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PROCESS FOR CHROMIUM PLATING

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The present invention relates to chromium plating and more particularly relates to the use of novel catalysts in chromic acid baths for chromium plating.

Industrial chromium plating became possible with the discovery that chromium could be electrodeposited from aqueous chromic acid baths containing small amounts of a sulfate ion as a catalyst. About the same time, it was discovered that certain other materials also act as catalysts, with varying degrees of effectiveness. Such catalysts include borate ions, fluoride ions, chloride ions, etc. Silicofluoride and fluoroborate ions have been disclosed to be catalysts. Silicofluoride ($SiF_6^=$) has been successfully utilized whereas fluoroborate (BF_4^-) is not commercially utilized. In addition to the aforementioned catalysts, the technical and patent literature are replete with materials claimed to be useful as catalysts or additives in the chromium plating process, either alone or in combination with other catalysts. Experience has proven that of the numerous materials claimed to be effective as catalysts, the only technically feasible and industrially acceptable materials are silicofluoride and sulfate, each of which has been known for about thirty years.

Although all materials which act as catalysts have in common the property that chromium may be electrodeposited from chromic acid baths when they are present in small amounts, each catalyst has somewhat distinct characteristics. Alone or in specific combinations, they govern and/or affect the current efficiencies, the hardness of the deposit, the appearance of the deposit including color, filming, the covering and throwing power of the solution, the soundness of the deposit, etc. Often it has not been possible to obtain deposits having specific desirable characteristics, or to operate under specific desired process conditions, with the known catalyst. I have now discovered three new and useful catalysts.

It is an object of the present invention to provide a process for chromium electrodeposition utilizing novel catalysts.

It is another object of the present invention to provide novel baths for chromium electrodeposition.

The invention also contemplates providing novel compositions of matter which when dissolved in water provide baths for chromium electrodeposition.

I have now discovered that certain complex fluorides, namely, fluoaluminate ions ($AlF_6^{\equiv}$), fluotitanate ions ($TiF_6^=$), and fluozirconate ions ($ZrF_6^=$), are effective catalysts in aqueous chromic acid solutions for chromium electrodeposition. These catalysts are effective when used as the sole catalyst in chromic acid baths, or when used in combination with one or more other catalysts. When used in baths containng sulfate, they provide superior baths for chromium electrodeposition.

Chromium plating baths are frequently designated as chromic acid baths. Herein the chromic acid content of the bath is usually referred to as CrO_3 (more accurately designated "chromic anhydride"). The bath may be made up by supplying CrO_3 in the form of chromic anhydride or in the form of compounds containing cations

which do not adversely affect the bath characteristics, including the chromates, dichromates, and polychromates of potassium, sodium, magnesium, and calcium. The CrO_3 may also be added in the form of chromic acid and/or dichromic acid in solution. Where alkali metal cations are present, the bath should not be neutralized in excess of 80% to the dichromate end-point.

Generally speaking, the conditions for electrodepositing chromium from CrO_3 baths containing those novel catalysts are similar to those employed when using sulfate catalyzed CrO_3 baths. The weight ratio of CrO_3 to total catalyst ions (herein referred to as "Ratio") is of great importance. Chromium may be electrodeposited from baths having a Ratio of between about 50:1 to about 200:1. Under specific conditions, a lower than 50:1 or higher than 200:1 Ratio may be used, but this is dependent on the basis metal; CrO_3 concentration; species, number and relative concentrations of catalyst ions used; temperature; desired properties of the electrodeposits and other factors. Although in some respects these novel catalysts are similar in their effect to sulfate, in others they are not. For purposes of increasing current efficiency, these novel catalysts are added in about 50 to 200% higher concentration (on a weight basis), depending on the particular plating conditions involved, than for sulfate for this purpose. This is an advantage since the optimum concentration limits for these novel catalyst ions are thereby made less critical than for sulfate. For purposes of promoting or inhibiting cracks in chromium electrodeposits, these novel catalysts (when used alone) have effects of the same general order of magnitude as sulfate. Their optimum concentrations with changing plating conditions, and their effects on haze, coverage, etching, and color characteristics differ somewhat from each other and from those attributed to sulfate. There are significant differences in regard to other properties of these three novel complex fluoride catalyst ions such as the solubility of their compounds versus temperature and chromic acid concentration.

