

May 26, 1953

J. E. STARECK

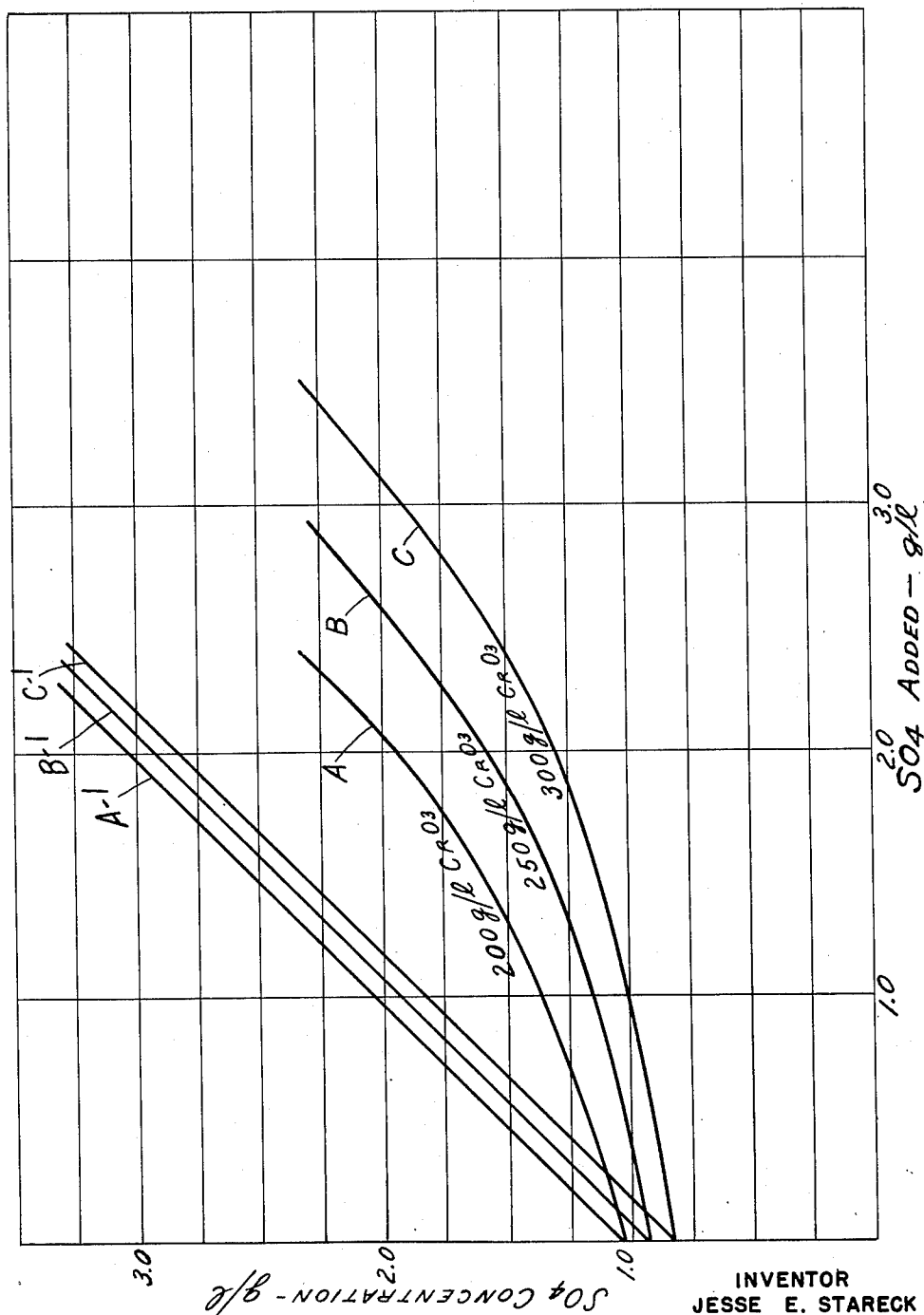
2,640,022

COMPOSITION, BATH, AND PROCESS FOR CHROMIUM PLATING

Filed Nov. 7, 1950

3 Sheets-Sheet 1

FIGURE 1.



