

[54] **ELECTROLESS CHROMIUM PLATING  
PROCESS AND COMPOSITION**

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[21] Appl. No.: **251,409**

[52] U.S. Cl. .... **106/1, 117/130 E, 148/6.2**

[51] Int. Cl. .... **C23c 3/00**

[58] Field of Search..... 106/1; 117/130 E; 148/6.2;  
204/51

[56] **References Cited**  
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[57] **ABSTRACT**

Articles being electroplated with zinc are rapidly coated with a resistant and well adhering electroless chromium plating by immersing the articles in an aqueous bath containing

- a. 8 to 15 liters of a solution of 250 to 350 g./l. of sodium dichromate and 200 to 300 g./l. of sodium nitrate, said solution being adjusted to pH .3 with nitric acid,
- b. 3 to 8 liters of a solution of 500 to 700 g./l. of 85 percent formic acid and
- c. .5 to 3 liters of glacial acetic acid and concentrated acetic acid respectively each per 100 liters and maintaining the pH value of the solution at a pH of 2.1 to 2.7.

**10 Claims, No Drawings**

## ELECTROLESS CHROMIUM PLATING PROCESS AND COMPOSITION

### BACKGROUND OF THE INVENTION

The invention relates to a process for chromating articles which have been electroplated with zinc in particular from acid baths, such as sulfuric acid containing plating baths.

It is known to provide zinc or articles electroplated with zinc with a passivating chromium coating. Thus it is possible to provide zinc and zinc coatings with a black chromium layer (by the so-called black chromium electroplating process) by using electrolytes which contain about 350 g./l. of chromium trioxide  $\text{CrO}_3$ , 5 g./l. of barium carbonate and 5 g/l of glacial acetic acid at high current densities of 100 to 200 amps/dm<sup>2</sup> and low temperatures from 12°C. to 18°C. The chromium coatings obtained in this manner contain 20 to 30 percent of chromium oxide but the process is costly and not generally applicable. Further brightening of zinc coatings may be performed by immersing the zinc plated articles in a solution of 100 g./l. of chromic acid, 10 g./l. of sulfuric acid and 5 g./l. of nitric acid. The chromium coatings obtained by this electroless chromium plating process are of a brown color. Frequently the underlying zinc coating is attacked by this process and it is not possible to obtain chromium coatings which are resistant to wiping and scratching and which are sufficiently adhering in particular on articles being electroplated with zinc from acid baths.

### SUMMARY OF THE INVENTION

It has been found that electroless plated passivating chromium coatings of olive to brown color which are resistant and well adhering may be provided to articles which had been electroplated with zinc by applying an aqueous plating bath containing particular ingredients in a particular concentration under particular conditions such as a specified pH range within very short immersing periods.

It is an object of the invention to provide a chromating process for articles electroplated with zinc comprising immersing said articles in an acid, aqueous bath said bath containing per 100 liters

- a. 8 to 15 liters of a solution of 250 to 350 g./l. of sodium dichromate and 200 to 300 g./l. of sodium nitrate, said solution being adjusted to a pH of 0.3 with nitric acid,
- b. 3 to 8 liters of a solution of 500 to 700 g./l. of 85 percent formic acid or an equivalent thereof and
- c. 0.5 to 3 liters of concentrated and or, respectively, glacial acetic acid and maintaining said bath at a pH of from 2.1 to 2.7.

It is a further object of the invention to provide a chromating bath for electroless plating of electroplated zinc articles and coatings, said bath containing the ingredients mentioned under a) to c) above and having a pH of from 2.1 to 2.7.

A further object of the invention is to provide a chromating process and an electroless plating bath for zinc articles or articles electroplated with zinc said bath containing per 100 liters

- a. 11 to 11.5 liters of a solution of about 300 g./l. of sodium dichromate and 250 g./l. of sodium nitrate, said solution being adjusted to a pH of 0.3 with nitric acid,

b. 5 liters of a solution of formic acid having a density of 1.133 at 20°C. and

c. 6 to 12 g./l. of glacial acetic acid, said bath having a pH from 2.1 to 2.7.

Further objects of the invention may be taken from the following description.

### DESCRIPTION OF THE INVENTION

It has been found that articles of zinc and articles electroplated with zinc, in particular from sulfuric acid containing electroplating baths may be chromated by applying to said article such an electroless plating bath, thereby carefully adjusting the pH range as mentioned above. Such adjustment may be effected by continuous pH measurement and, if desired, by the addition of fresh solutions to the exhausted bath. The process yields passivating chromium coatings of olive to brown color, having excellent resistance to cracking and wiping and adhering properties within a very short residence time in the bath. The color is mainly governed by the amount of acetic acid in the electroless chromium plating bath and is reproducible. The residence time in the bath amounts to less than 60 seconds such as 10 seconds or less. The resulting passivating chromium layer is completely resistant against wiping and scratching in the wet state and is resistant to cracks resulting from bending the article. It is well adhering in the dry state in particular at upset zones of zinc plated articles which have been provided with a chromium layer. This is of particular importance with articles electroplated with zinc and provided with an electroless chromium layer which articles are bent subsequently.

The ratio of trivalent chromium to hexavalent chromium ions in the bath is essentially constant when applying the process and bath of the invention. This contributes to superior properties of the chromium layer as obtained according to the invention.

The invention is illustrated by the following example.