Just as it is difficult to obtain from the literature precise limits of the various factors, and correlation of the interdependence of these factors that control and/or influence chromium electrodeposits from baths catalyzed with the known catalysts, it is difficult to set out precise limits for chromium electrodeposition using these novel catalysts. Chromium electrodeposition is affected by changes in concentration of CrO_3, by the temperature, by the current density, by Ratio, by the type of catalyst present, by the proportion of each catalyst present when using more than one catalyst, by the presence of other cations in the bath, etc. Generally speaking, the plating conditions and concentration ranges of bath components (other than these catalysts) are those generally accepted in the art for chromium plating from sulfate catalyst or sulfate-silicofluoride catalyzed CrO_3 baths. Detailed information concerning these conditions and bath components are set forth in the book, "Chromium Plating" by Morrisset et al., published by Robert Draper, Ltd. (1954).

Although baths containing from about 50 g./l. to over 600 g./l. of CrO_3 may be utilized in chromium electrodeposition, it is preferred to electrodeposit chromium from baths containing the novel fluoride catalysts (alone or together with known catalysts) and containing about 200 g./l. to about 450 g./l. of CrO_3, and having a total catalyst content governed by a Ratio of about 75:1 to about 150:1. When utilizing the preferred CrO_3 bath and conditions, and utilizing one of these novel catalysts in conjunction with sulfate as an auxiliary catalyst, superior chromium plating results are obtained. With this dual catalyst system, it is preferred that a minimum of at least 20% of the catalyst should be sulfate and that preferably at least 35% should be sulfate. Preferably the

sulfate should not be more than 75% of the total catalyst to obtain the benefits of the dual catalyst system. Although the three novel catalyst ions, fluoaluminate, fluotitanate, and fluozirconate, are generally treated as a single group herein, each has a distinct characteristic which affects the electrodeposition process and which makes one or the other more favored under particular conditions. It has been found that the solubility of K_2ZrF_6 in CrO_3 decreases as the temperature is raised from 32° C. to 43° C. and then increases as the temperature is raised to 55° C.; whereas the solubility of $K_2TiF_6 \cdot H_2O$ increases as the temperature is raised from 32° C. to 43° C. and then decreases as the temperature is further raised to 55° C.

The fluoaluminate, fluotitanate, and fluozirconate anions may be added to the bath as salts, associated with such cations as sodium, potassium, calcium, strontium, ammonium, barium, etc. They may be formed in situ by the introduction into a chromic acid bath of elements and/or compounds which in the bath environment react to form the desired catalyst ion. Baths containing fluoaluminate catalyst ions have been prepared by the introduction into a 400 g./l. CrO_3 bath of a small amount of aluminum added as the hydroxide or aluminate and a small amount of sodium fluoride.

By utilizing the principles disclosed in U.S. Patent Nos. 2,640,021 and 2,640,022, it has been possible to develop baths having extremely stable and even self-regulating characteristics using these novel complex fluoride catalysts in conjunction with a sulfate catalyst. In each case, the baths must be carefully tailored to give the desired result, taking into consideration the effects of many factors and interrelation of these factors on the chromium plating process. Thus, when a bath having both sulfate ion and a complex fluoride ion catalyst is desired, it is not possible to supply the complex fluoride in the form of its barium salt. If this were done, the barium would either partially or totally precipitate out the sulfate.

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative examples are given.

Standard test samples were obtained by electro-depositing chromium under varied conditions on metal sheet. In the examples, sound deposits were obtained. The bath composition and the process conditions are given in the table below.

