Sept. 13, 1960 J. E. STARECK ET AL 2,952,590

PROCESS FOR CHROMIUM PLATING

Filed Aug. 14, 1959

2 Sheets-Sheet 1

FIG. 1.

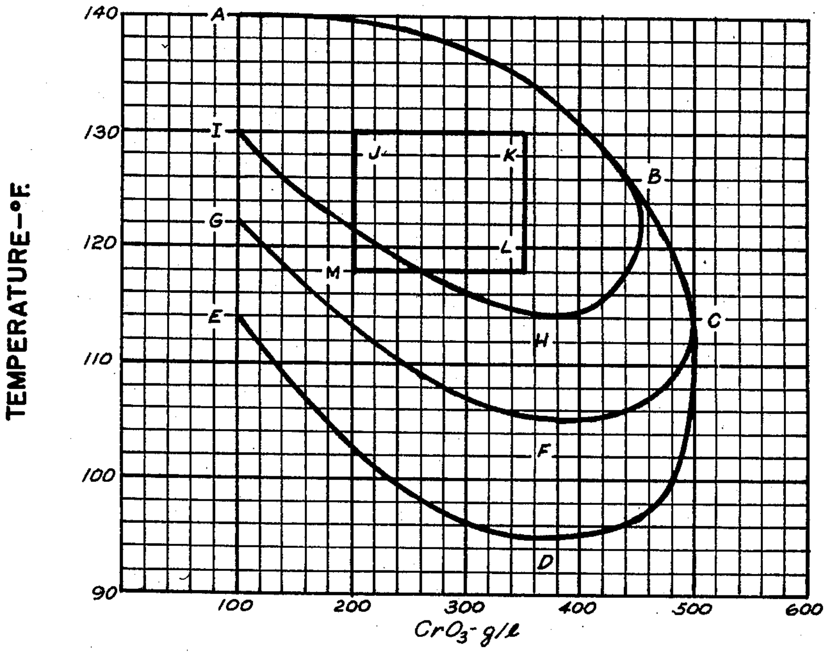
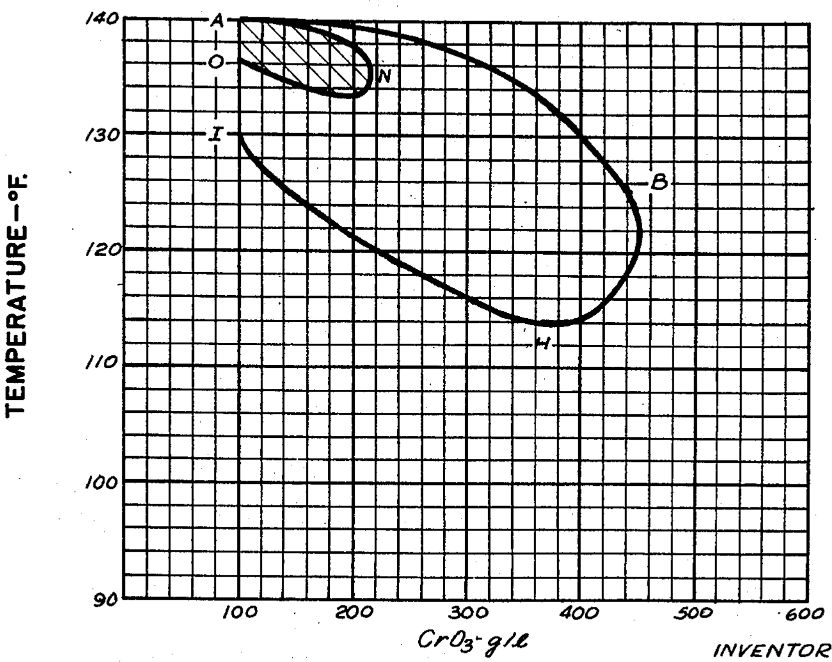


FIG. 2.



