Patented Dec. 7, 1937

2,101,580

UNITED STATES PATENT OFFICE

2,101,580

PROCESS FOR OBTAINING BRIGHT ZINC COATING

John A. Henricks, Chicago, Ill., assignor to Udylite Company, Detroit, Mich., a corporation of Indiana

No Drawing. Application May 2, 1936, Serial No. 77,527

10 Claims. (Cl. 204—18)

This invention relates to electrodeposition of zinc, particularly from an alkaline bath which has, or can be given, a bright lustrous appearance and to a composition of matter for forming such alkaline zinc plating solution.

It has been found previously that good zinc plates can be obtained only when the purity of the solution and the anodes are controlled. Such plates can be bright dipped in solutions of chromic acid, United States Patent 2,021,592 to George Dubpernell and Karl Gustaf Soderberg and application Serial No. 45,416 to the same inventors, acidified hydrogen peroxide application Serial No. 10,086 to Karl Gustaf Soderberg, bromic and allied acids, Serial No. 21,276 to David B. Stockton, and dilute nitric acid, United States Patent 1,816,837 to Carl L. Ganser. However, the plates obtained in this manner are not as lustrous as is sometimes desired. Thus, one object of this invention is to produce zinc plates which have a mirror-like lustre.

It has been found that plain zinc cyanide solutions are rather sensitive to impurities. Thus another object of this invention is to produce zinc plating solutions which will tolerate higher amounts of impurities, particularly lead and cadmium, and still produce bright or bright dippable plates.

I have found that these desirable results can be had by the addition to the zinc plating baths small amounts of ammonium thiocyanate-formaldehyde resins.

These ammonium thiocyanate-formaldehyde resins can be manufactured according to any of the processes heretofore known in the art or according to the following preferred methods which I have originated.

Twenty-five pounds of technical ammonium thiocyanate containing a minimum of 90% of NH_4CNS is placed in a 30 gallon steel tank. 4½ gallons of formaldehyde water solution, 37½% technical, is carefully added, with an exhaust fan running, to minimize objectionable fumes; then is added 1½ lbs. of caustic soda, technical, and 2½ lbs. of cresol, technical, and the mixture is thoroughly stirred with a wooden paddle. It is then boiled for 20 minutes with intermittent stirring to keep the brightener from precipitating too heavily around the heater coils. The mixture is then allowed to cool and when the supernatant liquor has clarified it is decanted into a convenient receptacle and the remaining brightener is allowed to dry and harden. It can then be removed from the tank and pulverized. The decanted liquor contains considerable amount of dissolved brightener. It may be used either together with the next batch or the dissolved resin may be precipitated by means of slow neutralization with an acid such as dilute sulphuric acid. The total yield is approximately 30 lbs. of brightener.

Purer chemicals may be used in the condensation but the ordinary technical grades are fully satisfactory and cheaper.

The function of the caustic soda in the above reaction is that of a catalyst. Any alkaline salt can be used for this purpose such as caustic potash, sodium and potassium carbonate, sodium and potassium sulphocyanate, cyanide of sodium or potassium, or sodium or potassium acetate, or other alkali salts of organic acids. The amounts required are proportional to the molecular weight of the salt.

One can also use an acid catalyst such as one-half pound of tartaric acid. Proportional amounts of citric, oxalic, acetic, furoic, may also be used with equal success, also small amounts of mineral acids.

The cresol is used for a solubilizer. It not only makes the resin more easily dispersible in the plating solution, but it also prevents the precipitation of insoluble zinc compounds with the resin. In its absence, the resin is slowly removed from the bath and gradually loses its effect. Among other similar compounds which have proven satisfactory are phenol and phenol-sulphonic acids, quinol, naphthol and naphthol sulphonic acids.

The resin may also be solubilized in other manners. One gram of the resin may be dissolved in 10 ml. of 66° Bé. sulphuric acid at room temperature. This mixture is poured into a solution containing 25 grams of sodium carbonate in 150 ml. of water, which neutralizes the excess sulphuric acid. This gives a flocculent precipitate of a sulphonated resin which dissolves to the extent of about 85% on boiling. Sulphonated resin gives good plate, although the lustre has been lessened slightly by the sulphonation.

Ten grams of the resin may be dissolved in 25 ml. of a solution containing 5 grams of urea, and the mixture boiled for 20 minutes. This gives a clear, yellow syrup which is completely dispersible in the zinc bath and which gives a lustrous deposit.

Another preferred formula comprises 380 g/l. of technical ammonium thiocyanate, 750 ml. of 37% of technical water solution of formaldehyde, 7.5 grams of tartaric acid. These three compositions are mixed and brought to boiling temperature, allowed to cool down to 150° F. The mixture is kept at this temperature (150° F.) for 20 minutes. About 400 grams of yellow resin precipitates and can be separated by decantation. This resin when added to the zinc plating baths, such as zinc cyanide plating baths, gave brilliant plates, the concentrations ranging from .6 to .9 gram per liter. However, this resin was not solubilized, and although it worked very well for three

or four days, at the end of such time part of the resin had precipitated and fallen to the bottom of the bath thereby requiring the addition of more resin to bring the bath into optimum operating condition.

