Patented Feb. 7, 1939 2,146,439

UNITED STATES PATENT OFFICE

2,146,439

ZINC PLATING

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No Drawing. Application May 6, 1935, Serial No. 20,054

9 Claims. (Cl. 204—18)

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

This application is a continuation in part of my co-pending applications, Ser. Nos. 752,703 and 752,704.

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 relatively low ductility and furthermore, the coating is of a dull color and less attractive in appearance than the galvanized coating. Such dull electroplated coatings 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. A further object is to produce by an electroplating process a smooth, bright, mirror-like zinc coating on iron, steel, or other electrically conductive bases. Other objects will be apparent from the following description of my invention.

In my above mentioned co-pending applications, Ser. Nos. 752,703 and 752,704, I have disclosed and claimed a method for electroplating zinc whereby relatively bright, highly ductile electrodeposits of zinc may be obtained. One feature of this electroplating process comprises purifying the electroplating solution by several alternative means, one of which consists in the addition of a reducing agent such as sodium bisulfite to the electroplating bath. In accordance with the process described and claimed in my above mentioned co-pending applications, by operating the purified electrolyte at cathode current efficiencies close to 100%, bright deposits are obtained which are of extremely high ductility. At somewhat lower cathode current efficiencies, e. g., 90–95%, the coatings produced, while still highly ductile, are more or less dull in color. These dull coatings in accordance with my previously described inventions may be brightened more or less by a mild oxidation treatment, e. g., by dipping in a dilute nitric acid solution or a sulfuric acid solution to which has been added hydrogen peroxide. These bright, ductile deposits produced by my prior inventions, whether by operating close to 100% current efficiency or by bright dipping, are, when compared with bright dipped plate hereinafter described, more accurately described as "semi-bright"; they do not have a mirror-like appearance unless they are buffed or burnished.

I have now discovered that in place of the purification treatments described and claimed in the above mentioned co-pending applications, I can obtain excellent purification of the bath by adding thereto certain sulfur compounds, hereinafter described, which appear to act to precipitate heavy metals from their solutions in the form of insoluble salts. I have further discovered that the use of such sulfur compounds to purify the bath leads to improved results in the obtaining of bright deposits by a bright dipping treatment after plating when the plating is done at cathode current efficiencies sufficiently low to produce dull coatings. More specifically, I have found that when the purified bath is used to electroplate iron, steel or other articles under such conditions that hydrogen is evolved from the cathode and the electroplated article has a brownish or yellowish thin coating on the electrodeposit, by subsequently bright dipping in an acidic oxidizing solution, the dull electroplate is transformed to a bright, smooth, substantially mirror-like finish without the necessity of burnishing, buffing or similar mechanical treatment. This result I have not been able to obtain by adding bisulfite or other reducing agent to the bath as described in the aforesaid co-pending applications.

Highly ductile zinc deposits may be obtained in

accordance with the present 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 adding certain sulfur compounds as 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, e. g. 60° C. or higher, 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 about 98%, deposits are formed which are slightly dull or have a thin yellow to brownish coating thereon. Such dull deposits may be transformed to bright, smooth, mirror-like plates 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, (but not mirror-like) crystalline electrodeposits of extremely high ductility are directly obtained without further treatment.

In accordance with the present invention, before using an alkaline electrolyte for zinc plating, I add thereto a sulfur compound soluble in the plating bath which is capable of precipitating heavy metals, e. g., lead, etc., from their solutions in the form of insoluble salts. The sulfur compounds which I have found suitable for this purpose may be either organic or inorganic and include soluble sulfides (including polysulfides), e. g., sodium sulfide, potassium sulfide, barium sulfide and hydrogen sulfide; zinc sulfide, soluble thiosulfates, e. g., sodium thiosulfate or potassium thiosulfate; soluble hydrosulfites, e. g., sodium hydrosulfite; soluble thiocyanates, e. g., sodium thiocyanate; soluble thiocarbonates, e. g. potassium ethyl xanthate or other soluble xanthates; the amides of thiocarbonates, e. g., thiourea; the thiuram sulfides, e. g. tetramethyl thiuram monosulfide ($((CH_3)_2NC:S.S.C:S.N(CH_3)_2)$). In order to purify the bath I merely add a small amount of one of these sulfur compounds. The required amount depends upon the amount of impurities to be precipiated. In general the amount of impurities present are very small and an amount of sulfur compound equivalent to a fraction of an ounce per gallon of solution ordinarily is sufficient to purify the bath and leave a small excess of the sulfur compound therein. Generally I prefer to add from 0.1 to 5 ounces per gallon of the sulfur compound. It is usually preferable, when possible, to add sufficient of the sulfur compound so that after purification is complete, a small excess of the sulfur compound is left in the bath. This is possible only when the sulfur compound does not precipitate zinc, e. g. by the use of a thiocyanate. If compounds which precipitate zinc are used, e. g. sulfides, the excess of sulfur compound soon appears to become completely reacted. When a considerable amount of impurities have been precipitated, it is preferable but not essential to filter the bath before using it. I have further found that it is often desirable to age the purified bath by subjecting it to electrolysis for a short time, e. g. from 15 minutes to several hours, before putting it into regular use; this appears to aid somewhat in obtaining more complete precipitation of the impurities. During extended periods of operation, it is advisable to add further small amounts of the sulfur compound from time to time (e. g., daily) or as required, to compensate for impurities which may enter the electrolyte. While I prefer to add not more than 5 ounces per gallon of sulfur compound per bath, larger amounts may be used if desired, since such excess ordinarily is not especially disadvantageous, except when the sulfur compound precipitates zinc in which case an excessive amount would unduly lower the zinc concentration.

