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ZINC PLATING

Leon R. Westbrook, Cleveland Heights, Ohio, assignor, by mesne assignments, to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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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 VI sub-group 1 of the Periodic System, and which, in addition, may also contain a metal of group VII sub-group 1 a metal of group VIII series 4, and organic addition agents. This invention, moreover, is also directed to the novel zinc deposits obtained by such processes.

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 satisfactory 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 deposits, 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 overvoltage 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 to which has been added a metal of group VI sub-group 1, of the Periodic System. In addition to using metals of group VI, I may use metals of group VII sub-group 1, and metals of group VIII series 4. My novel baths may also contain a suitable organic addition agent. The metal content of these baths may be maintained by using zinc anodes containing an adequate amount of the metal addition agent or agents.

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

The principal brightening agent of my invention is comprised of a metal of group VI sub-group 1 of Mendelejeff's periodic arrangement of the elements. The metals of this group, molybdenum, chromium, tungsten, and uranium, display a profound effect upon the character of a zinc electrodeposit. The metals, of course, must be present in the form of a compound which is soluble in the bath. They may be added to a bath, for instance, as a molybdate, chromate, tungstate, or uranate of sodium or potassium. While I may satisfactorily use any one or more of the members of this group, I have found molybdenum the most satisfactory and, accordingly, I prefer to use it as a metallic brightening agent.

The efficacy of metals of group VI sub-group 1 may be enhanced by employing in conjunction therewith a metal of group VII sub-group 1 and/or a metal of group VIII series 4 of Mendelejeff's Periodic System. The metals of group VII sub-group 1 tried are manganese and rhenium, and the metals of group VIII series 4 tried are iron, cobalt, and nickel. There is apparently some synergetic action between the metals of group VI and group VII or VIII series 4 which leads to results superior to those attributable to the individual action of the metals. The metals of group VII sub-group 1, or group VIII series 4, are, of course, added to the bath in the form of such alkali or cyanide soluble compounds as manganese sulfate, potassium perrhenate, potassium ferrocyanide, cobalt sulfate, nickel sulfate, cobalt oxide, and nickel oxide. The use of metals of group VII sub-group 1 and group VIII series 4 separate and apart from the metals of group VI sub-group 1, constitutes no part of the present invention.

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, or 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 an 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 of metals of group VI sub-group 1.

Manganese displays a considerable tendency to precipitate from the bath, and I have found that the addition of a small amount of a soluble iron compound tends to keep the manganese in solution. When used in conjunction with manganese, iron, then, acts both to keep the manganese in solution and to brighten the zinc deposit. A similar solubilizing tendency is exhibited on other metals of group VI sub-group 1 by other metals of group VIII series 4. To facilitate the deposition of zinc on cast iron articles, it may also be found desirable to employ a small amount of mercury in known manner.

The zinc deposits obtained according to the processes of my invention are not pure metallic zinc, but, rather, are alloys of zinc with small amounts of whatever metallic brightening agents are used. When molybdenum was used as the brightening agent, an amount in excess of five hundredths of one per cent of molybdenum was present in the zinc deposit. A much smaller amount of manganese was deposited with the zinc. It seems probable that the presence of a metal of group VI sub-group 1 renders the zinc deposit somewhat more resistant to corrosion, and, as the various novel characteristics of my novel zinc deposits are probably at least in part attributable to the presence of such brighteners, I regard the alloys of zinc with a metal of group VI sub-group 1, or with both such a metal and a metal of group VII sub-group 1, as an article 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 metallic 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 clearly to point out my invention.

Example I

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

	Grams per liter
Zinc oxide (ZnO)	45
Sodium hydroxide (NaOH)	38
Sodium cyanide (NaCN)	100
Molybdenum trioxide (MoO_3)	7

By the use of this bath, a bright, smooth zinc deposit was obtained. The bright current density range of the bath extended from about fifteen to seventy amperes per square foot. The zinc deposit obtained from the bath of this example was found to contain about one-tenth of one per cent of molybdenum. The molybdenum trioxide used corresponds to about four and seven-tenths grams per liter of molybdenum.

Example II

A zinc plating bath containing a metal of group VII sub-group 1, as well as a metal of group VI sub-group 1, was made up with the following composition:

	Grams per liter
Zinc oxide (ZnO)	45
Sodium hydroxide (NaOH)	38
Sodium cyanide (NaCN)	100
Molybdenum trioxide (MoO_3)	3
Manganese sulfate ($MnSO_4.4H_2O$)	1

Excellent results were obtained by the use of this bath. The deposit had a bright mirror-like surface with a slightly bluish hue. The molybdenum trioxide corresponds to about two grams per liter of molybdenum, and the manganese sulfate corresponds to about twenty-five hundredths of a gram per liter of manganese.

