

1

3,108,933

PROCESS AND COMPOSITION FOR CHROMIUM PLATING

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The present invention relates to a process for electrodepositing crack-free chromium, and more particularly to an improved process for electrodepositing bright crack-free chromium.

Bright chromium as electrodeposited from chromic acid baths in the conventional process for decorative plate usually cracks when the deposit reaches a thickness of about 0.00002 inch. The tendency to crack increases as the thickness increases. Several processes have recently been developed for electrodepositing bright crack-free chromium to a thickness of at least 0.00005 inch. Thick crack-free chromium electrodeposits have superior corrosion resistance.

It is an object of this invention to provide an improved process for electroplating thick crack-free chromium. It is another object of this invention to provide baths from which thick crack-free chromium may be deposited. Still another object of the invention is to provide novel compositions of matter useful for making up and maintaining chromic acid baths for the electrodeposition of crack-free chromium. The present invention also contemplates an improved process for obtaining thicker deposits of bright crack-free chromium.

Processes for the electrodeposition of industrial crack-free chromium are disclosed in U.S. Patent Nos. 2,686,756, 2,787,588, and 2,787,589. New processes have recently been developed for the electrodeposition of bright crack-free chromium from sulfate catalyzed baths as well as baths catalyzed with sulfate plus a complex fluoride, as disclosed in U.S. Patent Nos. 2,916,424 and 2,952,590, and in the Safranek et al. article in the May 1960 issue of Plating, vol. 47 (pages 513—519). I discovered that when electrodepositing chromium, using the conditions specified for each of these processes, and using the specified baths which had been modified only by the addition of lithium, a greater thickness of chromium was electrodeposited before cracking occurred. By utilizing baths containing lithium in the aforesaid processes, it is possible to broaden the conditions under which bright crack-free chromium may be electrodeposited to a minimum thickness of at least 0.00005 inch. It is known that lower plating temperatures tend to decrease the thickness at which cracking occurs. Higher concentrations of catalyst in the bath also tend to decrease the thickness at which cracking occurs. Lithium additions to the bath tend to counteract the above tendencies. Where suitable conditions have been determined for obtaining a specified thickness of bright crack-free chromium in a lithium-free bath, it is possible to obtain the same thickness using lower temperatures and/or lower ratios (of CrO_3 to catalyst ion) with a lithium-containing bath. In effect, processes utilizing lithium-containing baths under specified conditions to obtain a desired thickness of crack-free chromium are the equivalent of corresponding processes utilizing lithium-free baths at higher temperatures and/or higher ratios.

Relatively small additions of lithium to the bath increase the thickness which is plated before cracking occurs. Amounts as small as 1 g./l. (gram per liter) lithium in the bath yield substantial improvement in this respect. It is preferred that baths contain a minimum of 2 g./l. and preferably 4 g./l. of lithium to obtain substantial increases in the thickness of crack-free electrodeposit.

2

Substantially larger amounts of lithium in the bath may be tolerated and are even useful in increasing the thickness of plate before cracking occurs. The maximum amount of lithium in the bath is governed by the percent neutralization of the bath. For commercial practice, it is not contemplated that baths neutralized more than about 80% to the dichromate end-point will be used. For electrodeposition of bright crack-free chromium, it is preferred that baths have compositions within the following ranges: CrO_3 —between 100g./l. and 500 g./l. and preferably between 200 g./l. and 400 g./l.; sulfate ion—between 0.25 g./l. and 3.5 g./l. and preferably between 1 g./l. and 2.5 g./l.; complex fluoride ion—between 0.5 g./l. and 5 g./l. and preferably between 1 g./l. and 2.5 g./l.; and having a ratio between 70:1 to 150:1 and preferably between 85:1 to 130:1.

Chromium plating baths are frequently designated as chromic acid baths. Herein the chromic acid content of the bath is 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 soluble CrO_3 -containing compounds containing cations which do not adversely affect the bath characteristics. Such compounds include 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. The term CrO_3 is used herein to refer to the compound per se and to the CrO_3 -containing compounds as defined hereinabove, in solution and in solid form. Sulfate ions may be added in the form of sulfuric acid, or as soluble sulfate salt(s) with a cation that does not adversely affect bath characteristics. Similarly, the fluoaluminate, fluotitanate, fluozirconate, and/or silicofluoride anions may be added to the baths as the soluble salts or they may be formed in situ by the introduction into the chromic acid bath of the elements and/or compounds which in the bath environment react to form the desired ion. Lithium may be added to the bath in the form of the metal which dissolves as the cation, or it may be added in the form of a soluble compound such as lithium carbonate, lithium bicarbonate, lithium chromate, lithium dichromate, lithium hydroxide, and lithium oxide. It is preferably added in the form of the chromate and/or dichromate. The term "lithium" is used herein to define the element and ion in any of the aforementioned equivalents in solution and in solid form. The processes of electrodepositing of bright crack-free chromium require careful control of the bath components and particularly the CrO_3 , the catalyst anion, and the ratio between the two. My process also requires control of the lithium concentration. To accomplish this control it is preferred that the chromium plating baths be made up and maintained by the addition of compositions of matter which contain all the necessary bath components, i.e. the CrO_3 , the catalyst ions, and the lithium cation. Compositions of matter for making up and maintaining the baths preferably contain, in addition to the CrO_3 and the sulfate-supplying material and/or the complex fluoride-supplying materials, between about 0.2% and 5% of lithium cation. The compositions for the mixed catalyst baths contain between 70 parts and 95 parts of CrO_3 , between 0.5 part and 1.5 parts of sulfate anion, between 0.5 part and 5 parts of complex fluoride anions, and between 0.2 part and 5 parts (preferably 0.5 part and 2 parts) of lithium. These compositions may also contain some water and ancillary additives such as foam suppressants, etc. Using the above compositions of matter which are in solid form, the bath is made up with water to the desired chromic acid concentration for plating. The same compositions of matter are useful for maintaining the bath.

