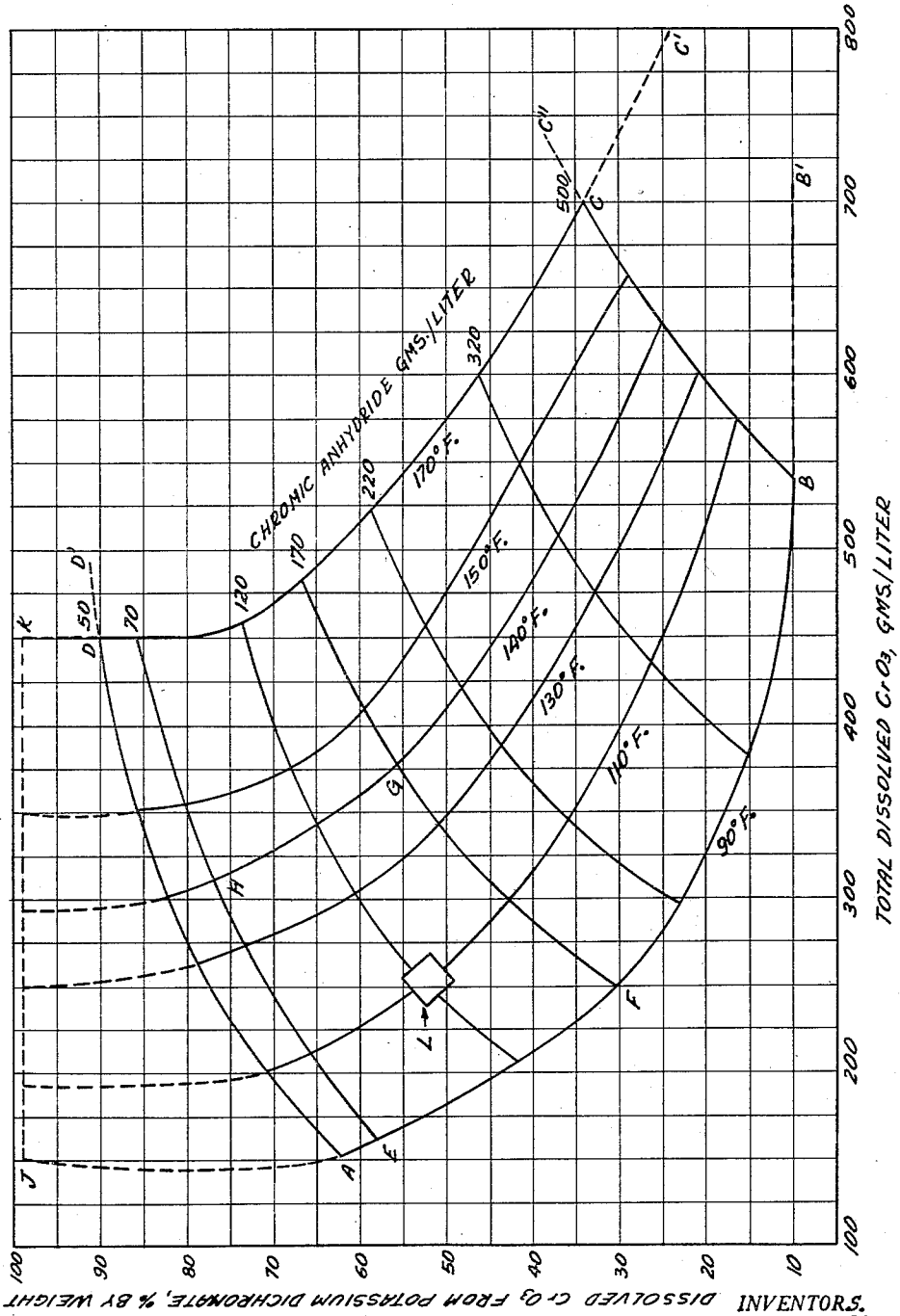
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CHROMIUM PLATING PROCESS AND BATH

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CHROMIUM PLATING PROCESS AND BATH

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This invention relates to chromium plating with a CrO_3-containing plating bath having sulfate and silicofluoride as mixed and cooperating catalysts which saturate the bath and whose concentrations are self-regulated.

More particularly, a portion of the total CrO_3 content is supplied by potassium dichromate, which also saturates the bath, so that the concentration of said portion of CrO_3 is self-regulated. The concentrations of the bath ingredients are thus self-regulated to a high degree. The bath is unusually constant in quantitative and qualitative composition over a substantial range of plating conditions, freeing the operator to a greater extent than heretofore possible of the necessity of closely watching the bath balance and of making frequent additions to maintain or correct the bath.

Over a substantial portion of its range of plating conditions the bath is characterized by having a ratio of CrO_3 to catalyst that is substantially constant, that is, it is substantially unaffected by changes in temperature and concentrations of CrO_3 and catalyst.