INVENTOR
JESSE E. STARECK

BY *Burges Ryan + Hinkle*
ATTORNEYS

May 26, 1953

J. E. STARECK

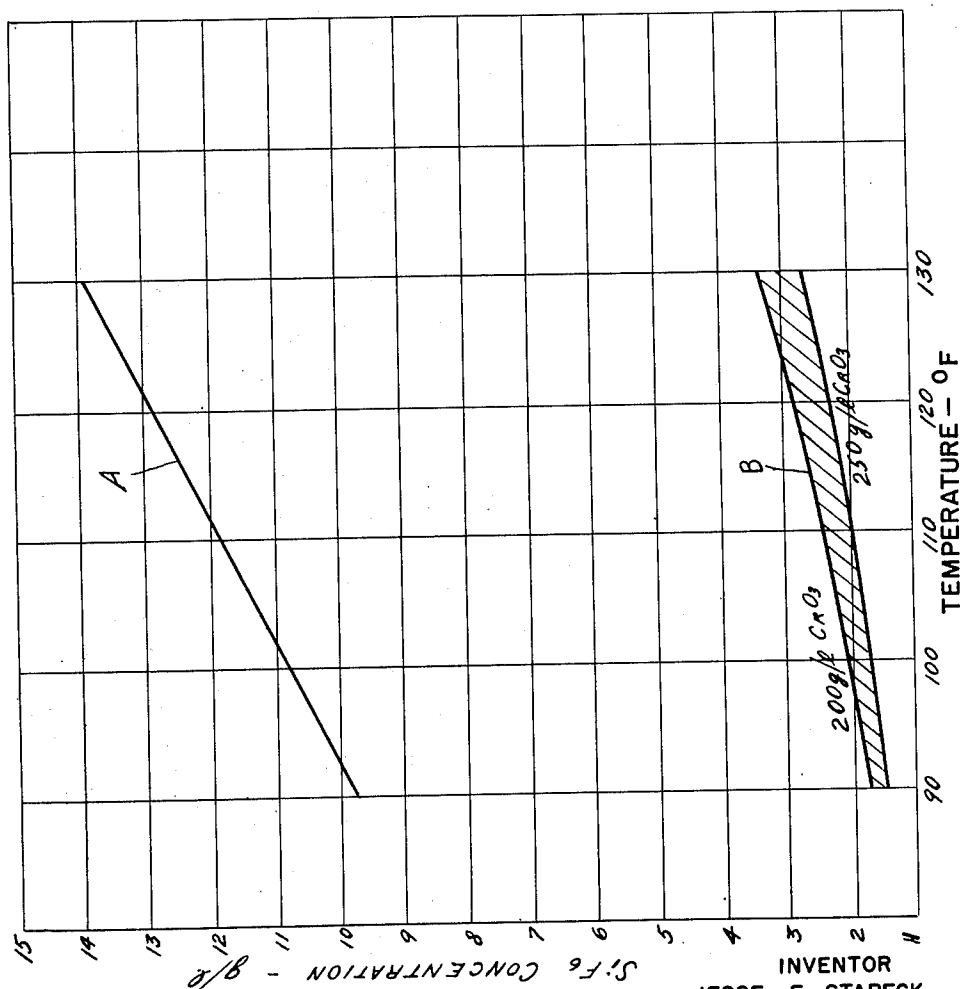
2,640,022

COMPOSITION, BATH, AND PROCESS FOR CHROMIUM PLATING

Filed Nov. 7, 1950

3 Sheets-Sheet 2

FIG. 2.



INVENTOR
JESSE E. STARECK
BY *Burgess Ryan + Hicks*
ATTORNEYS

May 26, 1953

J. E. STARECK

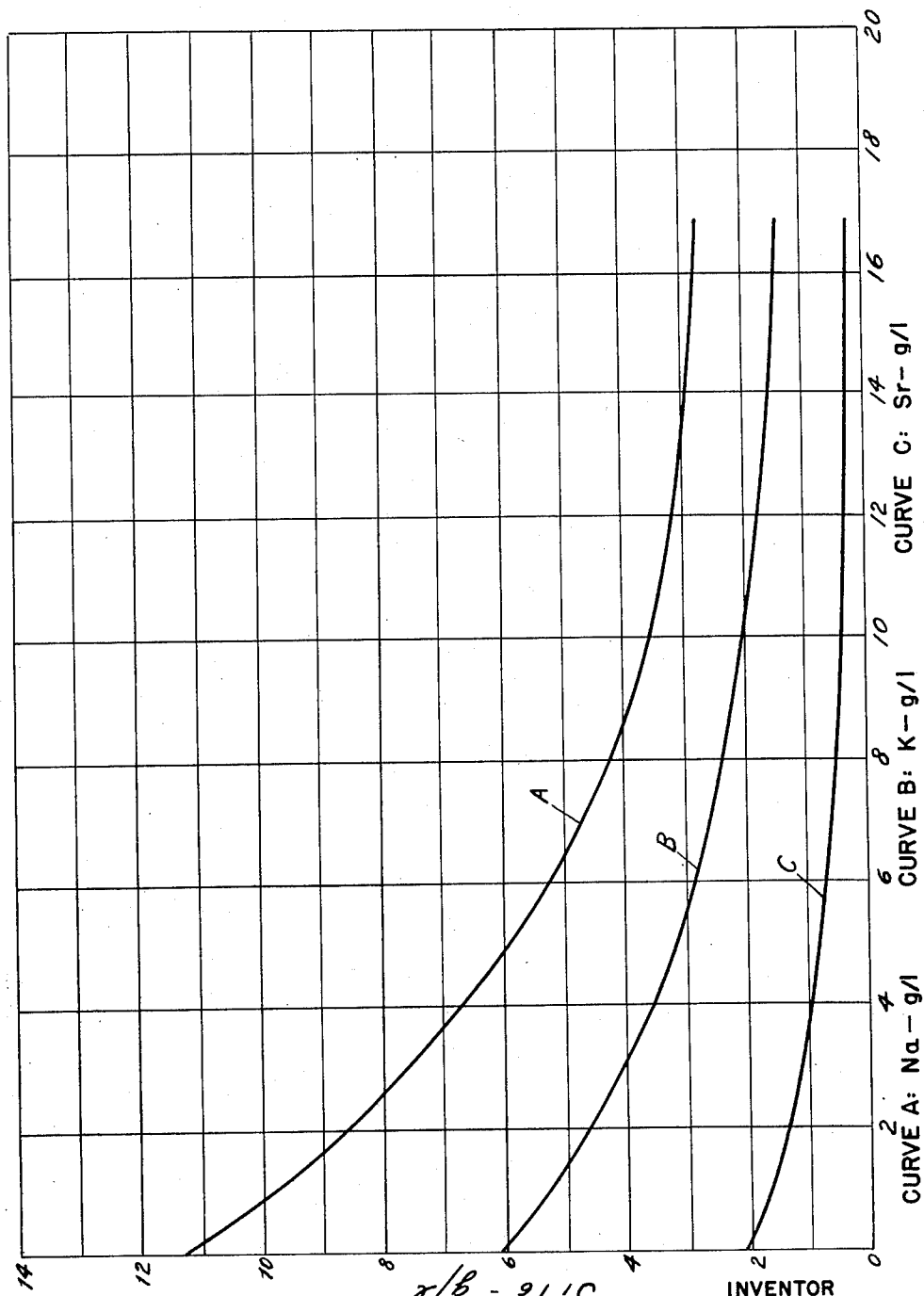
2,640,022

COMPOSITION, BATH, AND PROCESS FOR CHROMIUM PLATING

Filed Nov. 7, 1950

3 Sheets-Sheet 3

FIG. 3.



