

1

3,694,328

**COMPOSITION AND PROCESS FOR CHROMIUM PLATING**

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12 Claims

**ABSTRACT OF THE DISCLOSURE**

A composition and process for the electrodeposition of chromium from aqueous acidic hexavalent chromium solutions which contain sulfate ions and saturation concentrations of certain rare earth phosphofluorides. By the use of the phosphofluorides of these rare earths, a self-regulating chrome plating bath is produced having a higher fluoride ion content than has heretofore been possible. This is particularly desirable in the production of hard chrome plate, in that improved color of the plate is obtained.

This invention relates to a composition and process for the electrodeposition of chromium and more particularly it relates to an improved self-regulating chromium electroplating bath and to the process for electroplating using such bath.

It is well known that in the electrodeposition of chromium from acidic hexavalent chromium solutions, certain "catalyst" ions such as sulfate and/or fluoride ions, must be present. The use of mixed catalyst anions, such as combinations of sulfate ions and fluoride ions, both with and without boric acid, have been previously proposed in numerous U.S. Pats., such as 1,844,751; 1,864,013; 1,864,014; 1,952,793; 2,042,611; 2,063,197; 2,640,021; 2,640,022; and 2,952,590. It is further known that the concentrations of these catalyst ions in the chromium electroplating baths are relatively critical and that excessive amounts, particularly of the fluoride ions result in the decrease in the covering power of the chromium plate as well as the formation of discolored and iridescent films, particularly in low current density areas. To this end, many of the processes of the prior patents have been directed to attempts to make the chromium electroplating baths self regulating, i.e., to maintain the desired concentrations of the sulfate and fluoride catalyst ions in the bath substantially automatically, without the need for complex and time consuming controls.

One successful method for operating a self-regulating chromium plating bath is set forth in U.S. Pat. 3,334,033. In accordance with the process of this patent, the chromium plating bath contains saturation concentrations of "didymium" fluorides and/or complex fluorides, with the "didymium" fluosilicates being preferred. In this manner there is obtained a chromium plating bath in which the fluoride ion catalyst concentration is self regulating, which bath has improved chromium covering power, as compared to the chromium plating baths of the prior art. Although with these baths, the fluoride ion concentration is maintained substantially constant, the level at which it is maintained is such that, in some instances, and particularly where a hard chromium plate is being produced, the brightness of the chromium may not be a great as desired.

It is, therefore, an object of the present invention to provide an improved chromium electroplating bath, which bath is self regulating and will produce a hard chromium plate having excellent color.

A further object of the present invention is to provide an improved method for electroplating of chromium,

2

whereby a hard chromium electroplate having excellent color is produced from a self-regulating plating bath.

These and other objects will become apparent to those skilled in the art from the description of the invention which follows.

Pursuant to the above objects, the present invention includes a bath for the electrodeposition of chromium plate which comprises from about 100 to 500 grams per liter of chromic acid, sulfate ions in a concentration sufficient to provide a chromic acid to sulfate ion ratio of from about 75:1 to 300:1 and saturation concentrations of at least one inorganic phosphofluoride of a rare earth metal selected from neodymium, praseodymium, lanthanum, gadolinium, samarium, yttrium and cerium. Surprisingly, it has been found that by the use of the phosphofluorides of these rare earths, instead of other fluorides or complex fluorides as disclosed in U.S. Pat. No. 3,334,033 such as the fluosilicates, a self-regulating chrome plating bath is produced in which the fluoride ion concentration is maintained at a higher level, thus giving improved color to the chromium plate produced, particularly to a hard chromium plate.

More specifically, in the practice of the present invention, the rare earth phosphofluorides which are used in the chromium plating bath are the phosphofluorides of praseodymium, neodymium, lanthanum, samarium, gadolinium, yttrium, and cerium. The principal commercial source of these rare earth metals is the naturally occurring phosphate one known as monazite. In addition to the rare earth metals indicated above, this ore also contains, among other elements, thorium. The nomenclature and separation techniques involved in the refining of the monazite ore are described in a publication of the Lindsay Division of the American Potash and Chemical Corporation entitled, "Thorium, Rare Earth and Yttrium Chemicals." The rare earth mixtures derived from the monazite ore, as defined in this publication, are termed "didymium salt, neodymium salt and lanthanum salt." Didymium refers to the mixture of the rare earths obtained after the removal of cerium and thorium from the natural mixture of the rare earths found in the monazite ore. The approximate composition of the mixture, in terms of the oxides is 40 to 50 percent  $La_2O_3$ , 8 to 12 percent  $Pr_6O_{11}$ , 32 to 37 percent  $Nd_2O_3$ , 3 to 6 percent  $Sm_2O_3$ , 2 to 4 percent  $Gd_2O_3$ , as well as trace amounts of other rare earth metal oxides.