INVENTORS
JESSE E. STARECK
EDGAR J. SEYB, JR.
ANDY ALBERT JOHNSON
WILLIAM H. ROWAN
BY N.H. Goodman
ATTORNEY

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2 Sheets-Sheet 2

FIG. 3.

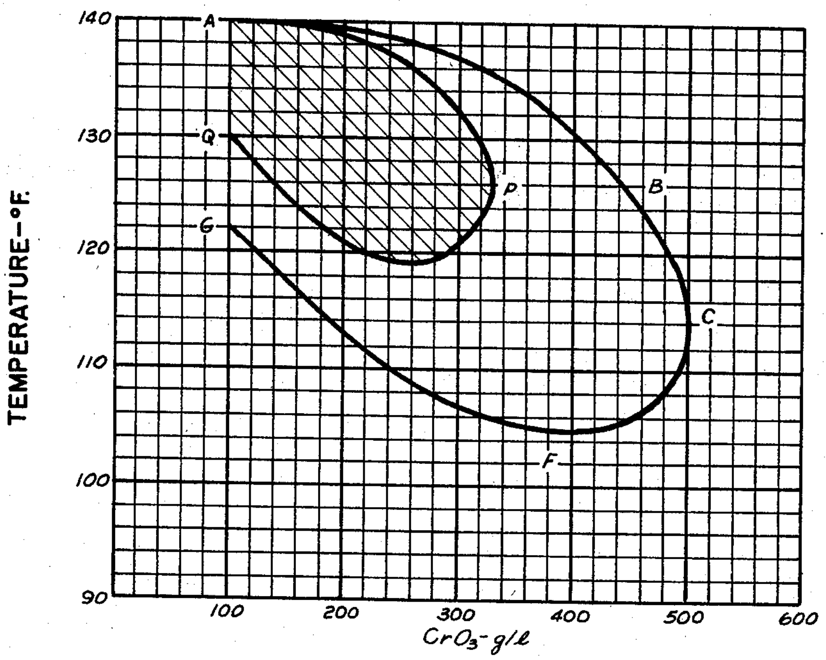
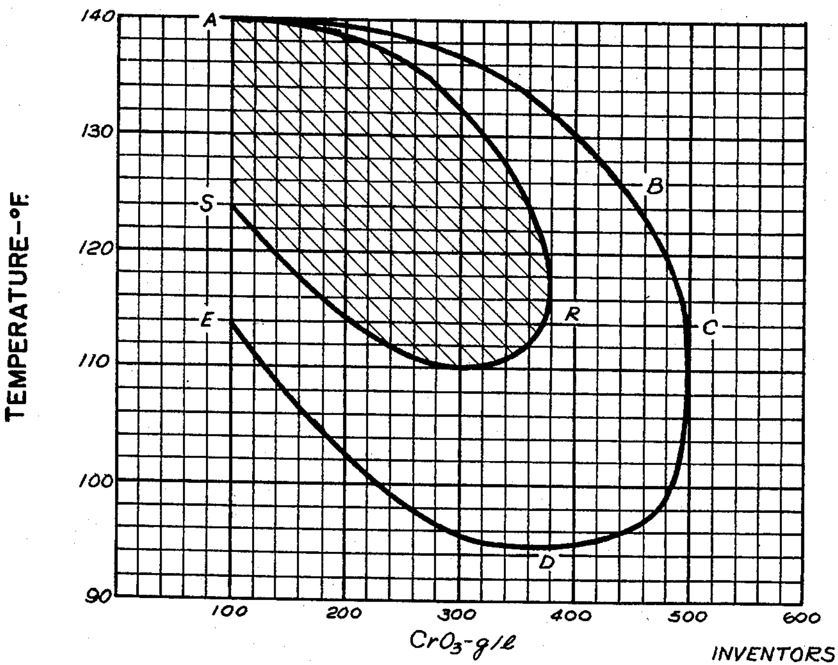


FIG. 4.



