United States Patent Office 3,723,261 Patented Mar. 27, 1973

3,723,261

BLACK CHROMIUM PLATING PROCESS AND COMPOSITION

Robert D. Byers, Syracuse, N.Y., and Winslow H. Hartford, Charlotte, N.C., assignors to Allied Chemical Corporation, New York, N.Y.

No Drawing. Filed Oct. 30, 1970, Ser. No. 85,701
Int. Cl. C23b 5/06, 5/48
U.S. Cl. 204—51 14 Claims

ABSTRACT OF THE DISCLOSURE

Black chromium plated articles are produced by the use of a novel electroplating bath, wherein a light and heat absorbing decorative and protective electroplate is applied to a basis metal or other conductive substrate. The bath comprises chromic acid, sodium or potassium ions, fluosilicate ions and an organic reducing agent.

This invention relates to a composition and method for the electrodeposition of black chromium coatings on a base metal to produce a smooth, adherent black surface having a low degree of reflectivity and a high degree of absorptivity for both heat and light. Furthermore, the composition of the plating bath of this invention is self-regulating with respect to the catalyst employed.

In general, black coatings fall into the following classifications:

(1) organic coatings;
(2) chemical treatments to product (a) oxide coatings and (b) precipitated films; and
(3) electrolytic treatments both anodic and cathodic.

The deposits obtained by the cathodic processes offer considerable opportunity for varying the characteristics and properties of the coating inasmuch as these properties are related to readily controllable factors such as time, temperature, current density and composition of the electrolyte. Furthermore, the most durable of all the electrodeposited black finishes are probably the chromium base plates since they have fairly good corrosion resistance and their mechanical properties are superior to those of many other black finishes.

Chromium coatings such as those produced by this invention may be used as coatings for food containers and the tin-free sheet stock (TFS) from which they are fabricated because the deposits are corrosion resistant and provide a surface receptive to the application of coatings such as paint, lacquer and the like. Black chromium electrodeposits find use as decorative black finishes, for example, on metal furniture, instrument cases, automobile and appliance parts, and plumbling supplies where their corrosion resistance coupled with their appearance makes them superior to other black finishes, such as paint. More specifically, these electrodeposited coatings find use in areas where their heat and light absorbing properties are important, as for example in the manufacture of non-reflective safety automotive trim, cameras and optical equipment, and in the production of non-reflective military hardware such as firearms, ordnance parts, communication equipment and military uniform fastenings.

In the past it has been the practice to produce black chromium electrodeposits by employing such plating baths as those containing chromic acid (CrO_3), acetic acid and fluoride-bearing ions. These are exemplified in U.S. Pat. 1,975,239 and British Pat. 408,097. However, it has been found that in using these baths it was necessary to operate them at temperatures as low as 50° F., and to employ high current densities, in the order of 900 to 2,000 amperes per square foot (a.s.f.). To successfully control and distribute such high current densities,

and at the same time maintain the relatively low bath temperatures required, was both costly and difficult.

Many of the methods disclosed in the prior art require the restriction or exclusion of the sulfate ion, which is replaced as a catalyst by either one or more of acetate, vanadate, nitrate, urea, fluosilicate, fluoride, fluoborate or the sulfamate ion. U.S. Pat. 2,824,829, for example, discloses a bath containing in addition to chromic acid, relatively small amounts of a soluble vanadium salt such as ammonium vanadate, and a carboxylic acid such as acetic acid. Here again a high current density is employed (400–2000 a.s.f.) and control is difficult and costly.

The plating bath disclosed in U.S. Pat. 2,623,847 requires the total absence of the sulfate ion in the plating bath. Since sulfate is present as a contaminant in essentially all commercial grades of chromic anhydride, it first must be precipitated and removed, generally as barium sulfate.

The application of the common ion effect to render a chromium plating bath self-regulating with respect to the contained catalyst is not new and has generally been employed to regulate the concentration of the sulfate ion or the fluosilicate ion, since these ions are frequently used as the catalyst. Usually a mixed catalyst has been used employing the potassium ion (K^+) as the regulator for the fluosilicate ion ($SiF_6^=$) and the strontium ion (Sr^{++}) as the regulator for the sulfate ion ($SO_4^=$). In connection with the development of the self-regulation concept with respect to the catalysts employed in chromium plating baths, we refer to U.S. Pats. 2,042,611; 2,640,021; 2,640,022; 2,950,234; 2,952,590 and 3,303,114. Although these self-regulating chromium plating electrolytes are designed to maintain the catalyst at a level such as to provide a bath capable of producing a uniform plate (usually a bright plate), none of these are designed to hold a chromium plating bath within the limits necessary to provide an adherent black chromium plate.