In testing the brightening effect of these resins, I used a zinc solution containing 4.5 oz./gal. of zinc, 9 oz./gal. of total cyanide, expressed as sodium cyanide, and 10 oz./gal. of total caustic soda. This bath had been prepared from a pharmaceutical grade of zinc oxide and good technical grades of sodium cyanide and caustic soda. In making a new zinc plating solution, preferably the ammonium thiocyanate formaldehyde resin, zinc salt (zinc cyanide or zinc oxide), caustic soda and sodium cyanide are mechanically mixed and this mechanical mixture is then dissolved in water to form the plating solution. The mechanical mixture can be, and preferably is, dissolved in water previously run into the plating tank. In preparing a new plating solution this mechanical mixing of the resin, zinc salts, sodium cyanide and caustic soda, prior to dissolving the same in water, is considerably more efficient and time saving than separately adding to, and dissolving in, the water each of the above-mentioned constituents of the new plating bath. Of course, as the resin, zinc salts, sodium cyanide and caustic soda are depleted by operation of the bath, each is separately added to the plating solution from time to time as required. The anodes employed were at least 99.97% pure zinc. Less pure grades may be employed if the solution is purified subsequent to make up and if the anodes are alloyed with mercury and such low current densities are applied that the mercury only amalgamates with the impurities and drops to the bottom of the tank and does not go into solution.

In the above bath we find that the optimum concentration of the standard resin is between .5 and 1.0 g/l. Bright plates are obtained at 10 amp./sq. ft. and very brilliant plates at higher current densities. At lower concentrations of brightener the plates tend to be streaky at low current densities; and at higher current densities the plates are not very bright, although there is a great deal of grain refinement. At higher concentrations only the low current density plates are bright while the plates obtained at higher current densities are ribbed or burned on the edges.

In general the solubility of ammonium thiocyanate formaldehyde resin in the plating bath is not critical. However, the brightening effect of the resin decreases with increasing solubility and vice versa the brightening effect of the resin increases with decreasing solubility of the resin. In other words, the greater the solubility of the resin the less brightening effect and the lesser the solubility of the resin the greater the brightening effect.

The use of larger amounts of solubilizer in preparing the resin makes it necessary to use higher concentration of resin in the bath. Slightly different optimum concentrations are found when different catalysts or solubilizers are employed, but generally the optimum concentrations vary between .1 and 2.5 g/l.

As stated before, the low current density plates are generally not as bright as the high current density plates, consequently the brightness of a deeply recessed part varies from the high current density points to the low current density points. If the concentration of brightener is too low, the lustre may not always be as high as desired and the plate may have a slightly brownish cast. These difficulties are overcome by the use of bright dips, as mentioned above, whereby the lustre is equalized or increased.

When the optimum amount of resin has been added to the zinc bath, its tolerance to copper is increased about six times; to cadmium more than three times; to lead, at least 25 times.

In general, the required concentration of brightener increases with increasing metal and caustic soda content in the bath and decreases with decreasing sodium cyanide content.

The substitution of other aldehydes, such as acetaldol and furfural, for formaldehyde produced resins which did not give any brightening effect. It is evident that the high lustre obtained with formaldehyde is specific.

I claim:

1. The method of electrodepositing zinc, comprising electrodepositing the said metal from a cyanide plating solution containing an ammonium thiocyanate formaldehyde resin which is soluble in the cyanide plating solution.

2. The method of electrodepositing zinc, comprising electrodepositing the said metal from a cyanide plating solution containing a solubilized ammonium thiocyanate formaldehyde resin.

3. The method of electrodepositing zinc, comprising electrodepositing said metal from a cyanide plating solution containing an ammonium thiocyanate formaldehyde resin formed by reacting ammonium thiocyanate and formaldehyde in the presence of a catalyst in the form of an alkaline salt.

4. The method of electrodepositing zinc, comprising electrodepositing said metal from a cyanide plating solution containing an ammonium thiocyanate formaldehyde resin formed by reacting ammonium thiocyanate and formaldehyde in the presence of a catalyst in the form of an acid.

5. The method of electrodepositing zinc, comprising electrodepositing the said metal from a plating bath consisting of a relatively pure cyanide solution and containing an ammonium thiocyanate formaldehyde resin which is soluble in the cyanide plating solution.

6. The method of electrodepositing zinc, comprising electrodepositing the said metal from a plating bath consisting of a relatively pure cyanide solution and containing an ammonium thiocyanate formaldehyde resin which is soluble in the plating bath and in the presence of a pure zinc anode.

7. A plating bath for electrodepositing zinc, comprising a cyanide solution of said metal and an ammonium thiocyanate formaldehyde resin soluble in the said cyanide solution.

8. A composition of matter comprising a mechanical mixture of zinc oxide, sodium cyanide, caustic soda, and ammonium thiocyanate formaldehyde resin.

9. A composition of matter comprising a mechanical mixture of zinc cyanide, caustic soda, sodium cyanide and ammonium thiocyanate formaldehyde resin.

10. A composition of matter comprising a mechanical mixture of a zinc salt, caustic soda, sodium cyanide and ammonium thiocyanate formaldehyde resin.

JOHN A. HENRICKS.