INVENTORS
JESSE E. STARECK
EDGAR J. SEYB, JR.
ANDY ALBERT JOHNSON
WILLIAM H. ROWAN
BY H.H. Goodman
ATTORNEY

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2,952,590
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2,952,590

PROCESS FOR CHROMIUM PLATING

Jesse E. Stareck, Westfield, N.J., Edgar J. Seyb, Jr., and Andy Albert Johnson, Oak Park, Mich., and William H. Rowan, San Diego, Calif., assignors to Metal & Thermit Corporation, Woodbridge, N.J., a corporation of New Jersey

Filed Aug. 14, 1959, Ser. No. 833,765

10 Claims. (Cl. 204—51)

The present invention relates to a novel process for electrodepositing chromium, and more particularly, to a process for electrodepositing bright crack-free chromium plate. This application is a continuation-in-part application of our patent application Serial No. 695,146, filed November 7, 1957, now Patent No. 2,916,424.

Chromium is widely used as a decorative and protective surface finish. Decorative chromium plate is usually of too small a thickness, in the order of 0.00001 inch, to be of substantial value for protecting the basis metal. When deposited in greater thicknesses, the plate contains a network of hair-like cracks extending through the chromium to the basis metal, destroying the plate's protective value. To coat metals with a corrosion resistant, decorative electrodeposit, copper and/or nickel are deposited on the basis metal to provide effective corrosion resistance, followed by deposition of the usual thin decorative chromium finish. "Thick" deposits of chromium are deposited directly on the basis metal or over a copper and/or nickel undercoat to provide fairly effective protection against corrosion and wear. These "thick" deposits are usually in the order of at least 0.002 inch. When chromium is electrodeposited to a thickness of between 0.00001 inch and 0.00002 inch (usually closer to 0.00002 inch), the deposit cracks, resulting in a crack pattern with many fine cracks extending through the entire thickness of the deposit. Chromium subsequently electrodeposited over the original cracked deposit "blankets" the cracks and, in effect, heals them. This occurs as the overall thickness is increased up to the order of 0.002 inch or more, which thickness is necessary to provide fairly effective protection against corrosion in the absence of a heavy undercoat serving this purpose. These thick deposits of chromium are not used for decorative applications. Recently a process has become available for electrodepositing dull crack-free chromium in thicknesses greater than 0.00002 inch (see U.S. Patent No. 2,686,756, No. 2,787,588, and No. 2,787,589).

Chromium deposits in the order of 0.00005 inch, 0.0001 inch and greater, which are bright and crack-free, as plated, are desirable for providing decorative chromium plates having good corrosion resistance. It has been found that for a given thickness of deposit, e.g., 0.00005 inch, 0.0001 inch and greater, the corrosion resistance of crack-free deposits is far superior to the corrosion resistance of deposits having a crack pattern, even including those deposits of sufficient thickness that the cracks are "healed." The art has not known how to obtain thick, bright crack-free chromium deposits and it appeared that it would be impossible to obtain them, except as disclosed in our aforesaid patent application No. 695,146. The known conditions for obtaining bright decorative deposits are, on the whole, the opposite of the conditions necessary to obtain crack-free deposits.

The term "bright" in describing bright crack-free chromium electrodeposits, as used herein, is limited to surfaces which have sufficient reflectivity to render a well defined and recognizable image. The bright range of deposits is divided into two subdivisions—deposits referred to as "mirror-bright" and deposits referred to as "bright." The mirror-bright deposits are those which have the reflectivity ordinarily associated with a good mirror. The bright deposits have a lesser degree of reflectivity than a good mirror, but sufficient reflectivity to render a well defined and recognizable image. These bright deposits are sufficiently bright as plated to be acceptable decorative finishes. Their degree of brightness may be improved by a buffing operation to achieve mirror brightness. The term "bright crack-free chromium" encompasses those deposits which are mirror-bright and bright, as defined herein.

It is an object of the present invention to provide a process for electroplating bright crack-free chromium deposits to a thickness of at least 0.00005 inch.

