

1

3,285,840

PROCESS AND COMPOSITION FOR ZINC
ELECTRODEPOSITION

Karl H. Lindemann, Richmond Heights, Ohio, assignor,
by mesne assignments, to Enthone, Incorporated, West
Haven, Conn., a corporation of Connecticut
No Drawing. Filed May 21, 1963, Ser. No. 282,138
21 Claims. (Cl. 204—55)

This invention relates to an electrodeposition process, to a plating bath, and to an addition agent or additive for use therewith, particularly for acid-zinc plating.

In electrodeposition processes, the techniques commonly in use frequently depend on observed phenomena that are not well understood. In general, analysis of a given problem from a theoretical standpoint is of little value in arriving at a solution; rather, it is necessary to rely almost exclusively on empirically derived data to determine the conditions under which a given process is likely to prove practicable. Because results are rarely predictable in advance, improvements tend to be of the nature of discoveries. Except for the widely accepted proposition that techniques that are known to be useful in a given field such as cyanide-zinc plating are likely to be of little value in a different field such as acid-zinc plating, there are few rules of general application.

In common with many other improvements that have been made in the past in the electrodeposition of zinc from acid-zinc media, the present invention is of the nature of a discovery. It stems out of the finding that hydrolyzed meat of animal origin, particularly a protein hydrolysate of the kind produced by the action of a proteolytic enzyme, can be used to excellent advantage as a brightener. Not only does hydrolyzed meat, so used, tend to produce a brighter deposit directly from the plating bath, but for reasons not understood its use makes it possible to employ in plating baths of the acid-zinc type brighteners of kinds that in the past have been found to be useful only in cyanide-zinc plating.

Thus aldehyde brighteners of kinds heretofore employed in cyanide-zinc plating impart greater brightness, give improved leveling, and yield a more refined crystal structure when used in conjunction with hydrolyzed meat in an acid-zinc plating bath. Their use also serves to enlarge the effective range of the plating bath both in respect of the temperature and in respect of the hydrogen ion concentration (pH). Other features, advantages and objects of the invention will be apparent from the description which follows.

Conventionally, a typical acid-zinc plating bath of a kind that may be used in the present invention contains water as a solvent or continuous phase, zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) in an amount between about 40 and about 46 ounces per gallon, an inorganic acid such as boric acid (H_3BO_3) in an amount in the neighborhood of 4 ounces per gallon, and often a conductive salt such as ammonium chloride (NH_4Cl) or ammonium fluoride (NH_4F), likewise in an amount in the neighborhood of 4 ounces per gallon. Zinc chloride, zinc acetate and aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) are sometimes used in amounts of the order of about 2 to 4 ounces per gallon. If the addition agent of the present invention is added as below described, such a bath can be used over a temperature range which may go as low as 80° and as high as 130° F. In a typical case, its hydrogen ion concentration (pH) will be between 3 and 4.

In the practice of the invention, it is convenient and usually desirable to include in the plating bath a conventional anti-pitting agent such as the sodium salt of

2

dodecylated oxydibenzene disulphonate. In water solution, this compound operates as an anionic surfactant or surface-active agent. It is available in the form of a 45% solution under the trademark Benax 2A1. While it may be omitted entirely if desired, in the normal practice of the invention it is incorporated in the plating bath by adding to each 1000 gallons from 4 to 8 gallons of the solution obtained by diluting 20 gallons of the commercial product with 180 gallons of water.

It will be convenient to take up next the novel addition agent that is one of the features of the present invention. Generally speaking, it comprises water, a surface-active agent of the nature of a wetting agent, and, present in a discrete or discontinuous phase, degraded meat of animal origin, more particularly the protein hydrolysate obtained therefrom by subjecting to the meat the action of a pancreatic or similar proteolytic enzyme. Enzyme-degraded meats, certain of which are used as bacteriological nutrients, are readily available on the commercial market.

A shipped, degraded meat of this kind takes the form of a dry powder containing up to about 5% of water. Approximately 95% of the commercial product consists largely of not entirely of hydrolyzed meat protein, fatty acids and hydrocarbons. Fatty acids, hydrocarbons and the like can total as much as 30% of the commercial product. The remainder, approximately 65% of the commercial product, is proteinaceous material that is virtually completely hydrolyzed. The commercial product contains about 14% total nitrogen, of which about one fifth is believed to be amino nitrogen. Inasmuch as the hydrolyzed meat is known to be present in colloidal form in the addition agent, it can probably be accurately described as a protective colloid.