Example III

As has been noted above, organic addition agents may advantageously be used with the baths of my invention. A cyanide-zinc bath containing an organic addition agent as well as a metal of group VI sub-group 1 was made up with the following composition:

	Grams per liter
Zinc oxide (ZnO)	45
Sodium hydroxide (NaOH)	34
Sodium cyanide (NaCN)	100
Ammonium sulfate ($(NH_4)_2SO_4$)	18
Molybdenum trioxide (MoO_3)	4
Furfural	3

Excellent results were obtained with the bath of this example. The molybdenum trioxide used corresponds to about two and seven-tenths grams per liter of molybdenum.

Example IV

Another bath containing an organic addition agent was made up with the following composition:

	Grams per liter
Zinc oxide (ZnO)	45
Sodium hydroxide (NaOH)	38
Sodium cyanide (NaCN)	80
Molybdenum trioxide (MoO_3)	1
Thiourea	10

An exceedingly smooth zinc deposit was obtained by the use of this bath, but the deposit had a slightly yellowish hue. To obtain a perfectly clear and bright finish, the articles plated in this bath were treated, briefly, with a bright dip made up of hydrogen peroxide and sulfuric acid. The ratio of H_2O_2 to H_2SO_4 in the bright dip was about 16 to 1 by weight. It is noted that the molybdenum trioxide used corresponds to about sixty-seven hundredths of a gram per liter of molybdenum.

Example V

As an example showing the use of another metal of group VI sub-group 1, chromium, a bath of the following composition is given:

	Grams per liter
Zinc oxide (ZnO)	45.
Sodium hydroxide (NaOH)	38.
Sodium cyanide (NaCN)	100.
Sodium chromate ($Na_2CrO_4 \cdot 10H_2O$)	0.25
Thiourea	10.

Quite satisfactory results were obtained with this bath. The thiourea, of course, can be omitted, or other organic addition agents may be used in lieu thereof. It is noted that the chromate used is equivalent to about thirty-eight thousandths of a gram per liter of chromium.

Example VI

A bath similar to that of Example V was made up with tungsten as the metal brightener. The bath had the following composition:

	Grams per liter
Zinc oxide (ZnO)	45
Sodium hydroxide (NaOH)	38
Sodium cyanide (NaCN)	100
Tungsten trioxide (WO_3)	5
Thiourea	10

Very good results were obtained with this bath. The bath contained about four grams per liter of tungsten in the form of a soluble compound.

Example VII

A cyanide-zinc bath with about one and seven-tenths grams per liter of uranium as the brightener is given:

	Grams per liter
Zinc oxide (ZnO)	45
Sodium hydroxide (NaOH)	38
Sodium cyanide (NaCN)	80
Uranium oxide (U_3O_8)	2

Example VIII

A bath of the following composition illustrates the use of metals of group VIII series 4 of the Periodic System, together with a metal of group VI sub-group 1.

	Grams per liter
Zinc oxide (ZnO)	45
Sodium hydroxide (NaOH)	38
Sodium cyanide (NaCN)	110
Molybdenum trioxide (MoO_3)	2
Cobalt sulfate ($CoSO_4 \cdot 7H_2O$)	1
Phenylthiourea	20

Very good results were obtained by the use of this bath. The thiourea addition agent may be omitted, if desired, or another organic addition agent may be used in lieu thereof. It is noted that the molybdenum trioxide introduced about one and three-tenths grams per liter of molybdenum, and the cobalt sulfate about twenty-one hundredths gram per liter of cobalt.

Example IX

The following cyanide-zinc bath shows the use of an iron brightener to solubilize manganese:

	Grams per liter
Zinc oxide (ZnO)	45
Sodium hydroxide (NaOH)	38
Sodium cyanide (NaCN)	100
Manganese-cyanide	10
Potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$)	5
Molybdenum trioxide (MoO_3)	4
Thiourea	8

The bath contained about two and seven-tenths grams per liter of moylbdenum, about sixty-six hundredths of a gram per liter of iron, and about one gram per liter of manganese. It is noted that the manganese was added in the form of a complex which was made by adding sodium cyanide to manganese sulfate.

It will be noted that in Example IV, sodium cyanide is used in about the known proportion for baths of this character. However, in the bath of Example IX, for instance, a considerably larger proportion of sodium cyanide is used. 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 VI sub-group 1 are shown in about an optimum amount in each of the above examples, the quantities used may be greatly varied. Generally speaking, the metals of group VI 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, in view of their high price, it would not at the present time be commercially feasible to employ very large amounts of these relatively expensive metals. More specifically considered, the metals of group VI sub-group 1 should be used in amounts not substantially less than about one hundredth gram per liter, and no more than about forty grams per liter can economically be used. Molybdenum has proved the most satisfactory of the metals of this group, and I generally prefer to use from about one-fourth to twenty-five grams per liter of this metal. More specifically, the best results are obtained when molybdenum is used in amounts from about one to twelve grams per liter. It will be understood that, while reference is made to the amount of metal used, the metal is present in the bath in the form of a soluble compound.