For the purpose of giving those skilled in the art a bet-

ter understanding of the invention, the following illustrative examples are given:

A standard Hull Cell or its equivalent was used to determine the thickness to which chromium plate can be electrodeposited without cracking. The Hull Cell is a container with an anode perpendicular to the sides and an inclined cathode. The current density on the cathode varies inversely with the distance from the near end where the current density is highest and the electrodeposit is thickest. The chromium plated cathode was examined for cracks and for brightness, and a thickness measurement made at the region where the crack pattern begins. Bright crack-free chromium was electrodeposited from all the baths to the specified thickness, noted in the table.

Example No.	CrO ₃ , g./l.	SO ₄ ²⁻ , g./l.	Fluoride Complex		Temp., ° F.	Li ⁺ , g./l.	Thickness to Crack-ing, 10 ⁻³ inches
			Anion	g./l.			
1	292	2.71	---	---	121	0	57
2	292	2.71	---	---	119	3	74
3	292	2.71	---	---	120	6	80
4	295	1.23	SiF ₆	1.56	120	0	65
5	295	1.23	SiF ₆	1.56	118	3	70
6	295	1.23	SiF ₆	1.56	119	6	107
7	295	1.23	AlF ₃	1.56	118	0	85
8	295	1.23	AlF ₃	1.56	119	3	102
9	295	1.23	AlF ₃	1.56	120	6	131
10	295	1.23	TiF ₄	1.56	118	0	97
11	295	1.23	TiF ₄	1.56	118	3	101
12	295	1.23	TiF ₄	1.56	122	6	115
13	295	1.23	ZrF ₄	1.56	120	3	98
14	295	1.23	ZrF ₄	1.56	119	6	106
15	250	2.5	---	---	119	0	39
16	250	2.5	---	---	119	1	45
17	250	2.5	---	---	119	8	60
18	250	3.0	---	---	119	0	31
19	250	3.0	---	---	119	2	38
20	250	3.0	---	---	119	8	49
21	301	0.95	SiF ₆	1.97	115	4.17	47
22	301	0.95	SiF ₆	1.97	115	8.34	59
23	299	0.95	AlF ₃	1.97	115	4.17	77
24	299	0.95	AlF ₃	1.97	115	8.34	93
25	388	1.9	SiF ₆	1.5	115	0	81
26	388	1.9	SiF ₆	1.9	115	10	166

The examples illustrate the advantages to be gained by the addition of lithium to the baths. In the examples, a comparison is made of the thickness to which chromium is electrodeposited before cracking occurs, with and without lithium addition, and/or a comparison showing the superior results obtained by a larger lithium addition over a smaller one. The presence in the bath of certain other materials such as chlorides are known to promote cracking. Such materials must be kept out of the bath or held to a minimum concentration.

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. In a process for electrodepositing crack-free chromium from an aqueous bath at a temperature of at least 115° F. and containing between 100 g./l. and 500 g./l. of CrO₃, at least one catalyst ion selected from the class consisting of sulfate, silicofluoride, fluoaluminate, fluotitanate, and fluozirconate, in an amount between 0.5 g./l. and 3.5 g./l., and having a ratio of CrO₃ to total catalyst ions of between about 85:1 to 150:1, the improvement which comprises adding to said bath sufficient lithium so that the bath contains at least 1 g./l. of lithium ion.

2. In a process for electrodepositing bright crack-free chromium from an aqueous bath at a temperature of at least 115° F. and containing between 100 g./l. and 500 g./l. of CrO₃, between 0.25 g./l. and 3.5 g./l. of sulfate ion, between 0.5 g./l. and 5 g./l. of a complex ion selected from the class consisting of silicofluoride, fluoaluminate, fluotitanate, and fluozirconate, the ratio of CrO₃ to the total of the sulfate and complex ions being between 85:1 and 150:1, the improvement which com-

prises adding to said bath sufficient lithium so that the bath contains at least 1 g./l. of lithium ion.