One of the most satisfactory black chromium plating baths of the prior art, and one which may be employed to produce black chromium deposits having excellent characteristics, is the so-called "Graham-Pinkerton" bath. (Graham, A. K., Proc. Am. Electroplaters' Soc., 46, 61 (1959); U.S. Pat. 2,985,567, H. L. Pinkerton, 5-23-61.) This bath may be characterized as follows:

CHARACTERIZATION—"GRAHAM-PINKERTON" BATH

[Composition and operating conditions]

	Range	Preferred
CrO_3 (g./l.)	Over 60	200–300.
A fluorine bearing ion such as $SiF_6^=$.	1:125 to 1:4000 of the CrO_3 content.	0.25 H_2SiF_6 g./l.
Current density, (a.s.f.)	70–450	300.
Temperature, ° F.	70–100	80–95.

Although this bath is more easily controlled than many other formulations, it is still extremely sensitive to sulfate contamination, catalyst ratio and temperature. No more than 0.01 g./l. of sulfate ion can be tolerated in this bath.

It is an object of the present invention to provide an improved electroplating bath composition for the deposition of black chromium-containing electrodeposits.

It is a further object of the present invention to provide an electroplating bath and process for electroplating an adherent black chromium-containing coating, in which process the concentration of the fluosilicate catalyst is automatically controlled.

It is another object of the present invention to provide a process for electrodepositing an adherent, black chromium coating wherein minor amounts of impurities, such as sulfate ions in amounts up to about .02% based on the

CrO_3 content, can be tolerated in the electrolyte without adversely affecting the coating.

It is still a further object of this invention to provide corrosion resistant plated articles having a black, adherent chromium and chromium oxide electroplate to which other coatings may subsequently be applied.

These and other objects are accomplished according to our invention wherein an adherent black chromium coating is electrodeposited on a basis metal from a bath having the following composition:

BLACK CHROMIUM PLATING BATH

[Composition and operating conditions]

	Range	Preferred
CrO_3 (g./l.)	300–500	350–450
Na^+ (g./l.)	6–52	10–35
Ratio CrO_3 to Na^+	10:1–50:1	13:1–35:1
or		
K^+ (g./l.)	10–90	17–60
Ratio CrO_3 to K^+	5.5:1–30:1	7.5:1–20:1
SO_4 (g./l.)	<0–0.10	<0–0.08
SiF_6 (g./l.)	0.2–3.0	0.4–1.0
An organic reducing agent such as sucrose (g./l.)	1.0–3.0	1.5–2.5
Temperature (° F.)	60–100	70–90
Current density (a.s.f.)	40–500	100–400

In general, high Na or K ion concentration should correlate with high CrO_3 concentration, as indicated by the above ratios. The Na or K cations can be added as their hydroxides or combined with other compatible anions. For example, they can be introduced in part by employing sodium or potassium chromates or bichromates rather than chromic anhydride, and/or sodium or potassium fluosilicate rather than fluosilicic acid.

As indicated above, the weight ratio of the CrO_3 to the Na ions falls between 10:1 to 50:1 for the general range, and between 13:1 and 35:1 for the preferred range. Correspondingly, the ratio of CrO_3 to the K ions falls between 5.5:1 and 30:1 for the general range while the preferred range lies between 7.5:1 and 20:1.

It was unexpectedly found that the above bath will produce a smooth, black adherent chromium deposit and has a considerably greater tolerance for sulfate than do typical electrolytes for deposition of the black chromium plate of the prior art. Also, it was unexpectedly found that no appreciable brightening of the electroplate followed the addition of fluosilicic acid in excess of 1.0 g./l. as would normally be expected with an excess of catalyst ion. The fact that a satisfactory black chromium coat can surprisingly be obtained, even in the presence of an excess of fluosilicic acid, is believed attributable to the fact that the bath of the present invention is self-regulating with respect to the catalyst ion. This self-regulation is brought about by the presence in the bath of a high concentration of either sodium ions or potassium ions, which by common ion effect limits the solubility of the sodium or potassium fluosilicate in the bath. The effect is more striking with the potassium ion than with the sodium ion, for K_2SiF_6 is even less soluble than Na_2SiF_6.