The bath is further characterized by exhibiting a substantially reduced tendency to etch an article being plated and by producing chromium plate of improved clarity and brightness, these effects being particularly apparent in the low current density plating range. Other advantages will appear hereinafter.

Generally speaking, the bath solution comprises chromic anhydride (CrO_3 per se), two catalyst-supplying compounds, namely, strontium sulfate and potassium silicofluoride, each having a limited solubility in the bath solution, and potassium dichromate. The strontium sulfate and potassium silicofluoride are each present in an amount sufficient to saturate the bath with dissolved catalytic sulfate and silicofluoride and to provide therein an undissolved residue of each compound. The potassium dichromate has several purposes or effects, one of which is to control the concentration of the dissolved silicofluoride in the bath by suppressing such concentration, the dissolved potassium dichromate acting by the common ion effect to decrease the solubility of the potassium silicofluoride. The concentrations of the dissolved sulfate and silicofluoride are the saturation concentrations, and both are self-regulated owing to the presence of undissolved residues of strontium sulfate and potassium silicofluoride in equilibrium therewith. The sulfate concentration, however, is normally the unsuppressed saturation concentration, while the silicofluoride has a suppressed saturation concentration.

While the use of strontium sulfate and potassium silicofluoride in saturating amounts is taught in U.S. Patents Nos. 2,640,021 and 2,640,022, and the suppression of the silicofluoride is taught in No. 2,640,022, these patents do not disclose the use of saturation concentrations of potassium dichromate and the effects thereof, as described below.

The potassium dichromate is present in an amount sufficient to saturate the bath and to provide therein an undissolved residue in equilibrium therewith; it provides concentrations of dissolved potassium and dissolved CrO_3 which not only saturate the bath but which are self-regulated. As described, the dissolved potassium is responsible for decreasing the solubility of the potassium silicofluoride, i.e., suppressing the concentration of the dissolved silicofluoride; while the dissolved CrO_3 constitutes a substantial portion of the total dissolved CrO_3 in the bath. The saturation concentration of the dissolved potassium has been found to be particularly suitable for controlling the concentration of the silicofluoride within desired limits.

As may therefore be apparent, the concentrations of the dissolved sulfate and silicofluoride are self-regulated, that of silicofluoride is suppressed by dissolved potassium whose concentration is also self-regulated, and the concentration of dissolved CrO_3 supplied by potassium dichromate is self-regulated, which in effect means that so long as undissolved dichromate is present, the total dissolved CrO_3 concentration is self-regulated. These automatically controlled concentrations mean that the bath is self-adjusting for drag-out of all essential ingredients: catalysts, CrO_3, and suppressor, providing a bath of unusual stability having wide application in chromium plating, particularly in barrel plating where high drag-out losses are encountered, and where, too, owing to the improved tolerance of the bath to concentration changes, less frequent correction is required. These advantages are generally realized in other applications of the bath.

The bath is frequently designated a chromic acid chromium plating bath, but since its chromium content is supplied by at least one other compound besides chromic acid (more accurately called chromic anhydride), the bath is referred to herein as a CrO_3-containing bath. Its CrO_3 content is supplied by CrO_3 per se, usually referred to as chromic anhydride or chromic acid, and by the amount of CrO_3 present in the dissolved potassium dichromate.

Numerically, the total concentration of dissolved CrO_3 in the bath solution may be about 150 to about 700 g./l. The concentration generally increases with the temperature, which may vary from room temperature to the boiling point of the solution, more particularly from 90 to 170° F. Of the total dissolved CrO_3, about 10 to about 90% by weight is supplied by potassium dichromate, and the balance is supplied as chromic anhydride. These quantities vary with respect to one another in the manner defined by the area ABCDA of the graph shown in the accompanying drawing. It is apparent from the graph that total dissolved CrO_3 increases with increasing chromic anhydride; at a given chromic anhydride concentration, and as temperature increases, total dissolved CrO_3 increases with increasing CrO_3 supplied by dichromate; and CrO_3 from dichromate increases with increasing temperature and decreases with increasing chromic anhydride. As also illustrated by the graph, the chromic anhydride ranges from 50 to 500 g./l.

The upper limit of 700 g./l. for the total dissolved CrO_3 is a preferred limit, as this quantity may range to 800 g./l. and more, provision for operation at the latter concentration levels being made by increasing the chromic anhydride concentration and/or increasing the temperature, and in such case it will be understood that for the overall range of 150 to 800 g./l. the area ABCDA will substantially define the relationships of the variables as before except that the line BC and/or the line DC will be disposed somewhat to the right of the position shown; thus, BC may assume a position joining the points B′ and C′, and DC may assume a position joining the points D′ and C″.