The above described bath purification method 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 the preferred embodiment of my invention, further impurities which exist in the anode or in electrolyte material thereafter added to the bath may be 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, tin and/or lead. The presence of extremely small amounts of such impurities appears to be deleterious in my process and such small amounts are effectively removed by the above described purification method.

In order to prevent impurities in the anodes from dissolving in the bath, I have found that the plating conditions must be such that the current efficiency at the anode must be substantially not lower than 100%. Under these conditions, the impurities appear to precipitate on the anode and/or fail to go into solution and finally drop to the bottom of the plating tank. I prefer to use zinc anodes containing a small percentage of mercury alloyed therewith, as the mercury, probably by amalgamation, appears to aid in settling out the impurities precipitated on the anode surface. Alternatively, instead of operating at 100% anode current efficiency, I may use absolutely pure zinc anodes. However, anodes of such high purity are difficult to obtain, and I prefer to operate at 100% anode current efficiency.

The conditions required to attain 100% anode current efficiency are well known to the electroplaters; such conditions will vary with various plating bath formulae. In general, it may be stated that to obtain 100% efficiency, the current density at the anode should not be too high for a given plating solution; and if the anodic current efficiency falls below 100%, this may be corrected by lowering the anodic current density and/or increasing the bath temperature. By way of example, I have obtained 100% anodic current efficiency by operating in the cold, at average anode current densities of 15 to 25 amperes per square foot, baths containing 6 to 12 oz. per gal. of zinc cyanide, 3 to 8 oz. per gal. of sodium cyanide and 6 to 10 oz. per gal. of sodium hydroxide. If these baths are operated hot, i. e. at 60° C. or higher, the average anodic current

densities may vary from 25 to 40 amperes per square foot to obtain 100% anodic current efficiency.

If the anodic current efficiency should be allowed to fall below substantially 100% for sufficient time to foul the bath with impurities, the bath may readily be repurified by the addition of a sulfur compound as above described.

By way of illustration, one method of practicing my invention to obtain a highly ductile zinc electrodeposit will be described. A solution is made up which contains from 6–12 ounces per gallon of zinc cyanide, 3–6 ounces per gallon of sodium cyanide and 6–16 ounces per gallon of sodium hydroxide. This solution then is purified by adding a small amount of one of the above mentioned sulfur compounds, whereupon the impurities are precipitated. Preferably the amount of sulfur compound added is sufficient to leave an excess, preferably an excess of at least 0.1 ounce per gallon, of the sulfur compound in solution. The solution then is employed as electrolyte for electroplating zinc with soluble zinc anode at an elevated temperature, e. g. above 60° C. and at such cathode current density that a cathode current efficiency of at least 90% is obtained. Preferably, the bath is allowed to stand to settle out the precipitate and/or filtered before using.

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 the sum 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 0.6 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, other conditions being unchanged. 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 allowable cathode current density for the production of ductile zinc 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 in my purified bath, I may produce 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 (although not mirror-like) 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 hereinbefore 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, so-

dium 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, e. g. 8 to 12 ounces per gallon, 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, highly 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 operated at a given 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.