The electroplating baths provided by the present invention may be characterized as containing chromic acid (CrO_3) which need not be treated for the removal of traces of sulfate ion unless they exceed 0.02% and a sodium or potassium ion concentration as follows: The sodium ion concentration should be at least 6 g./l., with a range to about 52 g./l., (preferably between 10 and 35 g./l.), or the potassium ion concentration should be at least 10 g./l. with a range to about 90 g./l., (preferably between 17 and 60 g./l.). A Na^+/CrO_3 ratio of at least about 1:50 or a K^+/CrO_3 ratio of at least about 1:30 is necessary to maintain the fluosilicate ion within the range required for a black chromium deposit.

Although the sodium and potassium ions are given as probably the two most practical, any alkali metal ion not contraindicated by the composition of the bath or detrimental to the electroplate, the fluosilicate of which is sparingly soluble in the bath, may be employed as a catalyst regulator.

Although the sodium and potassium ions are preferably added in the form of their hydroxides, many other soluble sodium or potassium salts, not detrimental to the electrolyte or the chromium plate, may be used to supply at least part of the required sodium or potassium ion; for example, the chromate, dichromate, carbonate, bicarbonate or fluosilicate of sodium or potassium.

Furthermore, although the fluosilicate ion is preferred as the fluorine-bearing catalyst, there are several others that may be similarly employed, such as the fluoaluminate, fluotitanate, fluozirconate, fluoride and fluoborate anions. To be suitable in chromium plating baths as a "regulated catalyst," the first requirement is that the chosen anion and its regulating cation be in no way detrimental to the plating bath or the resulting plate; the second, that the salt of the catalytic anion and the regulating cation be sparingly soluble in the plating bath so that control by common ion effect is possible.

The upper limit of the catalyst regulator of the present invention is not critical, although 52 g./l. of Na^+ or 90 g./l. of K^+ may be considered an upper practical limit for depositing acceptable black chromium deposits. If a reduction in the $SiF_6^=$ concentration is indicated by too gray or too bright a plate, the concentration of the Na or K ions should be increased.

The sucrose is preferably included in the composition as an example of an organic reducing agent which, through its action, insures the presence of a small amount of trivalent chromium in the plating bath. Trivalent chromium ions are present during normal plating operations, and the presence of sucrose makes it possible for the plating process to begin somewhat faster than would be possible without it. It serves to initiate the plating process, for without it, the trivalent chromium would have to be formed from the chromic acid by electrolysis, before electrodeposition of the chromium could begin. Other organic reducing agents could be used such as maltose, methanol, glycollic acid, glucose, and levulose, but sucrose is readily available and preferred.

In carrying out the process of our invention, preferably 350–450 g./l. of chromic acid (CrO_3) containing no more than about 0.02% SO_4 is dissolved to produce each liter of the plating bath. In the event that more than .02% SO_4 is present in the CrO_3 or more than 0.10% g./l. of SO_4 in the bath, it should be removed by precipitation with Ba^{++}, as a satisfactory black plate cannot be obtained in the presence of appreciably more than .02% SO_4. The bath also contains preferably 10 to 35 g./l. of Na ion, 0.4–1.0 g./l. of fluosilicate ion as catalyst, and 1.5 to 2.5 g./l. of sucrose.

In practice, a basis metal which has been thoroughly cleaned so as to be free of traces of grease, is used as the cathode. The current density employed may vary between 40 and 500 a.s.f., preferably between 100 and 400 a.s.f., and the plating temperature may vary between 60° and 100° F., preferably between 70 and 90° F. The above plating bath of the present invention will provide a smooth, non-reflective, adherent, black chromium electroplate, the surface of which may provide a base for subsequent coatings, such as electroplates, paints, lacquers or the like. As noted above, an adherent, non-reflective, black chromium plate is obtained with this plating bath, even when the quantity of fluosilicate in the bath is in excess of 2.5 g./l. and/or the sulfate concentration present in the bath is up to 0.10 g./l. of 0.02% by weight, based on the weight of the chromic anhydride (CrO_3) employed. Under either of theese circumstances, a grey or bright plate would normally be obtained.