The didymium salt mixture may be further processed and the lanthanum portion or salt removed therefrom, which portion consists mainly of lanthanum oxide. The remainder of the didymium salt mixture from which the lanthanum has been removed, is termed the "neodymium salts" and has the following composition in terms of the oxides: 65 to 70 percent  $Nd_2O_3$ , 12 to 16 percent  $Pr_6O_{11}$ , 10 to 13 percent  $Sm_2O_3$ , 3 to 5 percent  $Gd_2O_3$ , and trace amounts of other rare earth oxides. The neodymium salts can be further refined to provided a variety of mixtures of the remaining rare earth metals or the individual rare earth metals themselves can be obtained from this mixture. Although the phosphofluorides of any of these mixtures or of the individual rare earth may be used in the method of the present invention, the cost of the further separation of these rare earth metals becomes increasingly higher. Accordingly, it is generally preferred that for the chromium plating baths of the present invention, the phosphofluorides used are the phosphofluorides of didymium, neodymium and lanthanum, as defined above, and cerium.

The phosphofluorides of these rare earths may be prepared by reacting the rare earth salts, such as the chlorides, with an aqueous solution of a fluorophosphoric acid, such as difluorophosphoric acid, hexafluorophosphoric acid, or monofluorophosphoric acid, or an aqueous

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ous solution of the salts of the fluorophosphoric acid such as the ammonium salts. The reaction is quite straightforward and takes place with relative ease merely by heating the mixture to boiling and then allowing the reaction product to settle.

In a typical preparation, a solution of the ammonium salts of difluorophosphoric or hexafluorophosphoric acid ( $\text{NH}_4\text{PF}_2\text{O}_2$  or  $\text{NH}_4\text{PF}_6$ ) which solutions typically contain from about 100 g./l. to saturation of the ammonium compound, is added to a "didymium" or ceric chloride solution which typically contains the chloride compound from about 100 g./l. to saturation. Desirably, the two reactants are combined in at least stoichiometric amounts, with the use of an excess of the phosphofluoride compound being preferred. The resulting mixture is heated to boiling, typically for a period from about 1 to 3 hours, and is then allowed to settle. After centrifuging, the resulting rare earth phosphofluoride is recovered and washed to remove chloride ion and is then suitable for addition to the chromium plating baths of the present invention.

In using these rare earth phosphofluorides, they are desirably present in the chromium plating baths in saturation concentrations and are preferably used in amounts which will insure that an excess will be present undissolved in the bath. In general, it has been found that concentrations of the rare earth phosphofluorides of from about 5 to 10 grams per liter are more than sufficient to provide the saturation concentration and a sufficient, undissolved excess. Obviously, amounts of the rare earth phosphofluorides which are both less than and greater than the specific amounts indicated above may be used, as long as they provide for the saturation concentrations of the rare earth phosphofluorides in the plating bath.

The acidic hexavalent chromium plating baths for use in the present invention may be made up of chromic acid, chromic acid anhydride, or from mixtures of these with one or more chromates, dichromates, or polychromates. In general, it is preferred to use either chromic acid or chromic acid anhydride, as the presence of cations such as sodium, potassium, lithium, magnesium and calcium, except in very low concentrations, may be disadvantageous. Accordingly, in many instances, it has been found to be preferred if the chromium plating baths contain from about 100 to 500 grams per liter of chromic acid.

Additionally, these plating baths should contain sulfate ions in a concentration sufficient to provide a chromic acid to sulfate ion ratio from about 75 to 1 to 300 to 1. Although the sulfate ion may be added in any convenient form, such as sulfuric acid, various organic sulfates or the like, in the most preferred embodiment, the sulfate ions are added as strontium sulfate. In general, it has been found that saturation concentrations of the strontium sulfate will provide the proper concentration of sulfate ions to cooperate with the fluoride ions provided by the saturation concentrations of the rare earth phosphofluorides described hereinabove. This has been found to be particularly true for the lower range of bath concentrations of chromic acid. Where, however, an excess of sulfate ion concentration is inadvertently added to the bath, either in the form of the strontium sulfate alone or in combination with another source of sulfate ions, the sulfate ion concentration of the bath can be at least partially suppressed by the addition of strontium chromate, bichromate or carbonate. This has frequently been found to be desirable where the plating baths are low metal baths, such as those using from about 100 to 200 grams per liter of chromic acid or chromic acid anhydride.

In addition to the above components, the chromium plating baths of the present invention may also contain other components which are typically present in such plating baths, including anti-misting agents, such as perfluoro-n-octyl sulfonic acid and the like. Additionally, where the chrome plating baths are to be used on relatively passive bright nickel surfaces, the difficulties of plating on such surfaces can be minimized by including

4

in the chromium plating baths from about 0.5 to 5 grams per liter of an aliphatic or cycloaliphatic fluorocarbon acid such as the fluorocarbon sulfonic acid or fluorocarbon phosphonic acids. Exemplary of these "activators" which may be used are perfluorocyclohexyl sulfonic acid, perfluoro-para-methyl cyclohexyl sulfonic acid, perfluoro-para-ethyl cyclohexyl sulfonic acid, perfluorosuccinic acid, perfluoromethyl sulfonic acid or a fluoroalkyl phosphonic acid such as  $\text{H}(\text{CF}_2\text{CF}_2)_n\text{PO}(\text{OH})_2$ , in which  $n$  is 1 to 3.