As has been mentioned above, if the current efficiency of the plating bath during operation falls sufficiently low, hydrogen is evolved at the cathode and the cathodic deposit is more or less dull in appearance and usually is covered with a yellowish or brownish film. This is especially true when the current efficiency falls below 90% at the cathode and the cathodic hydrogen evolution is more or less vigorous. If the electroplating bath is operated under such conditions after having been purified by the addition of sulfur compounds as above described, bright dipping of the resulting electrodeposit in an oxidizing solution or other mild oxidation treatment results in a smooth, bright, substantially mirror-like plate. The characteristic yellowish brown coating which is formed in this process appears in the form of an extremely thin film covering the zinc deposit. Often, this film is sufficiently thin that the bright deposit underneath is fairly visible, thus producing a fairly bright, smooth plate which is satisfactory in appearance for many uses. The exact nature of this brownish film has not been determined and may possibly consist of insoluble impurities deposited by cataphoresis or it may be in the nature of interference colors caused by a slight film of oxide on a highly reactive surface layer of the deposited metal. In any event, if the conditions are such that this characteristic brown film is produced, subsequent bright dipping in an acidic oxidizing solution will produce an extremely bright, smooth, mirror-like finish which resembles a buffed or burnished surface. These mirror-like plates thus produced ordinarily are not highly ductile, their ductility in general being dependent upon cathode current efficiencies obtained while the plate is being deposited. They are, however, much more ductile than zinc coatings obtained by the hot dip method and have a much better appearance than such coatings. In general, they may be said to have substantially the same degree of ductility as ordinary zinc coatings produced by electroplating from unpurified zinc cyanide solutions.

In order to produce the mirror-like plate by the above described method the plating conditions preferably are such that visible cathodic hydrogen evolution occurs. While I prefer to operate under such conditions that the cathode current efficiency is not greater than about 90%, it is possible to produce the mirror-like coating by plating at higher current cathode efficiencies, especially if the bath is maintained at temperatures not greater than about 40° C. Under some conditions, especially at the lower temperatures, there may be substantially no visible hydrogen evolution and yet the electrodeposit will have the characteristic yellowish film and on bright dipping the mirror-like surface is obtained. For a given bath composition and concentration at a given operating temperature there will be a maximum cathode current efficiency, in amount not greater than about 98%, which should not be exceeded if it is desired to produce the mirror-like coating. If such maximum efficiency is exceeded, the coating is the semi-bright highly ductile deposit described above. It is difficult to predict with certainty just what the maximum current efficiency should be for a given solution operated at a given temperature to produce the mirror-like deposit by bright dipping. This is easily determined, however, by experimentation and in practical operation, if the deposits do not produce the desired results on bright dipping, the operator should take steps to reduce the current efficiency to a point where the desired result is obtained. The current efficiency may thus be decreased by (*a*) decreasing the temperature of the bath, (*b*) increasing the cathode current density, (*c*) diluting the bath to decrease the concentration of the ingredients thereof and/or (*d*) increasing the free cyanide content of the bath. Thus by varying these conditions the current efficiency of the bath may be adjusted as desired to produce either a semi-bright highly ductile plate or a somewhat dull plate covered with a yellowish film which on bright dipping acquires a mirror-like surface.

The operation for the transformation of the plate covered with the yellowish film to the bright mirror-like condition may comprise contacting the surface of the plated article for a short time with a dilute solution of an oxidizing agent, preferably at about room temperature, until the desired brightening effect is obtained. Other mild oxidation treatments, as hereinafter described, likewise may be used to remove the brown film. In general, I prefer to use an acidic oxidizing solution for this purpose. Also, it is preferable to thoroughly wash the plate to remove the alkaline plating solution therefrom before contacting it with the acid bright dip solution and if desired, the plate may be treated with

a non-oxidizing acid solution, e. g. dilute H_2SO_4 or HCl to remove all traces of alkali prior to bright dipping. Ordinarily, the brightening effect is obtained by immersion of less than one minute, e. g., 5 to 20 seconds, in the bright dip solution. 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:

	Per cent by weight
Sulphuric acid	2 to 5
Hydrogen peroxide (100 volume)	2 to 5

Solution C

Aqueous solution containing:

	Ounces per gallon
Chromic acid	16 to 32
Sulphuric 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 following examples illustrate specific methods of practicing the herein described invention:

Example 1

A zinc cyanide plating bath was made containing five ounces per gallon each of zinc cyanide, sodium cyanide and caustic soda, to which was added one ounce per gallon of sodium bisulfite. This solution was divided into two portions; to one portion was added one-half ounce per gallon of hydrated sodium sulfide (Na_2S+9H_2O) and to the other portion 0.8 gram per gallon of the hydrated sodium sulfide. The addition of the sulfide caused the formation of a precipitate; in the portion to which was added the larger amount of sulfide, the precipitate was voluminous and gray in color, indicating that some zinc sulfide had been precipitated. A brownish color was imparted to the bath to which 0.8 gram per gallon of sulfide had been added. Each portion of the solution was separately electrolyzed with zinc anodes and sheet steel cathodes for a period of about ten minutes. The baths were operated at room temperature with cathode densities of 20 to 50 amperes per square foot. In each case there was a voluminous evolution of hydrogen from the cathodes during the electrolysis. The resulting cathodic deposits were covered with a thin, brownish colored film. The cathodes were thoroughly washed in water and then were immersed for a few seconds in a 0.5% aqueous solution of nitric acid and following this, washed and dried. The nitric acid treatment completely removed the bronze film and the resulting plate in each case was smooth, bright and mirror-like.

Example 2

The procedure of Example 1 was repeated except that the solution used contained ten ounces per gallon each of zinc cyanide, sodium cyanide and caustic soda. Instead of the addition of sodium sulfide to one portion of the solution, ten grams per gallon of barium sulfide was added and another portion, fifteen grams per gallon of zinc sulfide. The electrodeposits secured from these solutions after treatment in one-half per cent nitric acid solution, had the same characteristics as the plates produced by the procedure of Example 1.

Example 3

To a zinc cyanide plating solution containing ten ounces each of zinc cyanide, sodium cyanide and caustic soda was added ten grams per gallon of potassium ethyl xanthate. Zinc deposits electro-plated from this solution and treated with nitric acid according to the procedure of Example 1 produced smooth, bright, mirror-like plates.

Example 4

The procedure of Example 3 was repeated, except that 180 grams per gallon of sodium thiocyanate was added to the solution in place of the xanthate. The results obtained were identical with the results of Example 3.

Example 5

The procedure of Example 3, employing ½ ounce per gallon of thiourea in place of the xanthate, produced smooth, bright, mirror-like plates.

Example 6

A zinc cyanide plating bath was made up containing 12 ounces per gallon of zinc cyanide, 9 ounces of sodium cyanide and 12 ounces per gallon of caustic soda. To this was added one ounce per gallon of sodium bisulfite and one-half ounce per gallon of sodium thiosulfate. This solution was used to electrodeposit zinc at various temperatures and at various cathode current densities, the cathode current efficiencies being determined for each run. By operating the bath at cathode current densities of 20 to 50 amperes per square foot at a temperature of about 25° C., plates having a bronze-like film similar to those produced in the above examples were obtained, which were transformed to smooth, bright, mirror-like plates by dipping in one-half per cent nitric acid.

The cathode current efficiencies obtained at the different current densities are shown in the following table:

Current density	Current efficiency
	Per cent
20 amperes per square foot	97.3
30 amperes per square foot	90.4
40 amperes per square foot	78.5
50 amperes per square foot	65.0

When the above solution was operated at a bath temperature of 45° C., deposits made at cathode current efficiencies in excess of 98% were

highly ductile but did not form mirror-like deposits on bright dipping in nitric acid. The deposits produced at current efficiencies below 98% produced the deposits having the characteristic bronze-like film which were transformed to the mirror-like appearance on bright dipping in dilute nitric acid. The following table shows the cathode current densities, cathode current efficiencies and the results obtained in a number of runs.

Current density	Current efficiency	Description of electrodeposit
	Per cent	
20 amperes per square foot	99.2	Highly ductile.
30 amperes per square foot	99.3	Do.
40 amperes per square foot	99.9	Do.
50 amperes per square foot	96.4	Mirror-like after bright dipping.
60 amperes per square foot	95.8	Do.

My herein described invention is not restricted to any particular alkaline zinc cyanide electrolyte nor to any particular range of concentrations or proportions of electrolyte ingredients, excepting the particular ranges of concentration and proportions required to obtain certain particular results as described hereinbefore, e. g., the production of highly ductile deposits at unusually high cathode current densities. Practically any cyanide electrolyte suitable for electroplating zinc may be adapted in practicing the present invention to produce the bright, mirror-like deposits. I prefer, however, to use solutions which contain approximately the same concentrations of zinc cyanide and sodium hydroxide or equivalent alkaline material, together with a concentration of alkali metal cyanide not substantially greater than that of the zinc cyanide. These preferred proportions may be varied within very wide limits to obtain very satisfactory results. For reasons of efficiency and economy I also prefer to operate electrolytes containing not less than about 4 ounces per gallon and not more than about 12 ounces per gallon of zinc cyanide.