INVENTOR

JESSE E. STARECK

BY

Burgess Ryan & Hicks
ATTORNEYS

UNITED STATES PATENT OFFICE

2,640,022

COMPOSITION, BATH, AND PROCESS FOR
CHROMIUM PLATING

Jesse E. Stareck, Birmingham, Mich., assignor to
United Chromium, Incorporated, New York,
N. Y., a corporation of Delaware

Application November 7, 1950, Serial No. 194,502

24 Claims. (Cl. 204—51)

1

This invention relates to chromium plating baths, compositions for making up and maintaining such baths, and to a chromium plating process.

The essential feature of my invention is the utilization of what I shall call suppression agents to maintain and regulate the catalyst acid radical content of a chromium plating bath of the chromic acid type. I give below several examples of compositions to be used in making up chromic acid baths and these compositions include suppression agents which have the effect of controlling the content of catalyst acid radicals in the bath from whatever source and controlling the solubility of the salts used to introduce such radicals into the bath. For instance, in Example I the suppression agents are potassium bichromate and strontium chromate.

The present invention provides a bath and process having numerous advantages, among which are:

1. Self-regulation of the catalyst acid radical content at or near the optimum concentration in baths of any desired chromic acid content;
2. Reduced or eliminated need for analytical control;
3. The ability to take up appreciable amounts of catalyst acid radical introduced as impurities or as drag-in without exceeding the operating limits in the bath for such radicals;
4. Superior covering power;
5. High operating efficiency such as low power consumption, minimum rejections and low operating costs;
6. Wide bright-plate range;
7. High plating speed;
8. Good cathode activating properties;
9. Bright plate direct on stainless steel;
10. Avoidance of iridescent film on articles only partly covered in chromium plating.

The bath and composition consist essentially of chromic acid (CrO_3), a sulfate radical bearing salt having a limited solubility in the chromic acid bath, a non-catalytic compound of the cation associated with the sulfate radical bearing salt, a silicofluoride bearing salt having a limited solubility in the chromic acid bath, and a non-catalytic compound of the cation associated with the silicofluoride salt. For instance, by adding the composition given in Example I below to water a chromic acid bath is produced which contains strontium sulfate and potassium silicofluoride, each in excess of its solubility in the bath, and also strontium chromate and potassium bichromate in solution.

2

In my invention, the total amount of catalyst acid radicals in solution is furnished from a plurality of substances, each supplying a portion of the total catalyst acid radical, the amount of each radical used being determined by the solubility of the particular salt used in introducing that acid radical into the bath. Thus, when the catalyst acid radical from the salt is depleted in the bath for one reason or another, the acid radical lost from the solution is replenished by acid radical from the catalyst acid radical bearing salt remaining in the bath as undissolved residue. The solubility of each of the catalyst acid radical bearing salts in the bath is in turn further regulated by the addition to the bath of other compounds having no catalyst acid radical but containing a cation common to that of the salts containing the catalyst acid radicals. The catalyst acid radicals are the sulfate and the silicofluoride radicals.

Examples of useful non-catalytic strontium and potassium compounds are SrCO_3 , $\text{Sr}(\text{OH})_2$, SrCrO_4 , etc., and KOH , K_2CO_3 , K_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, etc.

The control of the solubility of the catalyst acid radical salts in the bath is desirable in that self-regulation of the catalyst acid radical content of the bath at or near the optimum concentration may thus be achieved at any desired chromic acid concentration, with the advantages peculiar to these different concentrations.

Examples of compositions of matter formulated according to the present invention in percentages are:

Example I

Chromic acid	70	to	90
Potassium bichromate	5.5	to	15.5
Strontium chromate	0.6	to	3.6
Potassium silicofluoride	2.5	to	7.5
Strontium sulfate	1.4	to	3.4

Example II

Chromic acid	85	to	95
Potassium bichromate	2.5	to	7.5
Strontium chromate	0.5	to	1.5
Potassium silicofluoride	1.3	to	4.1
Strontium sulfate	0.7	to	1.9

Example III

Chromic acid	18	to	72.8
Sodium bichromate	23.4	to	70
Strontium chromate	0.8	to	3
Sodium silicofluoride	1.8	to	6
Strontium sulfate	1.2	to	3

3

Example IV

Chromic acid -----	59	to	86.4
Sodium bichromate -----	11.6	to	35
Strontium chromate -----	0.5	to	1.5
Sodium silicofluoride -----	1.0	to	3.0
Strontium sulfate -----	0.5	to	1.5

Example V

Chromic acid -----	85	to	95
Sodium bichromate -----	1.6	to	5
Strontium chromate -----	1.1	to	3.3
Sodium silicofluoride -----	1.9	to	5.5
Strontium sulfate -----	0.4	to	1.2

Example VI

Chromic acid -----	62.5	to	87.5
Potassium bichromate -----	5.7	to	17.7
Strontium chromate -----	4.3	to	12.3
Potassium silicofluoride -----	2.0	to	6.0
Strontium sulfate -----	0.5	to	1.5

Example VII

Chromic acid -----	85	to	95
Potassium bichromate -----	2.4	to	6.6
Strontium chromate -----	1.5	to	4.5
Potassium silicofluoride -----	0.9	to	2.5
Strontium sulfate -----	0.4	to	1.2

Example VIII

Chromic acid -----	85	to	95
Sodium bichromate -----	2.3	to	6.7
Strontium chromate -----	0.6	to	1.8
Potassium silicofluoride -----	1.5	to	4.5
Strontium sulfate -----	0.6	to	2.0

Example IX

Chromic acid -----	79	to	95
Sodium bichromate -----	2.3	to	11.7
Sodium silicofluoride -----	1.5	to	5.1
Strontium sulfate -----	1.2	to	4.2

Compositions given in Example I above are adapted to give satisfactory solutions over a range of chromic acid concentration from about 150 g./l. to about 400 g./l., the optimum varying somewhat with the basis metal upon which the chromium is plated and also with the type of application of chromium. For example, when chromium plating stainless steel, a chromic acid concentration of about 150 g./l. to about 200 g./l. is usually preferred. When plating over a nickel plate, a chromic acid concentration of about 200 g./l. to about 250 g./l. is usually preferred. For the production of a chromium deposit with maximum leveling action, a chromic acid concentration from about 250 g./l. to about 350 g./l. is usually preferred.

