 ounces per gallon of sodium hydroxide, the alkali metal cyanide concentration being not more than 0.6 times the zinc cyanide concentration, treating said solution to substantially completely precipitate soluble heavy metal impurities therefrom by adding to said solution sodium bisulfite in a concentration not less than about 0.25 ounces per gallon and thereafter employing the purified solution as electrolyte to electroplate articles of electrically conductive material at a temperature not lower than 60° C. with a cathode current density sufficiently low to obtain a cathode current efficiency not lower than about 90%.

17. A process for electroplating zinc comprising preparing an electrolyte containing zinc cyanide, alkali metal cyanide and an alkalining agent, treating said solution to substantially completely precipitate soluble compounds of heavy metals other than zinc and thereafter electroplating zinc from said solution.

18. A process for electroplating zinc comprising preparing an aqueous solution containing zinc cyanide, alkali metal cyanide and an alkalining agent, treating said solution to precipitate soluble heavy metal impurities therefrom by adding to said solution a soluble reducing agent in a concentration not less than that required to substantially completely precipitate said impurities and thereafter employing the purified solution as electrolyte to electroplate articles of electrically conductive material at a temperature not lower than 60° C. with a cathode current density sufficiently low to obtain a cathode current efficiency not lower than about 90%.

19. A process for electroplating zinc comprising preparing an aqueous solution containing zinc cyanide, alkali metal cyanide and an alkali metal hydroxide, treating said solution to precipitate soluble heavy metal impurities therefrom by adding to said solution a soluble reducing agent in a concentration not less than that required to substantially completely precipitate said impurities and thereafter employing the purified solution as electrolyte to electroplate articles of electrically conductive material at a temperature not lower than 60° C. with a cathode current density sufficiently low to obtain a cathode current efficiency not lower than about 90% and thereafter treating the electroplated articles with an acidic solution of an oxidizing agent.

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