It is believed that the high sodium or potassium ion concentration in the plating solution holds the concentration of the fluosilicate ions in the plating solution to within permissible limits (about 0.2–1.2 g./l., preferably 0.4–1.0 g./l.). The excess SiF_6 ions are precipitated as Na_2SiF_6 or K_2SiF_6, and the SiF_6 catalyst concentration is held below about 1.0 g./l., above which a bright plate

may form. This self-regulating action exemplified by good results regardless of whether or not an excess of the fluosilicic acid catalyst has been added, is brought about by the high concentration of the sodium or potassium ions and the relatively low solubility of Na_2SiF_6 or K_2SiF_6. By common-ion effect, the SiF_6 concentration is automatically held to a value between about 0.4 and 1.0 g./l, which is suitable for black chromium plating. If potassium is used, the potassium ion provides a plating bath with somewhat less working catalyst than does the sodium ion, since K_2SiF_6 is even more sparingly soluble than Na_2SiF_6. The chromium plating bath of the present invention is much less sensitive to sulfate contamination than many other baths of the prior art. Commercial chromic acid (CrO_3), generally contains sulfate (as SO_4= by deep black color, excellent adhesion and good corrosion resistance.

EXAMPLES 1–7

Table I below tabulates seven runs made on Hull cell test panels. The Hull cell provides a test panel in which the current density varies smoothly over a wide range, by virtue of the placement of the cathode at a fixed angle with respect to the anode. The standard Hull cell contains 267 ml. of plating bath solution so that a 2 gram addition corresponds to 1 oz./gal. (7.5 g./l.). The Hull cell and its operation are described in "Modern Electroplating" edited by F.A. Loweheim, 2d edition, 1963, pp. 525–528, which disclosure is specifically incorporated by reference.

TABLE I.—RESULTS OF HULL CELL TESTS ON SELF-REGULATING BLACK CHROME BATH

[All on Brass Hull Cell Panels]

Test number	1	2	3	4	5	6[1]	7[2]
CrO_3, g./l.	400	400	400	400	400	400	400
Percent SO_4 in CrO_3	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Ba $(OH)_2$ added to remove SO_4							
Na^+, g./l. (added as NaOH)	34.5	34.5	34.5	34.5	34.5	34.5	34.5
$SiF_6^=$, g./l. (added as H_2SiF_6)	1.0	1.5	2.0	2.5	2.5	2.5	2.5
Sucrose, g./l.	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Temperature, ° F.	68	68	68	68	77	86	95
Total amperage, amps	10	10	10	10	10	10	10
Time, mins.	5	5	5	5	5	5	5
Black-plate range, amps/ft.^{2}	45–420	45–420	45–420	45–420	45–420	45–420	45–420

[1] Some lightening of black. [2] Lightening of black.

in amounts up to about 0.05% by weight, although much is produced with no more than 0.02%. CrO_3 with 0.02% SO_4 or less may be used in the bath of the present invention without any prior purification step, whereas in baths of the prior art, e.g. U.S. Pat. 2,985,567, not more than 0.01% SO_4 contamination based on the CrO_3 can be tolerated. It is thought that the tolerance of our bath to traces of SO_4 and small amounts of other impurities that may be present, can be attributed to the presence of an excess of sodium ions in the bath of our invention.

The black chromium electrodeposit may be applied to any electrically conductive substrate, particularly copper, iron, zinc, nickel, lead, or to alloys of any of these. Unlike the process of U.S. Pat. 2,985,567 and others, a satisfactory black adherent chromium coatinng can be deposited on any of these, whereas in the method disclosed by the aforementioned patent, a strike coat of nickel must be deposited on the article to be chrome plated before the chrome plate is applied, except where the basis metal is nickel. If, however, such a strike or flash coat is used in connection with the process of the present invention, an improved black-plating range will be obtained. Such strike coats may be deposited from any Watts-type or other commercial nickel plating bath.

Black plates are commonly applied within 1–5 minutes at 100–400 a.s.f. The plate so formed is probably about 0.02–0.06 mil in thickness. Thicker plates are undesirable.

Insoluble anodes, preferably of lead or lead alloys of the type used for conventional chromium plating, may be employed. Plain iron or steel tanks offer reasonable service life, for there is essentially no corrosion problem at low temperatures and low SiF_6= concentrations.