The composition of Example II above is adapted to give satisfactory solutions over a range of chromic acid concentrations from about 250 g./l. to about 500 g./l. The chief use of the composition given in Example II is as a maintenance composition for baths made up from Example I, but it may also be used to make a plating bath. When used as a plating bath for chromium plating over nickel plate, the optimum chromic acid range is from about 275 g./l. to about 350 g./l. When used as a plating bath for producing heavy chromium deposits with maximum leveling action, a concentration range of about 350 g./l. to about 500 g./l. is usually preferred. The higher chromic acid concentrations made possible by Example II result in a bath having high conductivity with minimum treeing of deposits for heavy chromium plating.

4

Example III represents a composition corresponding to that in Example I except that sodium salts are used in place of potassium salts and all that has been said with respect to Example I applies to Example III.

Similarly, the composition of Example IV is the same as that of Example II with the exception that the sodium salts are used in place of potassium salts of Example II and what has been said with respect to Example II and the baths made therefrom applies to Example IV.

The composition of Example V is especially useful for barrel chromium plating. It may be used over a range of chromic acid concentration from about 300 g./l. to about 500 g./l., the optimum being about 400 g./l. These baths may also be used for ordinary decorative and for heavy chromium plating.

The compositions of Example VI above give satisfactory solutions over a range of chromic acid concentration from about 100 to about 250 g./l., with an optimum of about 150 g./l. The provision of a satisfactory bath having this low chromic acid concentration is one of the desirable features of my invention and gives the particular advantages of low cost and high efficiency.

The chief use of the composition given in Example VII is as a maintenance for baths made up from Example VI. However, it is also adapted to give satisfactory plating solutions over a range of chromic acid concentrations from about 200 g./l. to about 400 g./l.

Example VIII provides a composition which is useful in making chromium plating solutions over a range of chromic acid concentrations from about 250 g./l. to about 500 g./l., with an optimum of about 400 g./l. The main feature of this composition is that it is adapted to regulate the sulfate catalyst acid radical in particular by the use of a single suppression agent such as strontium chromate as distinguished from the previous examples where both the sulfate and the silicofluoride radicals are regulated by a plurality of suppression agents. In this example only the strontium chromate is a suppression agent, suppressing the sulfate content; the sodium bichromate does not function as a suppression agent inasmuch as the silicofluoride is present as the potassium salt, not the sodium salt, and the sodium from the sodium bichromate is present in insufficient quantity to have a suppressing effect on the silicofluoride; i. e., any sodium silicofluoride present would be in amount less than its solubility in this solution. The sodium bichromate merely supplements the chromic acid as a supplier of chromate. This composition can be used for decorative, barrel, and heavy chromium plating.

Example IX is similar to Example VIII except that in Example IX the silicofluoride radical in particular is controlled by the use of a single suppression agent such as sodium bichromate. This composition can be used for decorative, barrel, and heavy chromium plating.

As pointed out above, the suppression agents used in the composition of Example I are strontium chromate and potassium bichromate. These same agents are used in Examples II, VI, and VII. The suppression agents used in Examples III, IV, and V are sodium bichromate and strontium chromate. The suppression agent used in Example VIII is strontium chromate and that used in Example IX is sodium bichromate. The strontium in the suppression agents in all of the examples given herein suppresses directly the

5

sulfate content in the bath and the sodium or potassium of the suppression agents suppresses directly the silicofluoride content in the bath.

For those examples containing a non-catalytic potassium compound, it may be noted that the potassium content of such compound ranges from 0.64 to 4.7% by weight, while the strontium content of the non-catalytic strontium compound ranges from 0.21 to 5.3% by weight. In those examples having a non-catalytic sodium compound, the sodium content of such compound varies from 0.28 to 12.3% by weight, and the strontium content of the non-catalytic strontium compound varies from 0.21 to 1.4% by weight.

A special advantage of using a suppression agent for the silicofluoride radical is not only to adjust its concentration in solution to the desired value, but also to make it less affected by temperature changes and by changes in chromic acid concentration of the bath.

Certain of the superior features of the baths made up from the compositions given above (and from similar compositions) are illustrated by the curves attached hereto and made a part hereof.

In Fig. 1, curves A, B, and C illustrate the effect on the sulfate radical concentration of baths made up using the composition of Example I to give 200 g./l. chromic acid as CrO_3 , 250 g./l. chromic acid as CrO_3 , and 300 g./l. chromic acid as CrO_3 , respectively, by the addition (i. e. drag-in) of sulfate radical in amounts up to a little over 3 g./l. Curves A-I, B-I, and C-I illustrate the effect of the addition of sulfate radical (i. e. drag-in) on the sulfate radical concentration of ordinary solutions made up of only chromic acid and sulfate and with chromic acid and sulfate concentrations corresponding to those of the baths represented by curves A, B, and C, respectively. In solutions represented by curves A-I, B-I, and C-I, the sulfate radical concentration increases by the same amount as the sulfate acid radical drag-in. Thus for 1 g./l. of SO_4 drag-in, the SO_4 concentration as shown by the curve C-I, for example, is increased by 1 g./l. to a total value of about 1.83 g./l.; and likewise a 1 g./l. SO_4 drag-in affects the SO_4 concentration of solutions represented by curves A-I and B-I in the same manner and to the same extent.

By reference to curve C, it will be seen that a drag-in of 1 g./l. SO_4 will raise the SO_4 concentration of the bath represented by that curve from about 0.83 to about 1.0, or by 0.17 g./l. Thus the rise of the SO_4 concentration in consequence of the drag-in of the 1 g./l. SO_4 results in only about 20% increase of SO_4 concentration with a bath represented by curve C as against 120% increase of SO_4 concentration in a solution represented by curve C-I. The comparison is similar between curves A and A-I and between curves B and B-I.