The solubilized aldehyde or aldehydes may be any of a rather large class of aldehydes some of the members of which have in common the fact, inter alia, that they have been used successfully in the past in cyanide-zinc plating. In general, the most important of the latter group are anisic aldehyde, veratraldehyde, piperonal and vanillin. All can be used in the practice of the present invention; however, as will appear below, it is also feasible to use therein various other aromatic aldehydes such, for example, as hydroxybenzaldehyde and 2,4-dichlorobenzaldehyde and a number of aliphatic aldehydes containing five or more carbon atoms, for example, 2-methyl 2-ethyl 3-hydroxy propionaldehyde.

The aldehyde or aldehydes need not and in certain cases cannot be solubilized by reactions and techniques analogous to those heretofore employed in cyanide-zinc plating but should in each case be solubilized by reaction with an alkali metal bisulphite or some functionally equivalent solubilizer that is compatible with a plating bath of the acid-zinc type. Sodium bisulphite, if used as a solubilizer, should be used in quantities that are equimolar in relation to the aldehydes. An excess of an alkali metal bisulphite, if present, is objectionable for the reason that it tends to discolor the deposited zinc. An excess of aldehyde is of no value.

As already stated, the addition agent of the present invention also contains a surface-active agent of the nature of a wetting agent. For purposes of the invention, the best of the presently available surface-active agents is thought to be an alkali metal salt of a sulphate of a long chain aliphatic hydrocarbon. A good example is sodium tetradecyl sulphate, an anionic surface-active agent that is available under the trademark Tergitol 4. It is supplied in the form of an aqueous solution of 26 to 28% concentration. It is recognized as a wetting agent

lending itself to use in solutions containing relatively low concentrations of dissolved solids. In place of it may be used the sodium salt of 2-ethylhexyl sulphate. This product, which likewise is anionic, is sold under the trademark Tergitol 8. Offered in the form of an aqueous solution having a concentration of from 39 to 41%, it also is a recognized wetting agent.

In addition to the substances so far mentioned, the addition agent of the present invention preferably will contain a suitable commercial preservative. By incorporating such a preservative, the pot life of the addition agent may be extended from a few weeks to more than a year. The preferred preservative is Dowicide B, which is the sodium salt of 2,4,5-trichlorophenol.

Calculated on the basis of the dry weights of the four active constituents, the addition agent of the invention normally contains the following:

	Percent
(a) Protein hydrolysate	2.5 to 7.5
(b) Wetting agent (Tergitol 4 or Tergitol 8) ..	0.5 to 1.5
(c) Aldehyde (95% purity)	1 to 5
(d) Bisulphite (anhydrous)	1 to 5
(e) Water (by difference)	81 to 95
(f) Preservative, q.s.	

In the case of (c) and (d), the indicated upper limits may sometimes be exceeded provided equal percentages of the two are used.

Although prepared separately and added independently to the plating bath, the corresponding figures for the anti-pitting agent (Benax 2A1) are 5% to 20%, normally nearer the former than the latter.

Reverting again to the addition agent, 100 gallons can be made up by adding to sufficient water approximately 40 lbs. of enzyme-degraded meat, 8 lbs. of wetting agent solution, 16 lbs. of aldehyde, 12½ lbs. of anhydrous sodium bisulphite and 5 oz. of preservative. Most of the foregoing weights are on a non-dry or gross basis. An acceptable procedure calls for dissolving the enzyme-degraded meat in 60 gallons of water at 160° F. in a stainless steel vessel, adding sulphuric acid to lower the pH to 3.5, mixing for about one hour and adding the Tergitol 4 and Dowicide B and mixing for a further period of thirty minutes. To 30 gallons of water in a separate container the aldehyde and sodium bisulphite should be added, after which the solution should be mixed for thirty minutes. It should then be added to the original mixture in the previously mentioned stainless steel tank. The resulting mixture should be maintained at a temperature of between 140 and 150° F. for an hour, mixed in the meanwhile and then filtered through a suitable filter such as the Udylite filter.

Generally speaking, the addition of the aldehyde and the solubilizer for the aldehyde can best follow the addition of the meat. It may precede or follow the addition of the wetting agent. Assuming that the meat has already been added, the introduction of the aldehyde and the solubilizer for the aldehyde immediately produces a heavy precipitate that consists mainly of the fatty acids and hydrocarbons introduced as part of the meat. It is important that the precipitated fatty acids and hydrocarbons should be filtered off. If they are permitted to remain, they tend to produce pitting or at least to interfere with the action of the anti-pitting agent in the plating bath.

