

UNITED STATES PATENT OFFICE

2,080,479

PLATING OF ZINC

Elliott F. Hoff, Willoughby, Ohio, assignor, by
mesne assignments, to E. I. du Pont de
Nemours & Company, Wilmington, Del., a cor-
poration of Delaware

No Drawing. Application April 4, 1935, Serial
No. 14,588

13 Claims. (Cl. 204—18)

This invention relates to the electrodeposition of zinc and is particularly directed to processes wherein a bright, mirror-like zinc deposit is plated from cyanide-zinc baths which contain substantial amounts of a soluble compound of a metal of group VII sub-group 1 of Mendelejeff's Periodic System, and which may contain, in addition, an organic addition agent and a metal of group VIII series 4 of the Periodic System.

The electrodeposition of zinc, or electrogalvanizing, has been rather extensively employed, because electrodeposited zinc coatings, in addition to their low cost, display many characteristics which cause them to be particularly desirable as protective finishes. While zinc is not itself very resistant to corrosion, it does not accelerate the corrosion of iron or steel as do such metals as copper, nickel, and chromium. On the contrary, zinc, being higher in the electromotive series, will protect iron or steel against rust even after appreciable areas of the base metal are exposed. Despite their numerous advantages over many commonly used coating materials, electrodeposited zinc coatings have not enjoyed the use they deserve because they do not possess and do not retain a pleasing appearance and, consequently, for many purposes they are not acceptable.

The known methods of electrodepositing zinc almost invariably result in dark colored or dull plates and, even when the deposits at first are fairly satisfactory, they soon become dark and discolored. The poor appearance of electrodeposited zinc coatings has limited their use almost exclusively to purely protective applications, and those working in the art have turned to other protective materials when it was desired to produce a finish of pleasing appearance.

The electrodeposition of zinc has ordinarily been accomplished by the use of either an acid-zinc bath or a cyanide-zinc bath. With neither of these baths has it been possible to obtain satisfactorily smooth and bright deposits, but the acid-zinc bath is most commonly used because it leads to a brighter deposit with a better color than does the cyanide-zinc bath.

While, under favorable conditions, the deposits obtained from acid-zinc baths are relatively white, the deposits are still none too satisfactory because of their relatively coarse crystalline structure.

Numerous attempts have been made to improve the character of zinc deposits obtained from acid baths, and many addition agents, such as glycerine, dextrin, gum tragacanth, licorice,

naphthalene compounds, and aluminum compounds, have been used in conjunction therewith. While the use of addition agents improved the character of the deposits to some extent, the results were still none too satisfactory.

In addition to the fact that acid-zinc baths do not produce satisfactory results, there are numerous other disadvantages attendant upon their use. For one thing, acid-zinc baths have very poor throwing power, and it is exceedingly difficult satisfactorily to plate irregularly shaped objects. Another disadvantage of acid-zinc baths is their low cathode efficiency. As zinc is above hydrogen in the electromotive force series of metals, it is theoretically impossible to deposit zinc from acid solutions, but, of course, the rather great over-voltage of hydrogen does permit some zinc deposition. Concurrently with the deposition of zinc, however, there is a very considerable evolution of hydrogen.

While the deposits obtained from cyanide-zinc baths are poor in appearance, they have a relatively fine crystalline structure. A few addition agents, such as alum, gum arabic, and fluorides have been tried in cyanide-zinc baths, but the results obtained were none too satisfactory. Aside from the poor appearance of deposits obtainable therefrom, cyanide-zinc baths have a number of advantageous characteristics. They have good throwing power, and it is therefore possible to deposit a relatively uniform zinc coating on irregularly shaped and recessed articles. Cyanide-zinc baths, moreover, have a relatively high cathode efficiency which, of course, is very advantageous because the electric current applied to the bath is expended less upon the evolution of hydrogen, and more upon the deposition of zinc.

Despite the advantages of cyanide-zinc baths, they have not been much used by the art because of the poor appearance of zinc deposits obtainable therefrom. Regardless of the disadvantages in operation of acid-zinc baths, they have been favored by those working in the art because of the somewhat better appearing deposits obtainable by their use.

It is an object of my invention to provide processes by means of which bright, smooth zinc electrodeposits can be obtained. A further object of my invention is to provide processes by means of which the advantages of cyanide-zinc baths can be realized, and by means of which, at the same time, deposits of pleasing appearance can be produced. A still further object of my invention is to provide electroplating baths which

are characterized by good throwing power, and which will produce bright zinc deposits over a relatively extended range of current densities. A still further object of my invention is to provide processes which produce zinc deposits that will respond to dilute oxidizing bright dips. Further objects of my invention will become apparent hereinafter.