It is another object of the invention to provide a process for electrodepositing bright chromium having improved corrosion resistance.

It is still another object of the invention to provide a process for plating crack-free chromium surfaces of mirror-brightness to a thickness of at least 0.00005 inch.

Other objects and advantages will become apparent from the following description and drawings.

We have discovered that by controlling the several variables of the chromium plating process within relatively narrow, well-defined limits, bright crack-free deposits of chromium can be obtained in a thickness of at least 0.00005 inch using a plating bath of chromic acid and a catalyst mixture of a sulfate ion and at least one complex ion selected from the class consisting of fluoaluminate, fluozirconate, and fluotitanate. Catalyst ions in relatively high concentrations promote cracking. Nonetheless, relatively large concentrations of catalyst ions are required to obtain bright electrodeposits. The amount of catalyst ion that may be present in an operative bath is related to the CrO_3 concentration. It is specified as the ratio of the weight of CrO_3 to the total weight of all the catalyst ions (herein referred to as Ratio). We have discovered that the range of Ratios within which it is possible to obtain bright crack-free chromium plating is between 70:1 to 150:1, dependent upon the CrO_3 concentration and the temperature. In conjunction with the close control of catalyst concentration, we have found that the temperature must be maintained above 95° F. and below 140° F. With temperatures above about 114° F. and below 140° F., it is possible to obtain bright crack-free chromium electrodeposits utilizing any Ratio between 70:1 and 150:1. As the temperature is lowered, the tendency to crack increases markedly. To compensate for this increased tendency to crack at lower plating temperatures, baths having lower catalyst concentrations must be employed. Baths with very low catalyst concentrations, as noted by Ratios as high as 150:1, may be utilized at temperatures as low as 95° F. As the temperature is raised, the tendency to electrodeposit bright chromium decreases. Dull deposits are obtained at high temperatures. The upper temperature limit for obtaining bright chromium operative over most of the range of CrO_3 concentrations is 140° F. The temperature and Ratios at which bright crack-free chromium may be obtained are also related to the CrO_3 concentration of the bath. Baths containing from about 100 g./l. to about 500 g./l. are utilized. The tendency for the electrodeposition of chromium in a less bright condition increases as the CrO_3 concentration is increased. It is difficult to obtain mirror-bright deposits with baths having CrO_3 concentrations in the high portion of the range. Such baths may be utilized at lower temperatures. Baths with CrO_3 concentrations in the lower portion of the range yield mirror-bright deposits. The larger portion of the CrO_3 concentration range may be utilized at all temperatures above 114° F. and below 140° F. The overall relationship of temperature, CrO_3 concentration, and Ratio is defined by the area enclosed by the curves in Figure 1. The catalyst is a mixture of sulfate ions and complex fluoride ions. Of the total catalyst present, a minimum of 5% is sulfate and preferably at least 15% should be sulfate; the optimum baths contain at least 20% sulfate. The sulfate should not be more than 85% of the total catalyst and preferably not more than 70%; the optimum baths contain less than 55% sulfate.

As shown in Figure 1, bright crack-free chromium can be electrodeposited at temperatures between 95° F. and 114° F., by utilizing a high Ratio. At 105° F., a Ratio of about 100:1 is the limiting Ratio, whereas the limiting Ratio at 95° F. is 150:1. For baths utilizing Ratios between those illustrated in the graphs, the limiting Ratios and temperatures may be found by interpolation from the plotted data. For greater clarity the overall curves of Figure 1 are illustrated separately in Figures 2, 3 and 4. The conditions under which bright crack-free chromium can be electroplated at a Ratio of 70:1 are delineated in Figure 2; at 100:1 in Figure 3; and at 150:1 in Figure 4.