In Fig. 2, curve B illustrates the regulating effect of the suppression agents in baths of 200 g./l. and 250 g./l. chromic acid concentrations made with a composition of Example III, with respect to temperature variations. Curve A represents a bath made with a composition like that of Example III but without the suppression agents. Thus from curve B of Fig. 2, at 250 g./l. of chromic acid, for a temperature variation from 90° to 130° F. the SiF_6 content in solution varies only from about 1.4 to 2.7 (a difference of 1.3 g./l.), whereas from curve A it will be seen that for a like change in temperature the SiF_6 varies from 9.8 to 13.9 (a difference of 4.1 g./l.). Again, from curve B of Fig. 2, at 200 g./l. chromic acid,

6

the SiF_6 content varies only from 1.7 to 3.4 (a difference of 1.7 g./l.). As may be appreciated, for all of the baths contemplated by the invention, the SiF_6 content varies little with temperature changes. Similarly, the SO_4 content also varies little with temperature changes, the magnitude of the variation being even less than in the case of the SiF_6 .

Fig. 3 illustrates the effect of the suppression agents on the acid radical contents in solution. Curve A shows the effect of the sodium content from the suppression agent on the silicofluoride content. Curve B shows the effect of the potassium from the suppression agent on the silicofluoride content, and curve C shows the effect of strontium from the suppression agent on the sulfate content. The curves of Fig. 3 represent the effects described above in a bath having a chromic acid concentration of 250 g./l. at 110° F. Thus, for example, as shown on curve C, if to the bath containing 8 g./l. of excess strontium (this is the strontium from the suppression agent) which as shown by curve C contains 0.5 g./l. of sulfate, there is added an amount of sulfate (as from sulfuric acid, a common drag-in material) equivalent to 4 g./l. of strontium (i. e., 4.4 g./l. of sulfate), in the range of 8 to 4 g./l. of strontium on curve C, the amount of sulfate which will go into solution will be the difference between the sulfate concentrations at 8 g./l. strontium and at 4 g./l. strontium, i. e., 0.9 g./l. minus 0.5 g./l., or only 0.4 g./l. sulfate. Thus, only 0.4 g./l. sulfate goes into solution for a total addition of 4.4 g./l. sulfate, the balance being precipitated as strontium sulfate. As will be apparent, the drag-in effect has been effectively minimized. Similarly, from curves A and B it will be clearly understood that a similar relationship exists between the amount of SiF_6 added and the amount that goes into solution.

In this connection, and speaking in a general way, it may be observed from Fig. 3 that the concentration of sulfate radical may be depressed by addition of strontium radical to a concentration lower than the unsuppressed saturation concentration but above zero concentration, the unsuppressed saturation value being given on curve C at the point zero Sr, which point represents the sulfate content of the solution saturated with strontium sulfate in the absence of any other strontium or sulfate compound. In other words, sulfate radical concentration may be depressed anywhere in the range of 2.1 g./l. to 0.2 g./l., the latter value being taken at the right hand limit of the curve and being equivalent to about one-tenth of the unsuppressed saturation concentration. Of course, this value may be even lower if the curve is extended to the right. Similarly, the silicofluoride radical (see curve B) may be depressed by addition of potassium radical to a lower concentration but above zero, the concentration extending to as low as about one-fourth, or less, of the unsuppressed saturation concentration, and it may be depressed by sodium radical (curve A) to a concentration as low as about one-fourth, or less, of the unsuppressed saturation concentration. These observations are generally applicable to the invention.

It is preferred that the completed compositions as given in Examples I to IX, inclusive, be prepared and used, but obviously the advantages of my invention can be secured equally well by preparing the composition of Example I, for instance, omitting the chromic acid, the other ingredients of this example being added to a

7

chromic acid solution prepared independently. Similarly, the benefits of my invention may be secured by other combinations of the ingredients given in the various examples where one or more of the ingredients is added to the bath independently of the others. Also, as pointed out earlier, suppressing agents other than those specifically listed in the examples may be used equally well.

While I have given the compositions in the examples herein in terms of the percentages, it is understood of course that these may be expressed as "in parts" which may be readily calculated from the values given in the respective examples. Also, in view of the examples, wherein a portion of the total CrO_3 content is supplied by CrO_3 added as such and a portion is supplied by non-catalytic salts like sodium bichromate, strontium chromate, etc., the recitation in the claims of CrO_3 is, unless otherwise specified, intended to cover both the CrO_3 added per se to a composition or bath and also the CrO_3 added as part of a non-catalytic compound. The CrO_3 content may thus be seen to range from a low of about 72% in Example III to a high of about 97% in Example VII.

What is claimed is:

1. A composition of matter for making up an aqueous chromic acid bath for chromium plating in the range of 100 to 500 g./l. of CrO_3 , comprising essentially about 72 to 97 per cent by weight of CrO_3 , an amount of strontium sulfate sufficient to saturate said bath and to provide an undissolved residue of strontium sulfate in the bath, an amount of potassium silicofluoride sufficient to saturate said bath and to provide an undissolved residue of potassium silicofluoride in the bath, a soluble non-catalytic strontium compound in an amount containing 0.21 to 5.3 per cent by weight of strontium, and a soluble non-catalytic potassium compound in an amount containing 0.64 to 4.7 per cent by weight potassium.

2. A composition of matter for making up an aqueous chromic acid bath for chromium plating in the range of 250 to 500 g./l. of CrO_3 , comprising essentially 85 to 95 per cent by weight of CrO_3 , sodium bichromate 2.3 to 6.7 per cent by weight, an amount of strontium sulfate which provides an undissolved residue of strontium sulfate in the bath, an amount of potassium silicofluoride which provides an undissolved residue of potassium silicofluoride in the bath, and a soluble non-catalytic strontium compound in an amount containing 0.26 to 0.78 per cent by weight strontium.

3. A composition of matter for making up an aqueous chromic acid bath for chromium plating in the range of 250 to 500 g./l. of CrO_3 , comprising essentially 79 to 95 per cent by weight of CrO_3 , an amount of strontium sulfate which provides an undissolved residue of strontium sulfate in the bath, an amount of sodium silicofluoride which provides an undissolved residue of sodium silicofluoride in the bath, and a soluble non-catalytic sodium compound in an amount containing 0.4 to 2.0 per cent by weight sodium.