I accomplish my objects, briefly, by the use of cyanide-zinc baths which contain a soluble compound of a metal of group VII sub-group 1 of Mendelejeff's Periodic System, and which, in addition, may contain an organic addition agent and a metal of group VIII series 4 of the Periodic System.

Considering the features of my invention in greater detail, it is first noted that a cyanide-zinc bath must be employed if satisfactory results are to be obtained. Certain illustrative cyanide-zinc baths will be given hereinafter, but it will be understood that the principles of my invention are applicable to any of the cyanide-zinc baths known to the art.

According to the processes of my invention, a cyanide-zinc bath is modified by adding thereto a soluble compound of a metal of group VII sub-group 1 of Mendelejeff's Periodic System. The metals of this group, as manganese and rhenium, exercise a most profound influence upon the character of a zinc deposit obtainable from a given bath. When a small but substantial amount of a soluble compound of one of these metals is present in a cyanide-zinc bath, smooth, bright mirror-like zinc deposits are obtained.

I have also found that while metals of group VIII series 4 of the Periodic System have little or no effect upon the character of a zinc electrodeposit when used alone, these metals seem to exercise some synergetic action upon the metals of group VII sub-group 1, and the joint effect of metals from both groups is superior to the effects attributable to the action of the individual metals. The metals of group VIII series 4, iron, cobalt, and nickel, may be added to the bath in substantial amount in the form of bath-soluble compounds such as iron ferrocyanide, cobalt sulfate, nickel sulfate, and the like. In addition to their effect upon the characteristics of the deposit, the metals of group VIII series 4 also have the effect of keeping metals of group VII sub-group 1 in solution.

In addition to the metal brightening agents, the bath may contain suitable organic addition agents of known type. For instance, such addition agents as glue, dextrin, sulfite cellulose waste, licorice, gum arabic, gum tragacanth and furfural may be used. If it is desired to use an organic addition agent, I prefer to use thiourea, or a substituted thiourea. I may use any alkyl or aryl thiourea which is soluble in the bath, such as phenylthiourea or diphenylthiourea-disulfonic acid. It is to be understood that the use of thioureas constitutes no part of the present invention apart from the use with metals of group VII sub-group 1. It may sometimes be desirable to add small amounts of mercury, in known manner, to facilitate the deposition of zinc on cast iron articles.

The zinc deposits obtained according to the processes of my invention are not pure metallic zinc but are alloys of zinc with small amounts of whatever metallic brightening agent is used. When manganese was used as the brightening agent, an amount in excess of one one-thousandth per cent of manganese was present in the zinc

deposit. It seems probable that the presence of a metal of group VII sub-group 1 renders the zinc deposit somewhat more resistant to corrosion, and, in view of the fact that the characteristics of my novel zinc deposits are probably at least in part attributable to the presence of such metals, I consider such deposits a product of my invention.

In view of the fact that the metal brighteners are deposited with the zinc, it is necessary to add such metals to the bath from time to time. Instead of adding these metallic brighteners in the form of their soluble compounds, the bath may be constantly replenished by using an anode which contains an adequate amount of the brightener.

While the zinc deposits produced according to the processes of my invention are very bright and smooth, it may sometimes be desirable further to brighten them and, more particularly, to render them passive to finger staining and to other stains which might result from handling. The deposits produced according to the processes of my invention respond very satisfactorily to the action of oxidizing bright dip solutions, and by bright dipping a deposit in a mildly oxidizing solution, the deposit will be rendered brighter, any slight color will be removed, and the deposit will be rendered passive.

My novel zinc deposits are preferably bright dipped with an acidic hydrogen peroxide solution. Such a solution may be made by mixing sulfuric acid with hydrogen peroxide, the ratio of H_2O_2 to H_2SO_4 being about 48 to 1, to 4 to 1 by weight. More specifically, I prefer that the ratio of H_2O_2 to H_2SO_4 be about 16 to 1 by weight. While the best results may be obtained by the use of an acidic hydrogen peroxide solution, other bright dips such as an acidic chromic acid solution or a dilute nitric acid solution may be used.

The following illustrative examples are given more fully to point out my invention.