Operation is also possible when the dissolved CrO_3 supplied by potassium dichromate is as high as 99% by

weight of the total dissolved CrO_3, the balance of the latter being supplied by chromic anhydride; in this event it will be apparent that quantities of chromic anhydride less than 50 g./l., and going down, say, to about 5 g./l., will suffice. The broken or dash line JK identifies the limit of 99% by weight CrO_3 from dichromate, and the temperature lines are extended to it by broken lines. Thus, the overall range of dissolved CrO_3 from dichromate is about 10 to 99% by weight, and the preferred range is 10 to 90%. Operation is possible in the area ADKJA, but the more preferred area is ABCDA.

As noted, the amount of the potassium dichromate is always sufficient to saturate the bath and to produce an undissolved residue of the same. Preferably the dichromate is added to the bath per se; it may also be formed in situ in the bath by reaction between a bath-soluble CrO_3-containing compound and a bath-soluble potassium compound of a non-catalytic anion, these compounds being supplied in amounts that will provide potassium dichromate in excess of its solubility in the bath. The bath-soluble CrO_3-containing compound is selected from the group consisting of chromic anhydride and suitable CrO_3-containing compounds of a non-catalytic cation, such for example as chromic acid (H_2CrO_4) in solution, dichromic acid ($H_2Cr_2O_7$) in solution, etc. The bath soluble potassium compound of a non-catalytic anion may be potassium carbonate, potassium bicarbonate, potassium hydroxide, potassium chromate, etc.

Illustrative of the amount of potassium dichromate to be added to the bath solution is the observation that its saturation solubility at 110° F. in each of five aqueous solutions having dissolved therein, respectively, 100, 200, 300, 500, and 700 g./l. of chromic anhydride, is respectively about 199, 195, 191, 178, and 147 g./l. The amount of dichromate to be added to such solutions at 110° F., therefore, will always exceed these saturation solubilities so as to produce an undissolved residue of the dichromate in the solutions. The dichromate solubility increases with rising temperature, and vice versa, as indicated by the graph, so that this consideration must also be taken into account. These facts also apply when the dichromate is formed in situ.

For the broad ranges of CrO_3 and temperature noted above and as defined by the area ABCDA of the graph, the concentration of dissolved sulfate is the saturation concentration and that of dissolved silicofluoride is the suppressed saturation concentration. Numerically, the dissolved sulfate may vary from 1.16 to 2.60 g./l. and the dissolved silicofluoride from 0.25 to 1.81 g./l. Total catalyst varies from 1.5 to 4.5 g./l. It may be noted that the concentrations of both catalysts are low, particularly that of the silicofluoride. The low silicofluoride concentration is believed to contribute to the reduced etching tendency of the bath, and, together with the low proportion of silicofluoride to sulfate, is believed to contribute to the improved clarity and brightness of plate used for decorative applications.

The sulfate and silicofluoride are supplied in the form of strontium sulfate and potassium silicofluoride, as stated. The potassium silicofluoride is preferably provided per se. It may also be formed in situ in the bath by reaction between a bath-soluble silicofluoride-containing compound of a non-catalytic cation and a bath-soluble potassium compound of a non-catalytic anion, for example by the reaction between hydrofluosilicic acid or zinc silicofluoride and potassium carbonate. Similarly, strontium sulfate may be formed in situ but it is preferred to add it per se to the bath. Formation in situ of strontium sulfate and potassium silicofluoride is described in said Patent No. 2,640,021.

A preferred bath solution having more restricted concentrations than those described is one having a total dissolved CrO_3 concentration of about 150 to about 380 g./l. and operable at 90 to 140° F. About 30 to 77 percent by weight of the total dissolved CrO_3 is supplied by potassium dichromate, which saturates the bath and which is present in excess so as to provide an undissolved residue, and the balance is supplied by adding 70 to 170 g./l. of chromic anhydride. The relationship between these quantities is shown by the area EFGHE of the graph. The total catalyst is about 1.6 to about 3.6 g./l. dissolved sulfate concentration is 1.25 to 2.40 g./l., the dissolved, suppressed silicofluoride concentration is 0.30 to 1.20 g./l., and the silicofluoride/sulfate proportion is 0.22 to 0.55. With this bath it has been found that the ratio of total dissolved CrO_3 to the sum of dissolved sulfate plus ½ the dissolved silicofluoride, hereinafter referred to as the CrO_3/catalyst ratio, is substantially independent of changes in temperature and CrO_3 and catalyst concentrations. The ratio lies in the range of 115:1 to 140:1, and from a plating point of view a ratio that varies within this narrow range represents a substantially constant ratio. By virtue of its constant ratio, this preferred bath is well adapted to barrel plating.