4. A composition of matter for making up and maintaining an aqueous chromic acid bath for chromium plating in the range of 100 to 500 grams per liter of CrO_3 , said composition comprising essentially about 72 to 97% by weight of CrO_3 , two catalyst-supplying compounds, and a soluble non-catalytic compound, one of said catalyst-supplying compounds being strontium sulfate in an amount sufficient to saturate said

8

bath and to provide an undissolved residue of strontium sulfate in the bath, the other of said catalyst-supplying compounds being an alkali metal silicofluoride in an amount sufficient to saturate said bath and to provide an undissolved residue of alkali metal silicofluoride in the bath, said alkali metal being selected from the class consisting of potassium and sodium, said non-catalytic compound being present in an amount sufficient to suppress the concentration of one of said catalyst-supplying compounds in solution in said bath from the unsuppressed saturation concentration of the latter compound to a lower but greater than zero concentration, said non-catalytic compound being selected from the class consisting of a strontium compound and an alkali metal compound, and the alkali metal of said alkali metal compound being the same as the alkali metal of said alkali metal silicofluoride.

5. A composition of matter for making up and maintaining an aqueous chromic acid bath for chromium plating in the range of 100 to 500 grams per liter of CrO_3 , said composition comprising essentially about 72 to 97% by weight of CrO_3 , two catalyst-supplying compounds, and a soluble non-catalytic compound, one of said catalyst-supplying compounds being strontium sulfate in an amount sufficient to saturate said bath and to provide an undissolved residue of strontium sulfate in the bath, the other of said catalyst-supplying compounds being an alkali metal silicofluoride in an amount sufficient to saturate said bath and to provide an undissolved residue of alkali metal silicofluoride in the bath, said alkali metal being selected from the class consisting of potassium and sodium, said non-catalytic compound being a strontium compound in an amount sufficient to suppress the concentration of said strontium sulfate in solution in said bath from the unsuppressed saturation concentration of the latter compound to a lower but greater than zero concentration.

6. A composition of matter for making up and maintaining an aqueous chromic acid bath for chromium plating in the range of 100 to 500 grams per liter of CrO_3 , said composition comprising essentially about 72 to 97% by weight of CrO_3 , two catalyst-supplying compounds, and a soluble non-catalytic compound, one of said catalyst-supplying compounds being strontium sulfate in an amount sufficient to saturate said bath and to provide an undissolved residue of strontium sulfate in the bath, the other of said catalyst-supplying compounds being an alkali metal silicofluoride in an amount sufficient to saturate said bath and to provide an undissolved residue of alkali metal silicofluoride in the bath, said alkali metal being selected from the class consisting of potassium and sodium, said non-catalytic compound being an alkali metal compound in an amount sufficient to suppress the concentration of said alkali metal silicofluoride in solution in said bath from the unsuppressed saturation concentration of the latter compound to a lower but greater than zero concentration, and the alkali metal of said alkali metal compound being the same as the alkali metal of said alkali metal silicofluoride.

7. A composition of matter for making up and maintaining an aqueous chromic acid bath for chromium plating in the range of 100 to 500 g./l. CrO_3 , said composition comprising essentially about 72 to 97% by weight of CrO_3 , and the balance of the composition consisting essentially of the following four compounds: (1) strontium

sulfate in an amount sufficient to saturate said bath and to provide an undissolved residue of strontium sulfate in the bath, (2) an alkali metal silicofluoride in an amount sufficient to saturate said bath and to provide an undissolved residue of alkali metal silicofluoride in the bath, said alkali metal being selected from the class consisting of potassium and sodium, (3) a soluble non-catalytic strontium compound in an amount sufficient to suppress the concentration of the strontium sulfate in solution in said bath from the unsuppressed saturation concentration of the latter to a lower but greater than zero concentration, and (4) a soluble non-catalytic alkali metal compound in an amount sufficient to suppress the concentration of the alkali metal silicofluoride in solution in said bath from the unsuppressed saturation concentration of the latter to a lower but greater than zero concentration, and the alkali metal of said non-catalytic compound being the same as the alkali metal of said alkali metal silicofluoride.

8. A composition of matter for making up and maintaining an aqueous chromic acid plating bath for chromium plating in the range of 100 to 500 g./l. CrO_3 , said composition comprising essentially about 72 to 97% by weight of CrO_3 and the balance comprising the following four compounds: (1) strontium sulfate in an amount sufficient to saturate said bath and to provide an undissolved residue of strontium sulfate in the bath, (2) an alkali metal silicofluoride in an amount sufficient to saturate said bath and to provide an undissolved residue of alkali metal silicofluoride in the bath, said alkali metal being selected from the class consisting of potassium and sodium, (3) a soluble non-catalytic strontium compound in an amount sufficient to suppress the concentration of the strontium sulfate in solution in said bath from the unsuppressed saturation concentration of the latter to a lower concentration, said lower concentration being in the range extending from said unsuppressed saturation concentration to about one-tenth of the unsuppressed saturation concentration, and (4) a soluble non-catalytic alkali metal compound in an amount sufficient to suppress the concentration of the alkali metal silicofluoride in solution in said bath from the unsuppressed saturation concentration of the latter to a lower concentration in the range extending from said last-mentioned unsuppressed saturation concentration to about one-fourth thereof, and the alkali metal of said non-catalytic compound being the same as the alkali metal of said alkali metal silicofluoride.

9. A composition of matter for making up and maintaining an aqueous chromic acid bath for chromium plating in the range of 100 to 500 g./l. of CrO_3 , said composition comprising essentially about 72 to 97% by weight of CrO_3 , an amount of strontium sulfate sufficient to saturate said bath and to provide an undissolved residue of strontium sulfate in the bath, an amount of sodium silicofluoride sufficient to saturate said bath and to provide an undissolved residue of sodium silicofluoride in the bath, a soluble non-catalytic strontium compound in an amount equivalent to 0.21 to 1.4 per cent by weight of strontium, and a soluble non-catalytic sodium compound in an amount equivalent to 0.28 to 12.3 per cent by weight of sodium.