Example I

A cyanide-zinc bath containing a metallic brightening agent from group VII sub-group 1 was made up as follows:

	Grams per liter
Zinc oxide (ZnO)	45
Sodium hydroxide (NaOH)	38
Sodium cyanide (NaCN)	80.5
Manganese sulfate ($MnSO_4 \cdot 4H_2O$)	15

With this bath, a bright, smooth zinc deposit was obtained. The bright current density range of the bath extended from fifteen to sixty amperes per square foot. The zinc deposit obtained by the use of this bath was found to contain about 0.015 per cent of manganese. It is noted that the bath contained about three and seven-tenths grams per liter of manganese in the form of a soluble compound.

Example II

A bath similar to the one shown in Example I was made up with the following composition:

	Grams per liter
Zinc oxide (ZnO)	45
Sodium hydroxide (NaOH)	38
Sodium cyanide (NaCN)	90
Potassium perrhenate ($KReO_4$)	0.1

Excellent results were obtained by the use of this bath. The bath contained about sixty-five thousandths of a gram per liter of rhenium.

Example III

As an example showing the use of a metal of group VII sub-group 1 in conjunction with a thiourea, a bath of the following composition is given:

	Grams per liter
Zinc oxide (ZnO)-----	45
Sodium hydroxide (NaOH)-----	38
Sodium cyanide (NaCN)-----	100
Manganese-cyanide-----	15
Phenylthiourea-----	20

The manganese was added to the bath in the form of a manganese-cyanide complex which was precipitated from a water solution of manganese sulfate by adding a water solution of sodium cyanide thereto. The amount of the manganese-cyanide used is equivalent to about one and one-half grams per liter of manganese.

Example IV

A bath containing the preferred organic addition agent, thiourea, together with a soluble rhenium compound was made up with the following composition:

	Grams per liter
Zinc oxide (ZnO)-----	45
Sodium hydroxide (NaOH)-----	38
Sodium cyanide (NaCN)-----	80.5
Potassium perrhenate (KReO ₄)-----	0.1
Thiourea-----	10

The bath contained about sixty-five thousandths of a gram per liter of rhenium. Excellent results were obtained by the use of this bath, a bright, smooth zinc deposit being obtained. While the deposit was white, smooth, and bright, it had a slightly yellowish hue. To obtain a clear and bright finish, and to render the surface passive, the plated articles were treated by immersing them in an acidified hydrogen peroxide solution. The bright dip was made up with hydrogen peroxide and sulfuric acid, the ratio of H₂O₂ to H₂SO₄ being about 16 to 1 by weight.

Example V

The following bath illustrates the use of a metal of group VIII series 4 in conjunction with a metal of group VII sub-group 1:

	Grams per liter
Zinc oxide (ZnO)-----	45
Sodium hydroxide (NaOH)-----	38
Sodium cyanide (NaCN)-----	100
Manganese-cyanide-----	10
Potassium ferrocyanide-----	5
Thiourea-----	8

The manganese-cyanide, prepared as in Example III, was equivalent to about one gram per liter of manganese. The bath also contained about sixty-five hundredths of a gram per liter of iron. It will be noted that one-hundred grams per liter of sodium cyanide was used in the bath of this example, while only about eighty grams per liter were used in Example IV. I have found that electrodeposits of improved color are obtained with baths of this type if no less than about ninety grams per liter of sodium cyanide is employed. Generally, I prefer to use between about ninety and one-hundred and thirty grams per liter of sodium cyanide with baths having about the indicated amounts of zinc oxide and sodium hydroxide, while, more specifically, I prefer to use about one-hundred grams per liter, say ninety-five to one-hundred and five grams per liter. It will, of course, be understood that

the baths may be more dilute with a consequent reduction in the number of grams per liter of the constituents.

While the metals of group VII sub-group 1 are shown in about an optimum amount in each of the above examples, the quantities used may be greatly varied. Generally a soluble compound of a metal of group VII sub-group 1 should be used in substantial amount. The upper limit on the quantities of these metals is largely determined by economic considerations. Because of their high price, it would not be commercially feasible to employ very large amounts of these relatively expensive metals. More specifically considered, a metal of group VII sub-group 1 should be present in an amount not substantially less than about five hundredths of a gram per liter, and no more than about fifteen grams per liter can economically be used. Manganese has proved the most satisfactory of the metals of this group, from the standpoint of cost, and I generally prefer to use from about one to five grams per liter of this metal. More specifically, the best results were obtained when manganese was used in amounts from about one to three grams per liter.

The metals of group VIII series 4, similarly, should be used in substantial amount. I generally prefer to employ not substantially less than about five hundredths of a gram per liter of one of these metals in the form of a soluble compound. It is noted that when a metal of group VIII series 4 is used, a somewhat smaller quantity of a metal of group VII sub-group 1 is required for optimum results.