3. In a process for electrodepositing bright crack-free chromium from an aqueous bath at a temperature of at least 115° F. and containing between about 200 g./l. and 400 g./l. of CrO₃, between 1 g./l. and 2.5 g./l. of sulfate ion, between 1 g./l. and 2.5 g./l. of a complex ion selected from the class consisting of silicofluoride, fluoaluminate, fluotitanate, and fluozirconate, the ratio of CrO₃ to the total of the sulfate and complex ions being between about 85:1 and 130:1, the improvement which comprises adding to said bath sufficient lithium so that the bath contains at least 2 g./l. of lithium ion.

4. The process of claim 3 wherein the bath contains at least 4 g./l. of lithium ion.

5. In a process for electrodepositing bright crack-free chromium from an aqueous bath at a temperature of at least 115° F. and containing between 100 g./l. and 500 g./l. of CrO₃, between 0.25 g./l. and 3.5 g./l. of sulfate ion, and between 0.5 g./l. and 5 g./l. of silicofluoride ion, and having a ratio of CrO₃ to the total of the sulfate and silicofluoride ions between 85:1 to 150:1, the improvement which comprises adding to said bath sufficient lithium so that the bath contains at least 1 g./l. of lithium ion.

6. In a process for electrodepositing bright crack-free chromium from an aqueous bath at a temperature of at least 115° F. and containing between 200 g./l. and 400 g./l. of CrO₃, between 1 g./l. and 2.5 g./l. of sulfate ion, and between 1 g./l. and 2.5 g./l. of silicofluoride ion, and having a ratio of CrO₃ to the total of the sulfate and silicofluoride ions between about 85:1 to 130:1, the improvement which comprises adding to said bath sufficient lithium so that the bath contains at least 2 g./l. of lithium ion.

7. In a process for electrodepositing bright crack-free chromium from an aqueous bath at a temperature of at least 115° F. and containing between 100 g./l. and 500 g./l. of CrO₃, between 0.25 g./l. and 3.5 g./l. of sulfate ion, and between 0.5 g./l. and 5 g./l. of fluoaluminate ion, and having a ratio of CrO₃ to the total of the sulfate and fluoaluminate ions between 85:1 to 150:1, the improvement which comprises adding to said bath sufficient lithium so that the bath contains at least 1 g./l. of lithium ion.

8. In a process for electrodepositing bright crack-free chromium from an aqueous bath at a temperature of at least 115° F. and containing between 100 g./l. and 500 g./l. of CrO₃, between 0.25 g./l. and 3.5 g./l. of sulfate ion, and between 0.5 g./l. and 5 g./l. of fluotitanate ion, and having a ratio of CrO₃ to the total of the sulfate and fluotitanate ions between 85:1 to 150:1, the improvement which comprises adding to said bath sufficient lithium so that the bath contains at least 1 g./l. of lithium ion.

9. In a process for electrodepositing bright crack-free chromium from an aqueous bath at a temperature of at least 115° F. and containing between 100 g./l. and 500 g./l. of CrO₃, between 0.25 g./l. and 3.5 g./l. of sulfate ion, and between 0.5 g./l. and 5 g./l. of fluozirconate ion, and having a ratio of CrO₃ to the total of the sulfate and fluozirconate ions between 85:1 to 150:1, the improvement which comprises adding to said bath sufficient lithium so that the bath contains at least 1 g./l. of lithium ion.

10. In a process for electrodepositing bright crack-free chromium from an aqueous bath at a temperature of at least 115° F. and containing between 200 g./l. and 400 g./l. of CrO₃, between 1 g./l. and 2.5 g./l. of sulfate ion, and between 1 g./l. and 2.5 g./l. of fluoaluminate ion, and having a ratio of CrO₃ to the total of the sulfate and fluoaluminate ions between about 85:1 to 130:1, the improvement which comprises adding to said bath sufficient lithium so that the bath contains at least 2 g./l. of lithium ion.

11. A composition of matter for making up and main-

5

taining aqueous baths for use in an improved process for electrodepositing crack-free chromium, said composition of matter comprising between 70 and 95 parts of CrO_3 , between 0.5 and 1.5 parts of sulfate, between 0.5 and 5 parts of at least one complex fluoride selected from the class consisting of silicofluoride, fluoaluminate, fluotitanate, and fluozirconate; and between 0.2 and 5 parts of lithium.

12. A composition of matter as defined in claim 11, containing between 0.5 and 2 parts of lithium.

13. A composition of matter for making up and maintaining aqueous baths suitable for use in an improved process for electrodepositing bright crack-free chromium, said composition of matter comprising between 70 and

6

95 parts of CrO_3 , between 0.5 and 1.5 parts of sulfate, between 0.5 and 5 parts of silicofluoride, and between 0.2 and 5 parts of lithium.

14. A composition of matter as defined in claim 13 containing between 0.5 and 2 parts of lithium.

15. The process of claim 1 wherein the catalyst ion is sulfate.

References Cited in the file of this patent

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