10. A composition of matter for making up and maintaining an aqueous chromic acid bath for chromium plating in the range of 100 to 500 g./l.

of CrO_3 , consisting essentially of 90 to 70% by weight of CrO_3 per se, 1.4 to 3.4% by weight of strontium sulfate, 2.5 to 7.5% by weight of potassium silicofluoride, 0.6 to 3.6% by weight of strontium chromate, and 5.5 to 15.5 by weight of potassium bichromate.

11. A composition of matter for making up and maintaining an aqueous chromic acid bath for chromium plating in the range of 100 to 500 grams per liter of CrO_3 , consisting essentially of 95 to 85% by weight of CrO_3 per se, 0.7 to 1.9% by weight of strontium sulfate, 1.3 to 4.1% by weight of potassium silicofluoride, 0.5 to 1.5% by weight of strontium chromate, and 2.5 to 7.5% by weight of potassium bichromate.

12. A composition of matter for making up and maintaining an aqueous chromic acid bath for chromium plating in the range of 100 to 500 grams per liter of CrO_3 , said composition comprising essentially two catalyst-supplying compounds and a soluble non-catalytic compound, one of said catalyst-supplying compounds being strontium sulfate in an amount sufficient to saturate said bath and to provide an undissolved residue of strontium sulfate in the bath when said composition is added to said bath in the proportion of at least 5 parts of the composition to 95 parts of the chromic acid in said bath, the other of said catalyst-supplying compounds being an alkali metal silicofluoride in an amount sufficient to saturate said bath and to provide an undissolved residue of alkali metal silicofluoride in the bath when said composition is added to said bath in the proportion of at least 5 parts of the composition to 95 parts of the chromic acid in said bath, said alkali metal being selected from the class consisting of potassium and sodium, said non-catalytic compound being present in an amount sufficient to suppress the concentration of one of said catalyst-supplying compounds in solution in said bath from the unsuppressed saturation concentration of the latter compound to a lower but greater than zero concentration, said non-catalytic compound being selected from the class consisting of a strontium compound and an alkali metal compound, and the alkali metal of said alkali metal compound being the same as the alkali metal of said alkali metal silicofluoride.

13. A composition of matter for making up and maintaining an aqueous chromic acid bath for chromium plating in the range of 100 to 500 grams per liter of CrO_3 , said composition comprising essentially the following four compounds: (1) strontium sulfate in an amount sufficient to saturate said bath and to provide an undissolved residue of strontium sulfate in the bath when said composition is added to said bath in the proportion of at least 5 parts of the composition to 95 parts of the chromic acid in said bath, (2) an alkali metal silicofluoride in an amount sufficient to saturate said bath and to provide an undissolved residue of alkali metal silicofluoride in the bath when said composition is added to said bath in the proportion of at least 5 parts of the composition to 95 parts of the chromic acid in said bath, said alkali metal being selected from the class consisting of potassium and sodium, (3) a soluble non-catalytic strontium compound in an amount sufficient to suppress the concentration of the strontium sulfate in solution in said bath from the unsuppressed saturation concentration of the latter to a lower but greater than zero concentration, and (4) a soluble non-catalytic alkali metal compound in an amount sufficient to suppress the concentration of the alkali metal silico-

fluoride in solution in said bath from the unsuppressed saturation concentration of the latter to a lower but greater than zero concentration, and the alkali metal of said non-catalytic compound being the same as the alkali metal of said alkali metal silicofluoride.

14. A composition for use in making up and maintaining an aqueous chromic acid bath for chromium plating in the range of 100 to 500 grams per liter of CrO_3 , said composition comprising essentially about 2.4 to about 17.7 parts by weight of potassium bichromate, about 0.5 to about 12.3 parts by weight of strontium chromate, about 0.9 to about 7.5 parts by weight of potassium silicofluoride, and about 0.4 to about 3.4 parts by weight of strontium sulfate.

15. A composition for use in making up and maintaining an aqueous chromic acid bath for chromium plating in the range of 100 to 500 grams per liter of CrO_3 , said composition comprising essentially about 1.6 to about 70 parts by weight of an alkali metal bichromate, about 0.5 to about 12.3 parts by weight of strontium chromate, about 0.9 to about 7.5 parts by weight of an alkali metal silicofluoride, about 0.4 to about 3.4 parts by weight of strontium sulfate, said alkali metal being selected from the class consisting of potassium and sodium.

16. A composition for use in making up and maintaining an aqueous chromic acid bath for chromium plating in the range of 100 to 500 grams per liter of CrO_3 , said composition comprising about 1.6 to about 17.7 parts by weight of an alkali metal bichromate, about 0.9 to about 7.5 parts by weight of an alkali metal silicofluoride, about 0.4 to about 4.2 parts by weight of strontium sulfate, said alkali metal being selected from the class consisting of potassium and sodium.

17. A composition for use in making up and maintaining an aqueous chromic acid bath for chromium plating in the range of 100 to 500 grams per liter of CrO_3 , said composition comprising essentially about 1.6 to about 70 parts by weight of sodium bichromate, about 0.5 to about 3.3 parts by weight of strontium chromate, about 1.0 to about 6 parts by weight of sodium silicofluoride, and about 0.4 to about 3 parts by weight of strontium sulfate.

18. A composition for use in making up and maintaining an aqueous chromic acid bath for chromium plating in the range of 100 to 500 grams per liter of CrO_3 , said composition comprising essentially about 0.6 to about 1.8 parts by weight of strontium chromate, about 1.5 to about 4.5 parts by weight of potassium silicofluoride, and about 0.6 to about 2.0 parts by weight of strontium sulfate.