The process of the present invention has all the advantages of the aforementioned "Graham-Pinkerton" bath and improves upon it, in that the sulfate present in much of the available commercial chromic anhydride can be tolerated. Also, unlike the Graham-Pinkerton bath, the present bath is self-regulating with respect to the catalytic SiF_6=, and produces a black chromium plate characterized

In the tests here reported, the anode is lead, and the plating bath contains less than 0.08 g./l. of sulfate ion, and up to 2.5 g./l. of fluosilicate ion. The Hull cell cathodes are of brass.

In each case, the baths produce a uniform, hard, smooth, adherent wear-resistant, black chromium electroplate. In Examples 1–4, the temperature of the bath is held at 68° F., whereas in Examples 5, 6 and 7, the temperatures are 77°, 86° and 95° F., respectively. In the last two examples there is a noticeable lightening of the black coat produced, the effect being more pronounced at the higher temperature.

EXAMPLES 8–19

As with Examples 1 through 7, Examples 8 through 19 are run in a Hull cell. Reference is made to Table II, below. In Examples 8, 9, 10 and 11 the sodium ion content is 5.75, 11.5, 17.25 and 34.5 g./l., respectively. It will be noted that the minimum cathode current density required for black plate decreases as the amount of Na^+ increases. A satisfactory black plate is not obtained in any of these four runs at a low current density, however, as the SO_4 content of the CrO_3 used is in excess of 0.03%, based on the CrO_3.

An identical set is run, consisting of Examples 12, 13, 14 and 15, except in each case the SO_4 ion is removed by treatment with 3 g./l. of $BaCO_3$. The bath is stirred overnight before use and separated from the insoluble barium salts. A satisfactory, adherent, wear-resistant, black chromium electroplate is obtained in each instance over a wide range of current densities.

Examples 16, 17 and 18 correspond with Examples 9, 10 and 11, except that K^+ in the amount of 9.75, 19.15 and 29.2 g./l., respectively, is used. These quantities are the equivalent of 14, 28 and 42 g./l. of KOH. As in the case of Examples 9, 10 and 11, the SO_4 content based on CrO_3 is greater than 0.03% and a black plate is not obtained. A black plate could only be obtained under these conditions by employing a high current density.

TABLE II.—RESULTS OF HULL CELL TESTS ON SELF-REGULATING BLACK CHROME BATH

[All on Brass Hull Cell Panels Except as Noted]

Example number	8	9	10	11	12	13	14	15[1]	16	17	18	19
CrO_3, g./l.	400	400	400	400	400	400	400	400	400	400	400	400
Percent SO_4 in CrO_3	>0.03	>0.03	>0.03	>0.03	>0.03	>0.03	>0.03	>0.03	>0.03	>0.03	>0.03	>0.03
Ba $(OH)_2$ added to remove SO_4					Yes	Yes	Yes	Yes				Yes
Na^+, g./l. (added as NaOH)	5.75	11.5	17.25	34.5	5.75	11.5	17.25	34.5				
$SiF_6^=$, g./l. (added as H_2SiF_6)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
K^+, g./l. (added as KOH)									9.75	19.5	29.25	29.25
Sucrose, g./l.	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Temperature, ° F.	77	77	77	77	77	77	77	77	77	77	77	77
Total amperage, amps	10	10	10	10	10	10	10	10	10	10	10	10
Time, mins.	5	5	5	5	5	5	5	5	5	5	5	5
Black-plate range, amps/ft.[2]	>400	>360	>320	>250	150–400	120–450	100–400	180–420	>380	>300	>270	>300
$SiF_6^=$, g.p.l. (analysis)	1.00	0.97	0.73	0.56	0.81	0.61	0.66		0.94	0.47	0.44	

[1] This bath on Ni.

Example 19 corresponds to Example 14, except that 29.2 g./l. of K^+ are used, and once again, a smooth adherent black chromium plate is obtained, although no better black plating range was observed than in Example 14.

In the case of Examples 8–14 and 16–19, the $SiF_6^=$ present in the bath was determined in grams/liter by analysis.

In each instance where a satisfactory, uniform, hard, smooth, adherent, wear-resistant, black chromium electroplate is obtained, a relatively low cathode current density is used; hence, the process can be carried out in conventional plating equipment. The chromic acid input can be controlled by its density using a hydrometer. As previously noted, the catalyst anion concentration is automatically controlled, but if desired, can also be determined and controlled through chemical analysis. The continued operation of the bath can be checked as to black plating range by a Hull cell.