Many combinations of the three variables result in electrodeposits of bright crack-free chromium appreciably thicker than 0.00005 inch. These thicknesses may often be in the order of 0.0001 inch to 0.0002 inch, and in some cases as thick as .001 inch or more. As a general rule, for a given set of conditions, as the deposits get thicker, there is an increased tendency to crack and/or to obtain deposits of decreasing brightness. The shaded area located approximately in the upper central portion of each of the curves in Figures 2–4 define the limited conditions under which it is possible to electrodeposit bright crack-free chromium to a thickness of at least 0.0001 inch. As illustrated, at lower Ratios the area shifts to higher temperatures and decreases in size.

Electrodeposition of bright crack-free chromium between the temperatures of 105° F. and 135° F. is preferred. Within this range of temperatures, it is preferred to utilize CrO_3 concentrations between about 150 g./l. and about 450 g./l. and a Ratio between about 80:1 to 130:1. The relationship between these three variables must also fall within the areas defined by the curves in Figure 1.

Especially preferred conditions for electrodepositing bright crack-free chromium are those obtained within the rectangular area JKLM, at Ratios between about 85:1 and 120:1 utilizing baths having a CrO_3 concentration between about 200 g./l. and 350 g./l. and plating at temperatures between about 118° F. and 130° F.

Although it is possible by accurate analytical control, or by the use of self-regulating bath compositions, to control the Ratio within close limits during the plating process, it is recognized that many installations may not be able to maintain the desired close control for lesser or longer periods of time. When the temperature and CrO_3 concentration are maintained within the area defined by the closed curve ABHI in Figure 1, it is possible to deposit bright crack-free chromium at all Ratios between 70:1 and 150:1.

Chloride ion in the bath promotes the formation of cracks. Baths containing more than about 0.05 g./l. of chloride ion cannot be used to electrodeposit bright crack-free chromium to a thickness of 0.00005 inch. Less than this amount may be tolerated when electrodeposition is carried out, for a given temperature and CrO_3 concentration, at a Ratio selected from the high end of those allowable under the conditions specified. If it is desired to operate at a low Ratio (high catalyst ion content) selected from the allowable range, it is necessary to compensate for the presence of chloride by subtracting from the allowable catalyst ion content about fourteen times the amount of chloride ion present. When less than 0.005 g./l. of chloride is present, it may be ignored. It is preferable to operate with baths containing not more than 0.02 g./l. of chloride ion.

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 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. Where alkali metal cations are present the bath should not be neutralized in excess of 80% to the dichromate end point.

Sulfite ions may be added in the form of sulfuric acid, or as sulfate salt(s) with a cation that does not adversely affect bath characteristics, such as potassium, sodium, calcium, strontium, magnesium, chromium, etc. 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.

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.

Bright crack-free electrodeposits are obtained under the conditions of this invention using suitable current densities. The current densities vary between 0.5 a.s.i. (amperes per square inch) and 6 a.s.i., depending primarily on the plating temperature. These current densities are conventional and are described in "Chromium Plating" by Morrisset et al., published by Robert Draper Ltd., 1954, pages 351–363 and particularly page 354.

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

A standard Hull Cell was used to determine the thickness to which bright chromium plate can be electrodeposited without cracking. The cell is a box 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 and/or where the plate is no longer bright. Bright crack-free chromium was electrodeposited from all the baths listed below (defined by their CrO_3, sulfate ion and complex fluoride ion concentrations) at the specified conditions to the thickness, in all cases, of at least 0.00005 inch.