The amounts of the thioureas shown in the above examples are about an optimum, but the quantity used depends somewhat upon the character of the bath. Generally, from about one to twenty grams per liter of a thiourea should be used. More specifically, I prefer to use about ten grams per liter of thiourea. Known organic addition agents may be used according to the known practice.

As has been noted above, the zinc deposits produced according to the processes of my invention are characterized by the presence of a metal of group VII sub-group 1 of the Periodic System. Such deposits ordinarily contain not substantially less than about one thousandth of one per cent of a metal of group VII sub-group 1. According to the preferred processes of my invention, zinc deposits are obtained which contain from about one-hundredth of one per cent to one-tenth of one per cent of manganese.

As has been noted above, it may sometimes be advantageous to offset a depletion of the brightening agents in the bath by the use of zinc anodes which contain a small amount of such brightening agents. I have found, for instance, that the manganese content of a bath may satisfactorily be maintained by the use of alloys containing relatively small amounts of manganese. Specifically, I have prepared zinc-manganese alloys containing, respectively, 0.03%, 0.0011%, and 0.32% of manganese. It will be apparent that widely varying amounts of manganese may satisfactorily be used in the zinc alloy anodes and that the depletion of other metal brightening agents may also be offset by the introduction of such metals into the zinc anodes.

While I have given certain specific proportions and conditions in the foregoing, it will be readily understood that I do not intend to be limited

thereby, the scope of my invention being set forth in the following claims:

I claim:

1. A cyanide-zinc electroplating composition of a type adapted for the plating of a deposit comprised substantially of zinc, the composition containing a metal of group VII sub-group 1 of the Periodic System in the form of a soluble compound, said metal being present in such quantities as to produce a brightened zinc deposit.
2. A cyanide-zinc electroplating composition of a type adapted for the plating of a deposit comprised substantially of zinc, the composition containing manganese in the form of a soluble compound, the manganese being present in such quantities as to produce a brightened zinc deposit.
3. A cyanide-zinc electroplating bath of a type adapted for the plating of a deposit comprised substantially of zinc, the bath containing not substantially less than about one gram per liter of manganese in the form of a soluble compound.
4. A cyanide-zinc electroplating bath of a type adapted for the plating of a deposit comprised substantially of zinc, the bath containing from about one to five grams per liter of manganese in the form of a soluble compound.
5. A cyanide-zinc electroplating bath of a type adapted for the plating of a deposit comprised substantially of zinc, the bath containing a metal of group VII sub-group 1 and a metal of group VIII series 4 of the Periodic System in the form of soluble compounds, the metal of group VII sub-group 1 being present in such quantities as to produce a brightened zinc deposit.
6. A cyanide-zinc electroplating bath of a type adapted for the plating of a deposit comprised substantially of zinc, the bath containing a soluble manganese compound and thiourea.
7. In a process for the electrodeposition of a deposit comprised substantially of zinc, the step comprising depositing zinc from a cyanide-zinc bath in the presence of a metal of group VII sub-group 1 of the Periodic System in the form of a soluble compound, said metal being present in such quantities as to produce a brightened zinc deposit.
8. In a process for the electrodeposition of a deposit comprised substantially of zinc, the step comprising depositing zinc from a cyanide-zinc bath in the presence of manganese in the form of a soluble compound, the manganese being present in such quantities as to produce a brightened zinc deposit.
9. In a process for the electrodeposition of a deposit comprised substantially of zinc, the step comprising depositing zinc from a cyanide-zinc bath in the presence of not substantially less than about one gram per liter of manganese in the form of a soluble compound.
10. In a process for the electrodeposition of a deposit comprised substantially of zinc, the step comprising depositing zinc from a cyanide-zinc bath in the presence of from about one to five grams per liter of manganese in the form of a soluble compound.
11. In a process for the electrodeposition of a deposit comprised substantially of zinc, the step comprising depositing zinc from a cyanide-zinc bath in the presence of a metal of group VII sub-group 1 and a metal of group VIII series 4 of the Periodic System in the form of soluble compounds, the metal of group VII sub-group 1 being present in such quantities as to produce a brightened zinc deposit.
12. In a process for the electrodeposition of a deposit comprised substantially of zinc, the step comprising depositing zinc from a cyanide-zinc bath in the presence of a soluble manganese compound and thiourea.
13. An electrodeposit comprised substantially of zinc characterized by the presence of a metal of group VII sub-group 1 of the Periodic System, said metal being present in such quantities as to produce a brightened zinc deposit.

ELLIOTT F. HOFF.