With the benefit of the foregoing discussion, the preparation of the addition agent of the present invention will be readily apparent from the following representative examples:

Example I

	Percent
Meat protein hydrolysate	5
Tergitol 04	1
Anisic aldehyde	2
Sodium bisulphite	1.5
Water, q.s.	

Example II

	Percent
Meat protein hydrolysate	5
Tergitol 08	1
Anisic aldehyde	2
Sodium bisulphite	1.5
Water, q.s.	

Example III

Meat protein hydrolysate	5
Tergitol 04	1
Heliotropin aldehyde	2
Sodium bisulphite	1.5
Water, q.s.	

Example IV

Meat protein hydrolysate	5
Tergitol 04	1
Veratraldehyde	2
Sodium bisulphite	1.5
Water, q.s.	

Example V

Meat protein hydrolysate	5
Tergitol 04	1
2-methyl 2-ethyl 3-hydroxy propionaldehyde	2
Sodium bisulphite	1.5
Water, q.s.	

Example VI

Meat protein hydrolysate	5
Tergitol 04	1
2,4-dichlorobenzaldehyde	2
Sodium bisulphite	1.5
Water, q.s.	

Although each of the foregoing examples represents a composition that has been found empirically to give satisfactory results, variations are possible. Specific aldehydes are mentioned in Examples I to VI but there is a considerable range of equivalents, particularly among aldehydes characterized by a benzene ring with a para-position substituent of the nature of chlorine, a hydroxyl radical or an ether group and also among aldehydes characterized by a benzene ring with these or similar substituents in the 2,4 positions. Aliphatic aldehydes having less than 5 carbon atoms appear not to lend themselves to use for the purposes of the invention but straight and branched chain aliphatic aldehydes having a minimum of 5 carbon atoms are potentially useful.

Assuming the use of a plating bath containing zinc sulphate, boric acid and ammonium chloride, the preferred procedure is to add to 1000 gallons thereof equal volumes of the addition agent of the present invention and the previously described 5% solution of the anti-pitting agent. Depending on the temperature range, the two may be added in amounts of from 4 to 8 gallons, the smaller quantity being for use at the lower end of the temperature range (80° F.) and the greater for use at the upper end of the temperature range (130° F.). Maximum brightness can be obtained by using 8 gallons of each with 1000 gallons of a typical acid-zinc plating bath maintained at a temperature of about 130° F.

Thus the invention makes it possible to use in acid-zinc plating a group of aldehyde brighteners certain of which have gained acceptance in cyanide-zinc plating, wherein they have been highly valued because of the characteristics which they impart to the plated object. Heretofore, it has been assumed by those skilled in the plating arts that aldehyde brighteners could not be successfully used in acid-zinc plating. The foregoing description of the present invention amply demonstrates that this assumption is erroneous and that aldehydes, some of them of the very type used in the past in cyanide-zinc plating, can be used in acid-zinc plating provided they are solubilized in suitable fashion. However, it appears that these aldehydes, even when so solubilized, are not in and of themselves of a great deal of value in the absence of the protein hydroly-

sate described above. The latter seems to be the key to the invention in that, for reasons not understood, it makes it feasible to use a solubilized aldehyde in acid-zinc electro-deposition processes.

It is intended that the patent shall cover, by summarization in appended claims, all features of patentable novelty residing in the invention.

What is claimed is:

1. In the process for electrodepositing zinc upon a cathode from an acidic aqueous electrolyte, the improvement which comprises having present in said electrolyte as brightener an effective amount of an enzyme-degraded hydrolyzed meat protein and of an aldehyde selected from the group consisting of veratraldehyde, anisic aldehyde, piperonal, vanillin, 2,4-dichlorobenzaldehyde, and 2-methyl 2-ethyl 3-hydroxy propionaldehyde.

2. A process according to claim 1 wherein the hydrolyzed meat in the form in which it is used in the process consists essentially of an enzyme-degraded meat protein hydrolysate that is substantially free of fatty acids.

3. A process according to claim 2 wherein the hydrolysate is derived from meat that has been subjected to a degrading action induced by a proteolytic enzyme.

4. A process according to claim 3 wherein the enzyme is a pancreatic enzyme.

5. A process according to claim 1 further characterized in that an alkali metal bisulphite is present in the electrolyte in amount sufficient to solubilize the aldehyde.