The metals of group VII sub-group 1 and group VIII series 4, similarly, should be used in substantial amount. When a metal of one of these groups is employed, a smaller amount of the metals of group VI sub-group 1 is required for optimum results, as will appear from a consideration of the examples. Generally, I prefer to use no less than about five hundredths of a gram of a metal of group VII sub-group 1, and the metals of group VIII series 4, similarly, should be used in amounts not substantially smaller than five hundredths of a gram per liter. It will be readily understood that the optimum amounts of the various constituents of baths made according to my invention can best be determined for each particular bath by a few simple trials.

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

As has been noted above, it may sometimes be advantageous to offset a depletion of the bath of the metals used as brightening agents by the use of zinc anodes which contain a small amount of the metal.

Example X

To replace molybdenum removed from the bath, zinc-molybdenum alloys of the following composition were made up:

	Per cent
1. Molybdenum	0.0087
2. Molybdenum	0.03
3. Molybdenum	0.095
4. Molybdenum	0.11
5. Molybdenum	0.22
6. Molybdenum	0.39
7. Molybdenum	0.55

The preferred anode alloy is number 3, with 0.095% of molybdenum.

Similar alloys can be used, of course, when other metal brightening agents are employed. When two such brightening agents are used, it may prove advantageous to use zinc alloys which contain substantially the proper amounts of each agent used in the bath.

The zinc deposits produced according to the processes of my invention are characterized by the presence of a small but substantial amount of a metal of group VI sub-group 1. Such deposits usually contain no less than about two thousandths of one per cent of such a metal. More particularly, when molybdenum is used as a brightener according to my preferred processes, the zinc deposits obtained usually contain from five hundredths to one per cent of molybdenum. Deposits produced according to the processes of my invention may also contain other metals used as brighteners such as metals of group VII sub-group 1, for instance manganese.

While I have given certain specific proportions and have listed conditions in the foregoing, it will be 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 for plating a deposit comprised substantially of zinc, the composition containing a metal from group VI sub-group 1 of the Periodic System in the form of a soluble compound.

2. A cyanide-zinc electroplating composition for plating a deposit comprised substantially of zinc, the composition containing a substantial amount of molybdenum in the form of a soluble compound.

3. A cyanide-zinc electroplating bath for plating a deposit comprised substantially of zinc, the bath containing about one hundredth to forty grams per liter of molybdenum in the form of a soluble compound.

4. A cyanide-zinc electroplating bath for plating a deposit comprised substantially of zinc,

the bath containing about one-fourth to twenty-five grams per liter of molybdenum in the form of a soluble compound.

5. A cyanide-zinc electroplating bath for plating a deposit comprised substantially of zinc, the bath containing a substantial amount of a metal of group VI sub-group 1 of the Periodic System in the form of a soluble compound, and a thiourea.

6. A cyanide-zinc electroplating bath for plating a deposit comprised substantially of zinc, the bath containing a substantial amount of molybdenum in the form of a soluble compound, and thiourea.

7. A cyanide-zinc electroplating bath for plating a deposit comprised substantially of zinc, the bath containing a substantial amount of a metal of group VI sub-group 1 of the Periodic System, and a substantial amount of a metal of group VII sub-group 1 of the Periodic System, the metals being in the form of soluble compounds.

8. A cyanide-zinc electroplating bath for plating a deposit comprised substantially of zinc, the bath containing a substantial amount of a metal of group VI sub-group 1 of the Periodic System, and a substantial amount of a metal of group VIII series 4 of the Periodic System, the metals being present in the form of soluble compounds.

9. A cyanide-zinc electroplating bath for plating a deposit comprised substantially of zinc, the bath containing a substantial amount of molybdenum and a substantial amount of manganese.

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 a metal from group VI sub-group 1 of the Periodic System 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 substantial amount of molybdenum in the form of a soluble compound.

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 substantial amount of a metal of group VI sub-group 1 of the Periodic System in the form of a soluble compound, and thiourea.

13. 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 substantial amount of molybdenum and a substantial amount of manganese.

14. In a process for the electrodeposition of a deposit comprised substantially of zinc, the step comprising depositing zinc from a cyanide-zinc bath with an electric current introduced into the bath with a zinc alloy anode which contains a metal of group VI sub-group 1.

15. An electrodeposit comprised substantially of zinc and characterized by the presence of a substantial amount of a metal of group VI sub-group 1 of the Periodic System.

16. A cyanide-zinc electroplating bath made up with materials comprising about ninety to one-hundred and thirty grams per liter of sodium cyanide, a zinc compound and a soluble compound of a metal of group VI sub-group 1 of the Periodic System.

17. 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 substantial amount of a metal of group VI sub-group 1 and a substantial amount of a metal of group VIII series 4 of the Periodic System, the metals being present in the form of soluble compounds.

18. 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-hundredth to forty grams per liter of molybdenum in the form of a soluble compound.

19. 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-fourth to twenty-five grams per liter of molybdenum in the form of a soluble compound.

LEON R. WESTBROOK.