Ex. No.	CrO_3, g./l.	SO_4, g./l.	$SiF_6^=$, g./l.	$AlF_6^{\equiv}$, g./l.	$ZrF_6^=$, g./l.	$TiF_6^=$, g./l.	Temp., ° C.	C.D., amp./sq. dm.	Complex Fluorides added as—
1	400			2			43	7.75	Na_3AlF_6
2	400			8			43	15.5	Na_3AlF_6
3	175			2.70			43	11.6	Na_3AlF_6
4	320			2.75			38	15.5	$(NH_4)_3AlF_6$
5	250	0.3			2.9		43	24.8	K_2ZrF_6
6	400				2.9		38	12.4	K_2ZrF_6
7	400	2.0			3.6		49	15.5	K_2ZrF_6
8	250	1.5	2.2		5.8		43	15.5	$MgSiF_6$ + K_2ZrF_6
9	250					4	43	15.5	$K_2TiF_6 \cdot H_2O$
10	250	0.25				1.5	43	31	$K_2TiF_6 \cdot H_2O$
11	400	0.5	3.5			8.2	55	31	$MgSiF_6$ + $K_2TiF_6 \cdot H_2O$

Although the examples utilized the sodium, potassium and ammonium salts, such other salts as those of magnesium, strontium, and calcium are operative. The basis metal may be nickel, copper or copper base alloys, steel, zinc, aluminum or other structural metal.

As many embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention includes all such modifications and variations as come within the scope of the appended claims.

I claim:

1. An aqueous bath for chromium plating comprising between 50 and 600 g./l. of chromic acid and at least one complex ion selected from the class consisting of fluoaluminate, fluotitanate and fluozirconate ions, the Ratio of chromic acid to said complex ion being between 50:1 to 200:1.

2. An aqueous bath for chromium plating comprising between 50 and 600 g./l. chromic acid, sulfate ion, and at least one complex ion selected from the class consisting of fluoaluminate, fluotitanate and fluozirconate ions, the Ratio of chromic acid to the total of the sulfate ion and the complex ion being between 50:1 to 200:1.

3. The bath of claim 1, in which the Ratio is between 75:1 to 150:1.

4. The bath of claim 2, in which the Ratio is between 75:1 to 150:1.

5. The bath of claim 1, in which the complex ion is fluoaluminate.

6. The bath of claim 1, in which the complex ion is fluotitanate.

7. The bath of claim 1, in which the complex ion is fluozirconate.

8. A process of electrodepositing sound chromium comprising passing an electric current between an anode and a cathode immersed in an aqueous bath comprising between 50 and 600 g./l. of chromic acid and at least one complex ion selected from the class consisting of fluoaluminate, fluotitanate and fluozirconate ions, the Ratio of chromic acid to said complex ion being between 50:1 to 200:1.

9. A process of electrodepositing sound chromium comprising passing an electric current between an anode and a cathode immersed in an aqueous bath comprising between about 200 g./l. and about 450 g./l. of chromic acid, sulfate ion, and at least one complex ion selected from the class consisting of fluoaluminate, fluotitanate and fluozirconate ions, the Ratio of chromic acid to the total of the sulfate ion and the complex ion being between 50:1 to 200.1.

10. The process of claim 8, in which the bath has a chromic acid concentration of between about 200 g./l. and 450 g./l., and in which the Ratio is between 75:1 to 150:1.

11. The process of claim 9, in which the Ratio is between 75:1 to 150:1.

12. The process of claim 11, in which the complex ion is fluoaluminate.

13. The process of claim 11, in which the complex ion is fluotitanate.

14. The process of claim 11, in which the complex ion is fluozirconate.

15. The bath of claim 2 in which the complex ion is between 25% and 65% of the total of the complex ion and the sulfate ion concentration.

16. A composition of matter for making up and for maintaining aqueous chromic acid baths for chromium plating consisting essentially of chromic acid, and at least one salt of a complex anion selected from the class consisting of fluoaluminate, fluotitanate, and fluozirconate ions, the weight ratio of chromic acid to the complex anion of the salt being between 50:1 to 200:1, said composition being characterized by dissolving in water to produce a bath from which chromium is electrodeposited.

17. A composition of matter for making up and for maintaining aqueous chromic acid baths for chromium plating consisting essentially of chromic acid, a sulfate salt, and a salt of a complex anion selected from the class consisting of fluoaluminate, fluotitanate and fluozirconate ions, the weight ratio of chromic acid to the total sulfate and complex anion of the salt being between 50:1 to 200:1, said composition being characterized by dissolving in water to produce a bath from which chromium is electrodeposited.

References Cited in the file of this patent

UNITED STATES PATENTS

1,815,081	Sohn et al.	July 21, 1931
1,928,284	Fink et al.	Sept. 26, 1933