6. In an aqueous acid-zinc electroplating bath the improvement which comprises, having present in said bath an effective amount, sufficient to impart brightness to the zinc electroplate, of an enzyme-degraded hydrolyzed meat protein and of an aldehyde selected from the group consisting of veratraldehyde, anisic aldehyde, piperonal, vanillin, 2,4-dichlorobenzaldehyde and 2-methyl 2-ethyl 3-hydroxy propionaldehyde.

7. A plating bath according to claim 6 wherein the hydrolyzed meat consists essentially of a meat protein hydrolysate that is substantially free of fatty acids.

8. A plating bath according to claim 7 wherein the hydrolysate is derived from meat that has been subjected to a degrading action induced by a proteolytic enzyme.

9. A plating bath according to claim 6 further characterized in that an alkali metal bisulphite is present in the bath in amount sufficient to solubilize the aldehyde.

10. A plating bath according to claim 6 further characterized in containing a wetting agent.

11. A plating bath according to claim 10 further characterized in containing an anionic surface active anti-pitting agent.

12. An addition agent for a plating bath consisting essentially of water, an aldehyde selected from the group consisting of veratraldehyde, anisic aldehyde, piperonal, vanillin, 2,4-dichlorobenzaldehyde and 2-methyl 2-ethyl 3-hydroxy propionaldehyde, and an enzyme-degraded hydrolyzed meat protein.

13. An addition agent according to claim 12 wherein the hydrolyzed meat protein consists essentially of an enzyme-degraded meat protein hydrolysate that is substantially free of fatty acids.

14. An addition agent according to claim 13 wherein the hydrolysate is derived from meat that has been

subjected to a degrading action induced by a proteolytic enzyme.

15. An addition agent according to claim 14 wherein the enzyme is a pancreatic enzyme.

16. An addition agent for a plating bath consisting essentially of water, a wetting agent, an aldehyde selected from the group consisting of veratraldehyde, anisic aldehyde, piperonal, vanillin, hydroxybenzaldehyde, 2,4-dichlorobenzaldehyde and 2-methyl 2-ethyl 3-hydroxy propionaldehyde, and an enzyme-degraded hydrolyzed meat protein.

17. The addition agent of claim 16 wherein the hydrolyzed meat consists essentially of a meat protein hydrolysate that is substantially free of fatty acids.

18. The addition agent according to claim 12 further characterized in that an alkali metal bisulphite is present therein in amount sufficient to solubilize the aldehyde.

19. An addition agent for a plating bath consisting essentially of 2.5% to 7.5% of an enzyme-degraded hydrolyzed meat protein, 1% to 5% of an aldehyde selected from the group consisting of veratraldehyde, anisic aldehyde, piperonal, vanillin, 2,4-dichlorobenzaldehyde and 2-methyl 2-ethyl 3-hydroxy propionaldehyde, 0.5% to 1.5% of a wetting agent, 1% to 5% of an alkali metal bisulfite, and 81% to 95% of water, the percentage being by weight.

20. An aqueous electroplating bath for acid zinc plating consisting essentially of between about 40 and about 46 ounces per gallon of zinc sulphate, about 4 ounces per gallon of boric acid, and about 4 ounces per gallon of ammonium chloride, and having added thereto per 1,000 gallons thereof, from 4 to 8 gallons of the addition agent of claim 19 and from 4 to 8 gallons of a 5% aqueous solution of an anionic surface active anti-pitting agent, the additive agent and the anti-pitting agent aqueous solution being added in equal volume to the acid zinc bath.

21. An addition agent for a plating bath consisting essentially of an enzyme-degraded hydrolyzed meat protein and an aldehyde selected from the group consisting of veratraldehyde, anisic aldehyde, piperonal, vanillin, 2,4-dichlorobenzaldehyde and 2-methyl 2-ethyl 3-hydroxy propionaldehyde.

References Cited by the Examiner

UNITED STATES PATENTS

2,898,449	6/1961	Mackey et al.	204—55
3,088,884	5/1963	Passal	204—55

FOREIGN PATENTS

580,302	7/1959	Canada.
---------	--------	---------

OTHER REFERENCES

Bray, J. L., et al., "Addition Agents in the Electrodeposition of Zinc," Transactions of the Electrochemical Society, vol. 78, pp. 309-316 (1940).

Lyons, E. H. Jr., "Acid Zinc Plating," Transactions of the Electrochemical Society, vol. 80, p. 387-398 (1941).

60 JOHN H. MACK, *Primary Examiner.*

G. KAPLAN, *Assistant Examiner.*