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.

We claim:

1. A composition of matter comprising an aqueous electrolyte consisting essentially of 300 to 500 grams per liter of CrO_3 containing up to 0.02% by weight of SO_4 ion based on the CrO_3 content, 0.2 to 3.0 grams per liter of SiF_6 ion, 1.0 to 3.0 grams per liter of a water soluble organic reducing agent, selected from the group consisting of maltose, methanol, glycollic acid, glucose, levulose and sucrose, and at least one member selected from the group consisting of sodium and potassium ions, wherein said sodium ion is present in the bath in a concentra tion from 6 to 52 grams per liter and in a weight ratio with respect to the CrO_3 of from 1:10 to 1:50, and said potassium ion is present in the bath in a concentration from 10 to 90 grams per liter and in a weight ratio with respect to the CrO_3 of from 1:5.5 to 1:30.

2. The composition of claim **1** wherein the SiF_6 ion in the electrolyte is held between 0.2 and 1.2 g./l.

3. The composition of claim **1** wherein the SiF_6 ion in the electrolyte is held between 0.4 and 1.0 g./l., and the SO_4 content does not exceed 0.08 g./l.

4. The composition of claim **1** wherein the electrolyte contains 350 to 450 grams per liter of CrO_3, and said sodium ion is present in the bath in a concentration from 10 to 35 grams per liter and in a weight ratio with respect to the CrO_3 of between 1:13 and 1:35.

5. The composition of claim **1** wherein the electrolyte contains 350 to 450 grams per liter of CrO_3, and said potassium ion is present in the bath in a concentration from 17 to 60 grams per liter and in a weight ratio with respect to the CrO_3 of between 1:7.5 and 1:20.

6. The composition of claim **1** wherein the organic reducing agent is sucrose.

7. A method of electrodepositing an adherent black chromium coating on an electrically conductive substrate, which process comprises the steps of making said substrate to be plated the cathode in an aqueous electrolyte consisting essentially of 300 to 500 grams per liter of CrO_3 containing up to 0.02% by weight of SO_4 ion based on the CrO_3 content, 0.2 to 3.0 grams per liter of SiF_6 ion, 1.0 to 3.0 grams per liter of a water soluble organic reducing agent, selected from the group consisting of maltose, methanol, glycollic acid, glucose, levulose and sucrose, and at least one member selected from the group consisting of sodium and potassium ions, wherein said sodium ion is present in the bath in a concentration from 6 to 52 grams per liter and in a weight ratio with respect to the CrO_3 of from 1:10 to 1:50, and said potassium ion is present in the bath in a concentration from 10 to 90 grams per liter and in a weight ratio with respect to the CrO_3 of from 1:5.5 to 1:30, passing a direct current between the anode and cathode to provide a cathode current density of from 40 to 500 a.s.f. while maintaining the temperature of said electrolyte between 60 and 100° F.

8. The method of claim **7** wherein the sodium and potassium cations are added in combination with any water soluble anion compatible with the electrolyte and said method.

9. The method of claim **7** wherein the sodium and potassium cations are added as their hydroxides.

10. The method of claim **7** wherein the sodium and potassium cations are added wholly or in part as their fluosilicates.

11. The method of claim **7** wherein the sodium and potassium cations are added wholly or in part as their chromates.

12. The method of claim **7** in which the direct current provides a cathode current density of 100 to 400 a.s.f.

13. The method of claim **7** in which the plating temperature is maintained between 70 and 90° F.

14. The method of claim **7** in which the aqueous electrolyte contains 350 to 450 grams per liter of CrO_3, 0.4 to 2.5 grams per liter of SiF_6, ion, 1.5 to 2.5 grams per liter of sucrose and at least one member selected from the group consisting of sodium and potassium ions wherein said sodium ion is present in the bath in a concentration from 10 to 35 grams per liter and in a weight ratio with respect to the CrO_3 of from 1:13 to 1:35, and said potassium ion is present in the bath in a concentration from 17 to 60 grams per liter and in a weight ratio with respect to the CrO_3 of from 1:7.5 to 1:20.

References Cited

UNITED STATES PATENTS

3,157,585	11/1964	Durham	204—41
3,475,294	10/1969	Seyb et al.	204—51
3,511,759	5/1970	Nelson	204—51

FREDERICK C. EDMUNDSON, Primary Examiner