### EXAMPLE

A solution A consisting of 30 kg. of sodium dichromate and 25 kg. of sodium nitrate, filled up to 100 liters with deionized water and adjusted to a pH of 0.3 with nitric acid was prepared. The density of the solution amounted to 1.326 at 20°C.

Further, a solution B consisting of 65.8 kg. (53.8 liters) of 85 percent formic acid, filled up to 100 liters with deionized water was prepared. The density of the solution amounted to 1.133 at 20°C.

11.2 liters of solution A, 5 liters of solution B and 690 cm<sup>3</sup> of 98 percent acetic acid were filled up to 100 liters using deionized water.

In the electroless chromium plating bath thus obtained there were immersed iron articles provided with an electroplated zinc coating obtained from a sulfuric acid containing electrolyte. After 13 seconds of residence time the articles were taken from the bath. There was obtained a finely crystalline chromium coating of olive color which was resistant against wiping and scratching in the wet state and which adhered very strongly in the dry state. The articles could be bent without peeling of the chromium layer at the place of bending.

The bath was continuously controlled with a digital pH control instrument. When the pH value exceeded

2.7, fresh solutions A and B and acetic acid were added. It was possible to chromitize articles continuously over long periods without observing changes in color and quality of the chromium coatings obtained.

What is claimed is:

1. In a process of chromitizing zinc articles and zinc electroplated articles, the step which comprises immersing said articles in an acid aqueous chromitizing bath for a period of time less than 60 seconds, said bath containing per 100 liters

a. 8 liters to 15 liters of an aqueous solution of 250 g./l. to 350 g./l. of sodium dichromate and 200 g./l. to 300 g./l. of sodium nitrate, said solution being adjusted to a pH of 0.3 by the addition of nitric acid;

b. 3 liters to 8 liters of an aqueous solution of 500 g./l. to 700 g./l. of 85 percent formic acid or equivalent amounts thereof, and

c. 0.5 liters to 3 liters of glacial acetic acid or concentrated acetic acid,

the pH-value of said bath being maintained at a pH between 2.1 and 2.7.

2. The chromitizing process of claim 1, in which the zinc electroplated articles to be chromitized are articles that have been electroplated from a bath comprising sulfuric acid and zinc.

3. The chromitizing process of claim 1, in which the chromitizing bath is a bath containing per 100 liters

a. 11.0 liters to 11.5 liters of an aqueous solution of about 300 g./l. of sodium dichromate and 250 g./l. of sodium nitrate, said solution being adjusted to a pH of 0.3 by the addition of nitric acid,

b. 5 liters of an aqueous formic acid solution of a density of 1.133 at 20° C., and

c. 6 g./l. to 12 g./l. of glacial acetic acid,

the pH-value of said bath being maintained at a pH between 2.1 and 2.7.

4. An electroless chromium plating bath comprising an aqueous solution containing per 100 liters

a. 8 liters to 15 liters of an aqueous solution of 250 g./l. to 350 g./l. of sodium dichromate and 200 g./l. to 300 g./l. of sodium nitrate, and nitric acid in an

amount sufficient to adjust the pH of the solution to 0.3;

b. 3 liters to 8 liters of an aqueous solution of 500 g./l. to 700 g./l. of 85 percent formic acid or equivalent amounts thereof, and

c. 0.5 liters to 3 liters of glacial acetic acid or concentrated acetic acid,

said bath having a pH between 2.1 and 2.7.

5. The electroless chromium plating bath of claim 4, said bath comprising an aqueous solution containing per 100 liters

a. 11.0 liters to 11.5 liters of an aqueous solution of about 300 g./l. of sodium dichromate and 250 g./l. of sodium nitrate, and in an amount sufficient to adjust the pH of the solution to 0.3,

b. 5 liters of an aqueous formic acid solution of a density of 1.133 at 20° c., and

c. 6 g./l. to 12 g./l. of glacial acetic acid, said bath having a pH between 2.1 and 2.7.

6. An article with a zinc surface, said article being provided with a chromium layer deposited on said zinc surface in an electroless manner by a process as claimed in claim 1.

7. An article with a zinc surface, said article being provided with a chromium layer deposited on said zinc surface in an electroless manner by a process as claimed in claim 2.

8. An article with a zinc surface, said article being provided with a chromium layer deposited on said zinc surface in an electroless manner by a process as claimed in claim 3.

9. A chromitized article with a zinc surface, said article being provided with a chromium layer deposited on said zinc surface in an electroless manner by immersing the article in the electroless chromitizing bath of claim 4.

10. A chromitized article with a zinc surface, said article being provided with a chromium layer deposited on said zinc surface in an electroless manner by immersing the article in the electroless chromitizing bath of claim 5.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,816,142 Dated June 11, 1974

Inventor(s) KARL H. LINDEMANN

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

After "[21] Appl. No.: 251,409" there should be inserted:  
-- Claims priority, application Germany,  
January 19, 1972, P 22 02 457.3 -- ;

Abstract of the Disclosure, line 7: ".3" should read  
-- 0.3 --;

Abstract of the Disclosure, line 11: ".5" should read  
-- 0.5 --;

Column 4, line 14: After "and" there should be inserted  
-- nitric acid --.

Signed and sealed this 29th day of October 1974.

(SEAL)

Attest:

McCOY M. GIBSON JR.  
Attesting Officer

C. MARSHALL DANN  
Commissioner of Patents