If desired, various reducing agents, e. g. bisulfites and/or various addition agents such as organic colloids may be added to the plating bath in practicing the herein described invention. Moreover, the herein described method of bath purification may be used to supplement bath purification accomplished by the method described in my copending applications hereinbefore mentioned.

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 from a zinc cyanide solution containing alkali metal cyanide and alkali metal hydroxide comprising adding to said solution a soluble sulfide in an amount sufficient to substantially completely precipitate dissolved heavy metal impurities and thereafter electroplating zinc from said solution.

2. A process for electroplating zinc from a zinc cyanide solution containing alkali metal cyanide and alkali metal hydroxide comprising adding to said solution a soluble sulfide in an amount sufficient to substantially completely precipitate dissolved heavy metal impurities and thereafter electroplating zinc from said solution at a cathode current density sufficiently low to obtain a cathode current efficiency of not less than about 90%.

3. A process for electroplating zinc comprising preparing a solution containing zinc cyanide, alkali metal cyanide and an alkali metal hydroxide, adding to said solution a soluble sulfide in an amount sufficient to substantially completely precipitate dissolved heavy metal impurities in said solution and thereafter electroplating zinc from said solution at a cathode current density sufficiently low to obtain a cathode current efficiency of not less than about 90%.

4. A process for electroplating zinc comprising preparing a solution containing zinc cyanide, alkali metal cyanide and an alkali metal hydroxide, adding to said solution a soluble sulfide in an amount sufficient to substantially completely precipitate dissolved heavy metal impurities in said solution and thereafter electroplating zinc from said solution at a cathode current density sufficiently low to obtain a cathode current efficiency of 90–100% and at an anode current density sufficiently low to obtain an anode current efficiency of not less than 100%.

5. A process for electroplating zinc comprising preparing a solution containing zinc cyanide, alkali metal cyanide and an alkali metal hydroxide, adding to said solution sodium sulfide in an amount sufficient to substantially completely precipitate dissolved heavy metal impurities in said solution and thereafter electroplating zinc from said solution at a cathode current density sufficiently low to obtain a cathode current efficiency of 90–100% and at an anode current density sufficiently low to obtain an anode current efficiency of not less than 100%.

6. A process for producing a zinc electrodeposit comprising purifying a zinc cyanide solution containing alkali metal cyanide and an alkali metal hydroxide by adding thereto a sulfur compound, capable of precipitating heavy metals in the form of insoluble salts, selected from the group consisting of thiocyanates, thiosulfates, xanthates and sulfides, soluble in said solution, in an amount sufficient to substantially completely precipitate heavy metal impurities in said solution, electroplating zinc from the so purified solution at a current density sufficiently high that hydrogen is evolved from the cathode, and thereafter dipping the resulting electrodeposit in a dilute solution of an oxidizing agent.

7. A process for producing a zinc electrodeposit comprising purifying a zinc cyanide solution containing alkali metal cyanide and an alkali metal hydroxide by adding thereto a sulfur compound, capable of precipitating heavy metals in the form of insoluble salts, selected from the group consisting of thiocyanates, thiosulfates, xanthates and sulfides, soluble in said solution, in an amount sufficient to substantially completely precipitate impurities in said solution, electroplating zinc from the so purified solution at a current density sufficiently high that hydrogen is evolved from the cathode, and thereafter dipping the resulting electrodeposit in a dilute nitric acid solution.

8. A process for producing a zinc electrodeposit comprising purifying a zinc cyanide solution containing alkali metal cyanide and an alkali metal hydroxide by adding thereto a sulfide, soluble in said solution, in an amount sufficient to substantially completely precipitate heavy metal impurities in said solution, electroplating zinc from the so purified solution at a current density sufficiently high that hydrogen is evolved from

the cathode and thereafter dipping the resulting electrodeposit in a dilute nitric acid solution.

9. A process for electroplating zinc comprising purifying a zinc cyanide solution containing alkali metal cyanide and alkali metal hydroxide by adding to said solution a sulfur compound, capable of precipitating heavy metals in the form of insoluble salts, selected from the group consisting of thiocyanates, thiosulfates, xanthates and sulfides, soluble in said solution, in an amount sufficient to substantially completely precipitate dissolved heavy metal impurities and thereafter electroplating zinc from said solution.

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