United States Patent Office 3,298,938 Patented Jan. 17, 1967



3,298,938

# ELECTRODEPOSITION OF ZINC

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No Drawing. Filed June 10, 1964, Ser. No. 374,178
Claims priority, application Japan, June 14, 1963, 38/30,527
5 Claims. (Cl. 204—55)

The present invention is concerned with improvements in the electrodeposition of zinc. More specifically, it is concerned with improvements realized by the expedient of carrying out the electrodeposition of zinc in an aqueous electrolyte composition, sometimes referred to as a "bath," containing as principal ingredient ammonia-alkaline zinc gluconate.

In the electrodeposition of zinc, e.g. in the electroplating or electrowinning of this metal, use has generally been made, as electrolytic bath, of an acidic zinc sulfate solution, of an alkaline zincate solution or of an alkaline zinc cyanide solution. The latter bath yields a smoother, more compact and more homogeneous deposit than the former. However, since the latter contains an extremely poisonous cyanide, the handling thereof is always accompanied by troublesome problems, e.g. disposal of cyanide-containing wastes.

It is a primary object of the present invention to embody an electrolitic bath for zinc which contains no poisonous material, such as a cyanide or the like and which yields, at the least, essentially the same result as an aqueous solution of alkali zinc cyanide in electrodeposition. This and other objects can be realized by employing an aqueous solution of ammonia-alkaline zinc gluconate.

The concentration of zinc gluconate in the baths useful according to the present invention for the electrodeposition of zinc can vary over a wide range from dilute solution to saturated solution, but a concentration ranging from 0.1 to 2 molal (gram mols per kilogram of water) is preferable and a concentration ranging from 0.5 to 1.5 gram mols per kilogram of water.

The concentration of ammonia in the baths according to the present invention can also be varied in a wide range from dilute solution to saturated solution; it is preferred, however, that the pH of the bath be in the range of from 7.5 to 10 at 25° C.

A convenient method of preparing an electrolytic bath according to this invention is as follows:

Zinc oxide, zinc hydroxide, zinc carbonate or the like is added to an aqueous solution of gluconic acid of a desired concentration, thereby yielding an aqueous solution of zinc gluconate. After filtration, gaseous ammonia is passed into the solution (filtrate) while measuring the pH, introduction of ammonia being discontinued when the pH reaches the desired value. The resulting solution is then ready to function as an electrolytic bath according to this invention.



Alternatively, the bath can be prepared by dissolving zinc gluconate in water, after which aqueous ammonia is added until the pH of the resulting ammoniacal solution attains the desired value. The so-prepared solution is then also ready to function as an electrolyte bath according to the invention.

The electrolytic bath according to the invention can contain minor amounts of other additaments, such as ammonium gluconate, ammonium carbonate, surfactant, cobalt salt, dextrine, etc., without impairing the capability of the bath to result in good electrolytic precipitation of zinc.

The mechanism of the electrodeposition is conventional. The electrolyte compositions according to the invention may be used to deposit zinc on a variety of objects to be zinc-plated, e.g. steel plates, steel tools or machine parts may be plated. The object to be coated is made to constitute the cathode in usual manner, the anode being made of zinc and the direct current employed being introduced through the latter.

The plating solutions of the invention may be operated over a wide range of temperatures; best results being obtained at temperatures from about 15° to 40° C. The current density may also vary considerably, as will be seen from the illustrative examples which follow. These examples set forth presently preferred embodiments for obtaining glossy zinc deposits.

*Example 1*

An aqueous ammonia-alkaline bath solution is prepared containing the following ingredients:

| | | |
|---|---|---|
| Zinc gluconate | gram mols | 1.5 |
| Water | kilograms | 1 |

The pH of the solution is adjusted to 8 by the introduction of gaseous ammonia.

A steel stamping is connected up as cathode, and a zinc rod is used as anode. The electroplating operation is carried out at an electrolite solution temperature of 16° C. Voltage of the electrolysis is 36 volts; current density of the electrodeposition (a./dm.$^2$) is 25 amperes per square decimeter.

At the end of 2 minutes, the electrodeposited zinc coating is glossy, smooth and silver white.

*Examples 2 to 4*

These are carried out as described in Example 1, with the differences shown in the following Table:

| No. of Examples | Example 2 | Example 3 | Example 4 |
|---|---|---|---|
| Electrolyte solution: Zinc gluconate | 0.3 gram mol and 0.5 gram of dextrin. | 1.5 gram mol | 1.5 gram mol and 0.1 gram mol of hexaoxyethylene laurylether. |
| Water | 1 kg. | 1 kg. | 1 kg. |
| PH controlled by the addition of ammonia. | 8.5 | 8 | 8. |
| Temperature of electrolyte solution. | 15° C. | 30° C. | 40° C. |
| Voltage of electrolysis | 10 v. | 2.7 v. | 3.6 v. |
| Current density of electrodeposition. | 0.5 a./dm.$^2$ | 3 a./dm.$^2$ | 4 a./dm.$^2$. |
| Time of electrodeposition | 10 minutes. | 10 minutes. | 8 minutes. |
| Textures of electrodeposited zinc. | Semi-glossy; slightly rough; grey. | Glossy; crystalline; silver white. | Glossy; slightly crystalline; silver white. |

An electrolytic bath according to the present invention presents the following advantages:

(1) It makes possible electrodeposition of zinc of an excellence at least equal to that obtained with an aqueous

solution of zinc cyanide, and sometimes of greater excellence.

(2) It yields a glossy zinc plating.

(3) It is bound up with ease of handling, since no special precautions have to be taken such as are necessary when handling poisonous cyanide.

(4) Notwithstanding the simplicity of the bath composition, it results in excellent and stable electrolytic precipitation of zinc; moreover, disposition of the liquid is easy.

Having thus disclosed the invention, what is claimed is:

1. In a process for electrodepositing zinc wherein an electric current is passed from a zinc anode to a cathode on which the zinc is to be electrodeposited through an aqueous electrolyte solution, the improvement wherein the said solution consists essentially of water, zinc gluconate, and sufficient ammonia to give a pH of 7.5 to 10.

2. Electrolytic bath for electrodepositing zinc consisting essentially of water, zinc gluconate, and sufficient ammonia to give a pH of 7.5 to 10.

3. Electrolytic bath for electrodepositing zinc consisting essentially of water, zinc gluconate, and sufficient ammonia to give a pH of 7.5 to 10, the concentration of zinc gluconate being in the range from 0.1 to 2 gram mols per kilogram of water.

4. Electrolytic bath for electrodepositing zinc consisting essentially of water, zinc gluconate, and sufficient ammonia to give a pH of 7.5 to 10, the concentration of zinc gluconate being in the range from 0.5 to 1.5 gram mols per kilogram of water.



5. Aqueous electrolytic bath for electrodepositing zinc consisting essentially of water, zinc gluconate, and ammonia, the concentration of the zinc gluconate being in the range from 0.5 to 1.5 gram mols per kilogram of water, and the pH of said bath being in the range from 7.5 to 10, measured at 25° C.


**References Cited by the Examiner**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,485,563 | 10/1949 | Chester et al. | 204—55 |
| 2,537,032 | 1/1951 | Chester et al. | 204—55 |
| 2,576,997 | 12/1951 | Chester | 204—55 |
| 2,576,999 | 12/1951 | Chester et al. | 204—55 |
| 2,614,975 | 10/1952 | Chester | 204—55 |
| 2,615,030 | 10/1952 | Chester | 204—55 X |
| 2,632,728 | 3/1953 | Chester | 204—55 |
| 2,799,635 | 7/1957 | Chester et al. | 204—55 |


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