Example No.	CrO_3, g./l.	SO_4, g./l.	Second Catalyst	Second Catalyst, g./l.	Total Catalyst	Temp., ° F.
1	150	0.33	AlF_6	0.81	1.14	133
2	195	0.41	AlF_6	2.27	2.68	120
3	250	0.80	AlF_6	2.05	2.85	120
4	290	0.86	AlF_6	2.31	3.17	120
5	300	1.05	AlF_6	1.50	2.55	110
6	335	0.82	AlF_6	2.24	3.06	120
7	342	0.92	AlF_6	1.42	2.34	120
8	450	0.98	AlF_6	2.36	3.34	105
9	150	0.33	TiF_6	0.85	1.18	128
10	300	0.68	TiF_6	1.77	2.45	99
11	300	1.05	TiF_6	1.50	2.55	120
12	300	1.05	TiF_6	1.50	2.55	130
13	450	1.03	TiF_6	2.70	3.73	106
14	150	0.37	ZrF_6	0.94	1.31	111
15	300	0.68	ZrF_6	1.91	2.59	99
16	300	1.05	ZrF_6	1.50	2.55	110
17	300	1.05	ZrF_6	1.50	2.55	120
18	300	1.05	ZrF_6	1.50	2.55	130
19	450	0.98	ZrF_6	2.88	3.86	106

The fluoaluminate was added as the sodium salt; the fluotitanate as the potassium salt (hydrated); and the fluozirconate as the potassium salt.

We have discovered that other materials which may be found in the bath affect the ability to plate bright crack-free chromium. Certain materials which tend to promote cracking must be kept out of the baths or restricted to extremely low levels. Chlorides are such materials, as noted hereinbefore. Certain materials leached from ion exchange resins tend to promote cracking. Some of these materials may be found in the salts used to make up the bath. Care must also be exercised to avoid their introduction during operation, especially if bath purification is to be attempted utilizing basic ion exchange resins. Other materials tend to widen the conditions under which it is possible to plate bright crack-free chromium, or under given conditions result in the ability to plate a greater thickness of bright crack-free chromium. Such favorable materials are exemplified by the cations sodium, calcium and potassium.

Articles made of any of a variety of basis metals, such as plain carbon steels, alloy steels including stainless steel, iron, copper and copper alloys, nickel and nickel alloys, zinc and zinc alloys, etc., may be plated with bright crack-free chromium. In general, the basis metal may be any metal, or an undercoat on a metal, that can be chromium plated.

The basis metal does affect the thickness of chromium which may be plated bright and crack-free to a certain extent. This is illustrated by the slightly greater thickness of bright crack-free chromium which can be deposited directly on steel than can be deposited directly on copper under the same process and bath conditions. The greater thickness attainable under the same conditions on the steel is attributed to the greater hardness of the basis metal and the support it is thus able to give the electrodeposit.

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 process for electrodepositing bright crack-free chromium to a thickness of at least 0.00005 inch on a metal cathode comprising passing current from an anode to said cathode immersed in an aqueous chromium plating bath at a temperature between 95° F. and 140° F., said bath containing less than 0.05 g./l. of chloride ion and comprising essentially between 100 g./l. and 500 g./l of CrO_3, a total catalyst ion concentration of sulfate ions and at least one complex ion selected from the class consisting of fluoaluminate, fluozirconate, and fluotitanate, to achieve a Ratio of CrO_3 concentration to total catalyst ion concentration between 70:1 and 150:1, the sulfate ion content being between 5% and 85% of the total catalyst concentration, the CrO_3 concentration, Ratio and temperature having a relationship defined by the area enclosed by the curve ABCDE in Figure 1.

2. A process for electrodepositing bright crack-free chromium to a thickness of at least 0.00005 inch on a metal cathode comprising passing current from an anode to said cathode immersed in an aqueous chromium plating bath at a temperature between 105° F. and 135° F., said bath containing less than 0.02 g./l. of chloride ion and comprising essentially between 150 g./l. and 450 g/l. of CrO_3, a total catalyst ion concentration of sulfate and at least one complex ion selected from the class consisting of fluoaluminate, fluozirconate, and fluotitanate to achieve a Ratio of CrO_3 concentration to total catalyst ion concentration between 80:1 and 135:1, the sulfate ion content being between 15% and 70% of the total catalyst concentration, the relationship between the CrO_3 concentration, the Ratio and the temperature being within that defined by the area enclosed by the curve ABCDE in Figure 1.