19. An aqueous bath for chromium plating comprising essentially 100 to 500 g./l. of CrO_3 , two catalyst-supplying compounds, and a soluble non-catalytic compound, one of said catalyst-supplying compounds being strontium sulfate in an amount sufficient to saturate said bath and to provide an undissolved residue of strontium sulfate in the bath, the other of said catalyst-supplying compounds being an alkali metal silicofluoride in an amount sufficient to saturate said bath and to provide an undissolved residue of alkali metal silicofluoride in the bath, said alkali metal being selected from the class consisting of potassium and sodium, said non-catalytic compound being present in an amount sufficient to suppress the concentration of one of said catalyst-supplying compounds in solution in said bath

from the unsuppressed saturation concentration of the latter compound to a lower but greater than zero concentration, said non-catalytic compound being selected from the class consisting of a strontium compound and an alkali metal compound, and the alkali metal of said alkali metal compound being the same as the alkali metal of said alkali metal silicofluoride.

20. An aqueous bath for chromium plating comprising essentially 100 to 500 g./l. of CrO_3 , strontium sulfate in an amount sufficient to saturate said bath and to provide an undissolved residue of strontium sulfate in the bath, an alkali metal silicofluoride in an amount sufficient to saturate said bath and to provide an undissolved residue of alkali metal silicofluoride in the bath, said alkali metal being selected from the class consisting of potassium and sodium, a soluble non-catalytic strontium compound in an amount sufficient to suppress the concentration of the strontium sulfate in solution in said bath from the unsuppressed saturation concentration of the latter to a lower but greater than zero concentration, and a soluble non-catalytic alkali metal compound in an amount sufficient to suppress the concentration of the alkali metal silicofluoride in solution in said bath from the unsuppressed saturation concentration of the latter to a lower but greater than zero concentration, and the alkali metal of said non-catalytic compound being the same as the alkali metal of said alkali metal silicofluoride.

21. An aqueous bath for chromium plating comprising essentially 100 to 500 g./l. of CrO_3 , strontium sulfate in an amount sufficient to saturate said bath and to provide an undissolved residue of strontium sulfate in the bath, an alkali metal silicofluoride in an amount sufficient to saturate said bath and to provide an undissolved residue of alkali metal silicofluoride in the bath, said alkali metal being selected from the class consisting of potassium and sodium, a soluble non-catalytic strontium compound in an amount sufficient to suppress the concentration of the strontium sulfate in solution in said bath from the unsuppressed saturation concentration of the latter to a lower concentration, said lower concentration being in the range extending from said unsuppressed saturation concentration to about one-tenth of the unsuppressed saturation concentration, and a soluble non-catalytic alkali metal compound in an amount sufficient to suppress the concentration of the alkali metal silicofluoride in solution in said bath from the unsuppressed saturation concentration of the latter to a lower concentration in the range extending from said last-mentioned unsuppressed saturation concentration to about one-fourth thereof, and the alkali metal of said non-catalytic compound being the same as the alkali metal of said alkali metal silicofluoride.

22. A process of electrodepositing chromium comprising essentially passing current from an anode to an article-cathode immersed in an aqueous bath comprising essentially 100 to 500 g./l. CrO_3 , two catalyst-supplying compounds, and a soluble non-catalytic compound, one of said catalyst-supplying compounds being strontium sulfate in an amount sufficient to saturate said bath and to provide an undissolved residue of strontium sulfate in the bath, the other of said catalyst-supplying compounds being an alkali metal silicofluoride in an amount sufficient to saturate said bath and to provide an undissolved residue of alkali metal silicofluoride

13

in the bath, said alkali metal being selected from the class consisting of potassium and sodium, said non-catalytic compound being present in an amount sufficient to suppress the concentration of one of said catalyst-supplying compounds in solution in said bath from the unsuppressed saturation concentration of the latter compound to a lower but greater than zero concentration, said non-catalytic compound being selected from the class consisting of a strontium compound and an alkali metal compound, and the alkali metal of said alkali metal compound being the same as the alkali metal of said alkali metal silicofluoride.

23. A process of electrodepositing chromium comprising essentially passing current from an anode to an article-cathode immersed in an aqueous bath comprising essentially 100 to 500 g./l. CrO_3 , strontium sulfate in an amount sufficient to saturate said bath and to provide an undissolved residue of strontium sulfate in the bath, an alkali metal silicofluoride in an amount sufficient to saturate said bath and to provide an undissolved residue of alkali metal silicofluoride in the bath, said alkali metal being selected from the class consisting of potassium and sodium, a soluble non-catalytic strontium compound in an amount sufficient to suppress the concentration of the strontium sulfate in solution in said bath from the unsuppressed saturation concentration of the latter to a lower but greater than zero concentration, and a soluble non-catalytic alkali metal compound in an amount sufficient to suppress the concentration of the alkali metal silicofluoride in solution in said bath from the unsuppressed saturation concentration of the latter to a lower but greater than zero concentration, and the alkali metal of said non-catalytic compound being the same as the alkali metal of said alkali metal silicofluoride.

24. A process of electrodepositing chromium

14

comprising essentially passing current from an anode to an article-cathode immersed in an aqueous bath comprising essentially 100 to 500 g./l. CrO_3 , strontium sulfate in an amount sufficient to saturate said bath and to provide an undissolved residue of strontium sulfate in the bath, an alkali metal silicofluoride in an amount sufficient to saturate said bath and to provide an undissolved residue of alkali metal silicofluoride in the bath, said alkali metal being selected from the class consisting of potassium and sodium, a soluble non-catalytic strontium compound in an amount sufficient to suppress the concentration of the strontium sulfate in solution in said bath from the unsuppressed saturation concentration of the latter to a lower concentration, said lower concentration being in the range extending from said unsuppressed saturation concentration to about one-tenth of the unsuppressed saturation concentration, and a soluble non-catalytic alkali metal compound in an amount sufficient to suppress the concentration of the alkali metal silicofluoride in solution in said bath from the unsuppressed saturation concentration of the latter to a lower concentration in the range extending from said last-mentioned unsuppressed saturation concentration to about one-fourth thereof, and the alkali metal of said non-catalytic compound being the same as the alkali metal of said alkali metal silicofluoride.

JESSE E. STARECK.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,857,547	Humphries	May 10, 1932
2,040,881	Rojas	May 19, 1936
2,050,478	Wickenhiser	Aug. 11, 1936
2,095,995	Mardick	Oct. 19, 1937