In utilizing the chromium plating baths of the present invention, the baths are desirably operated at a temperature within the range of 30 degrees to 65 degrees centigrade and current density within the range of 100 up to 300 amps per square foot. When operating in this manner, it is found that a bright chromium plate of exceptional covering power is produced on nickel, brass, copper and steel. This bright chromium plate is produced over a very wide cathode current density range and the plate is further found to be substantially free of discoloration, with no formation of iridescent films, even in hard chrome (thick chromium) plating applications.

In order that those skilled in the art may better understand the present invention and the manner in which it may be practiced, the following specific examples are given. In these examples, unless otherwise indicated, parts and percents are by weight and temperatures are in degrees centigrade.

Aqueous chromium electroplating baths were formulated containing the components in the amounts indicated in the following examples:

## EXAMPLE 1

|  | Grams/liter |
|--|-------------|
| $\text{CrO}_3$ .....                                 | 300         |
| Strontium sulfate .....                              | 3           |
| Didymium hexafluorophosphate .....                   | 4           |
| Stearyl dimethyl amine N-propane sulfonic acid ..... | 0.002-0.020 |

## EXAMPLE 2

|                                   |            |
|-----------------------------------|------------|
| $\text{CrO}_3$ .....              | 400        |
| Strontium sulfate .....           | 3          |
| Cerium hexafluorophosphate .....  | 8          |
| N-perfluoro octyl sulfonate ..... | 0.005-0.02 |

## EXAMPLE 3

|                                    |     |
|------------------------------------|-----|
| $\text{CrO}_3$ .....               | 200 |
| Didymium hexafluorophosphate ..... | 2   |
| Strontium sulfate .....            | 2   |

## EXAMPLE 4

|  | Grams/liter |
|--|-------------|
| $\text{CrO}_3$ .....                       | 150         |
| Strontium sulfate .....                    | 3           |
| Didymium hexafluorophosphate .....         | 2           |
| N-perfluoro octyl sulfonate .....          | 0.006       |
| N-stearyl dimethyl N-propane sulfone ..... | 0.006       |

## EXAMPLE 5

|   |     |
|---|-----|
| $\text{CrO}_3$ .....  | 150 |
| $\text{CrO}_3/\text{SO}_4$ ratio, by adding $\text{H}_2\text{SO}_4$ , of 100:1. |     |
| Didymium hexafluorophosphate .....  | 3   |

The above baths were maintained at temperatures within the range of 30 degrees to 65 degrees centigrade and bright nickel surfaces were electroplated with an excellent chromium electroplate from each of the baths, using cathode current densities of from 100 to 300 amps/square foot. The above baths were also formulated using the corresponding lanthanum and neodymium compounds, as well as with the monofluoro- and difluorophosphates of didymium, cerium, lanthanum and neodymium, and similar results are obtained.

While there have been described various embodiments of the invention, it will be readily apparent to those skilled in the art that many variations and modifications

5

of the compositions and processes as hereinabove set forth may be made without departing from the spirit and scope of the invention as defined in the following claims.

What is claimed is:

1. A bath for the electrodeposition of chromium plate which comprises about 100 to 500 grams per liter of chromic acid, sulfate ions in a concentration sufficient to provide a chromic acid to sulfate ion ratio of from about 75 to 1 to 300 to 1 and saturation concentrations of at least one inorganic phosphofluoride of a rare earth metal selected from neodymium, praseodymium, lanthanum, gadolinum, samarium, yttrium, and cerium.
2. The bath as claimed in claim 1 which contains saturation concentrations of strontium sulfate.
3. The bath as claimed in claim 2 wherein the phosphofluoride is a didymium phosphofluoride.
4. The bath as claimed in claim 2 wherein the phosphofluoride is a neodymium phosphofluoride.
5. The bath as claimed in claim 2 wherein the phosphofluoride is a lanthanum phosphofluoride.
6. The bath as claimed in claim 2 wherein the phosphofluoride is a cerium phosphofluoride.
7. A method for electrodepositing chromium which

6

comprises electrolyzing an aqueous acidic hexavalent chromium solution as claimed in claim 1.

8. The method as claimed in claim 7 wherein the hexavalent chromium solution contains saturation concentrations of strontium sulfate.

9. A method as claimed in claim 8 wherein the phosphofluoride in the hexavalent chromium solution is a didymium phosphofluoride.

10. The method as claimed in claim 8 wherein the phosphofluoride in the hexavalent chromium solution is a neodymium phosphofluoride.

11. The method as claimed in claim 8 wherein the phosphofluoride in the hexavalent chromium solution is a lanthanum phosphofluoride.

12. The method as claimed in claim 8 wherein the phosphofluoride in the hexavalent chromium solution is a cerium phosphofluoride.

#### References Cited

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FREDERICK C. EDMUNDSON, Primary Examiner