3. A process for electrodepositing bright crack-free chromium to a thickness of at least 0.00005 inch on a metal cathode comprising passing current from an anode to said cathode immersed in an aqueous chromium plating bath at a temperature between 118° F. and 130° F., said bath containing less than 0.02 g./l. of chloride ion and comprising essentially between 200 g./l. and 350 g./l. of CrO_3, a total catalyst ion concentration of sulfate and at least one complex ion selected from the class consisting of fluoaluminate, fluozirconate, and fluotitanate, to achieve a Ratio of CrO_3 concentration to total catalyst ion concentration between 85:1 and 120:1, the sulfate ion content being between 20% and 55% of the total catalyst concentration, the CrO_3 concentration, Ratio and temperature having a relationship defined by the area JKLM of Figure 1.

4. A process for electrodepositing bright crack-free chromium to a thickness of at least 0.00005 inch on a metal cathode comprising passing current from an anode to said cathode immersed in an aqueous chromium plating bath at a temperature between 114° F. and 140° F., said bath containing less than 0.02 g./l. of chloride ion and comprising essentially between 100 g./l. and 450 g./l. of CrO_3, a total catalyst ion concentration of sulfate and at least one complex ion selected from the class consisting of fluoaluminate, fluozirconate, and fluotitanate, to achieve a Ratio of CrO_3 concentration to total catalyst ion concentration between 70:1 and 150:1, the sulfate ion content being between 5% and 85% of the total catalyst concentration, the CrO_3 concentration, Ratio and temperature having a relationship defined by the area enclosed by the curve ABHI in Figure 1.

5. The process of claim 1 in which the complex ion is a fluoaluminate ion.

6. The process of claim 1 in which the complex ion is a fluozirconate ion.

7. The process of claim 1 in which the complex ion is a fluotitanate ion.

8. The process of claim 2 in which the complex ion is a fluoaluminate ion.

9. The process of claim 2 in which the complex ion is a fluozirconate ion.

10. The process of claim 2 in which the complex ion is a fluotitanate ion.

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
2,916,424	Stareck et al.	Dec. 8, 1959

UNITED STATES PATENT OFFICE

Certificate of Correction

Patent No. 2,952,590 September 13, 1960

Jesse E. Stareck et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the drawings, Sheet 1, containing Figures 1 and 2, and Sheet 2, containing Figures 3 and 4, should appear as shown below instead of as in the patent—

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FIG. 1.

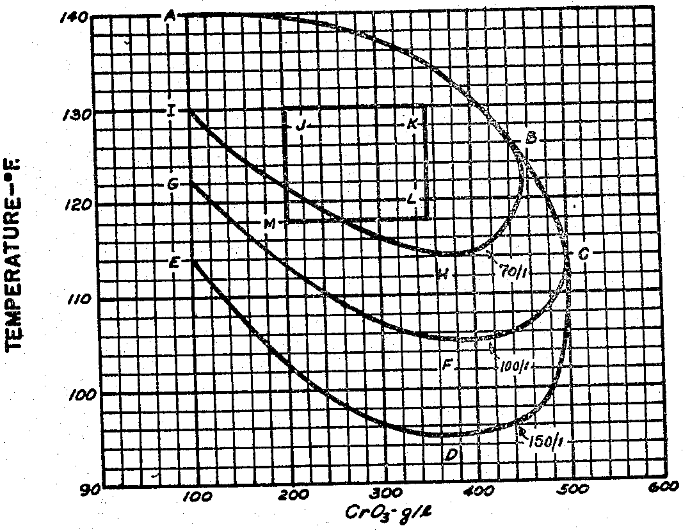
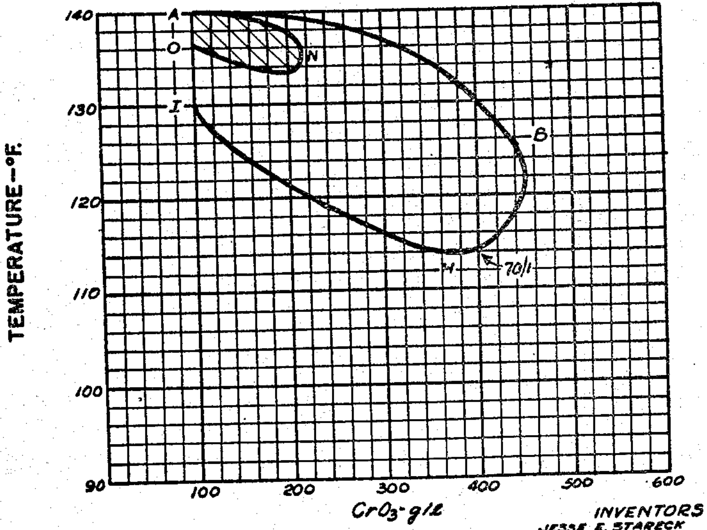


FIG. 2.



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BY H.H. Goodman
ATTORNEY

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FIG. 3.

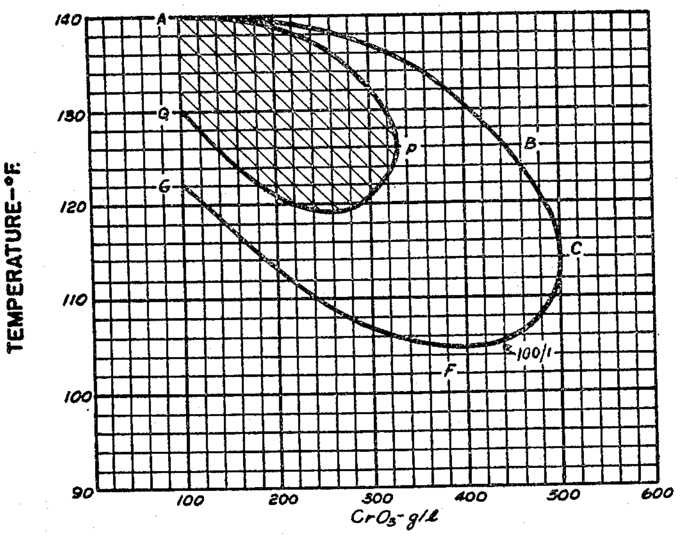
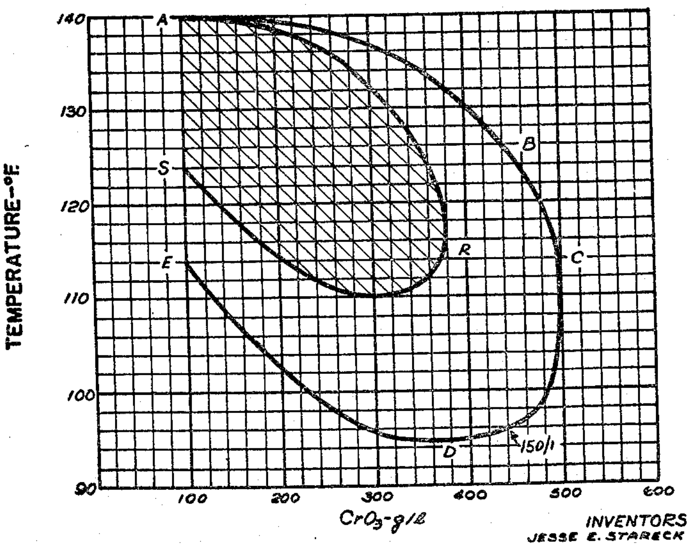


FIG. 4.



INVENTORS
JESSE E. STARECK
EDGAR J. SEYB, JR.
ANDY ALBERT JOHNSON
WILLIAM H. ROWAN
BY H.H. Goolman
ATTORNEY

column 4, line 26, for "Sulfite" read —Sulfate—.

Signed and sealed this 9th day of May 1961.

[SEAL]

Attest:
ERNEST W. SWIDER,
Attesting Officer.

DAVID L. LADD,
Commissioner of Patents.