The area on the graph designated by the arrow L represents an especially preferred bath solution operable at about 110° F. having a total dissolved CrO_3 concentration of about 250 to about 260 g./l. about 50 to 55% of the latter being supplied by potassium dichromate and about 120 g./l. being supplied as chromic anhydride. The total dissolved sulfate is about 1.68 to 1.94 g./l., the dissolved suppressed silicofluoride is 0.52 to 0.57 g./l., the silicofluoride-sulfate proportion is 0.29 to 0.31, and the CrO_3/catalyst ratio is 120:1 to 130:1. This bath composition is specially suitable for commercial operation because it employs the temperature and CrO_3 concentration ranges most normally used, and because of the constancy of the ratio, the latter having a value particularly adapted for barrel chromium plating.

In some cases the CrO_3/catalyst ratio may, if desired, be varied by the addition of a small amount of soluble strontium or soluble sulfate while still maintaining the sulfate concentration of the bath saturated and self-regulated. Addition of strontium increases the ratio by suppressing dissolved sulfate; and addition of sulfate decreases the ratio by providing additional dissolved sulfate. In both cases the addition can be made so as to maintain the total dissolved sulfate concentration of the bath both saturated and self-regulated. While the addition of sulfate involves the precipitation of some strontium as strontium sulfate, which may lead one to think that all the added sulfate will be so precipitated, actually it has been found that additional dissolved sulfate may be introduced to the bath so as to decrease the ratio. This procedure provides a convenient manner of changing the ratio, within limits, while retaining the property of self-regulation. In particular, the procedure is useful to extend the plating range of the bath. For example, by addition of sulfate, baths may be obtained having compositions more commonly used in hard chromium plating, that is, having a ratio range of 90:1 to 100:1, or a wider range of 70:1 to 100:1. As illustrated in Example 5, a bath having a ratio of 118:1 may be adjusted to a ratio of 92:1 or to a ratio of 221:1 in this way. The procedure applies to all the baths described herein, particularly to the preferred baths. The compound to be added to the bath should be more soluble therein than strontium sulfate and should provide a soluble ionic component of strontium sulfate. Suitable strontium compounds include strontium carbonate, strontium hydroxide, strontium chromate, strontium oxide, and strontium bichromate. Suitable sulfate compounds are sodium sulfate, sulfuric acid, ammonium sulfate, calcium sulfate, lithium sulfate, chromic sulfate, sodium bisulfate, etc. The amount of the sulfate compound can be as low as that equivalent to 0.1 g./l. strontium, and on the other hand it should be less than an amount which prevents the total dissolved sulfate from being self-regulated. When resort to this procedure is had, it is apparent that the sulfate concentration may be altered, so that the procedure con-

stitutes an exception to the general practice described above of not suppressing or altering the sulfate.

Where it is not desired to change the ratio, the bath is preferably maintained free of compounds acting to alter the concentration of the total dissolved sulfate.

The bath solution may be made up by adding, to a given volume of water, chromic anhydride, potassium silicofluoride, strontium sulfate, and potassium dichromate, each in the desired amount. The ingredients are preferably supplied in subdivided form, and stirring is used until equilibrium is obtained. Varying bath compositions may be made up by simply varying the amount of chromic anhydride and/or water, and an existing bath solution may be varied by adding chromic anhydride or water.

Current densities conventionally used in chromium plating are suitable, such for example as described in "Chromium Plating," by Morisset et al., published by Robert Draper Ltd., 1954, pages 351–363. Numerically, the current density may range from 0.2 a.s.i. (amperes per square inch) to 10 a.s.i., preferably from 0.2 to 6.0 a.s.i.

Conventional chromium deposits of any type can be plated, including decorative plate, hard plate, crack-free plate, and porous plate. The deposits may have varying thicknesses ranging from a thickness just sufficient to cover the pores of the basis metal to any practical desired thicker deposit for which a demand may exist.

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

The invention may be illustrated by the following examples. A brief explanation of some of the terms and abbreviations used in the examples may be given: "C.A." is chromic anhydride; "sulfate" is SO_4; "silicofluoride" is SiF_6; "catalyst proportion" or "cat. prop." is SiF_6SO_4; and "catalyst ratio" or "cat. ratio" is $CrO_3/SO_4+\frac{1}{2}SiF_6$.

EXAMPLE 1

This example illustrates mixtures for making bath solutions and the compositions of the latter, and it compares them with prior art mixtures and bath solutions.

A solid, finely divided mixture was made up consisting of 35.8% chromic anhydride, 59.7% potassium dichromate, 1.5% potassium silicofluoride, and 3.0% strontium sulfate, all on a weight basis. Two parts of the mixture were taken to prepare two aqueous solutions, Nos. 1 and 2. The equilibrium compositions of No. 1 at 90% F., and No. 2 at 110° F., are given below in Table 1.

Another solid, finely divided mixture was made up consisting of 27.6% chromic anhydride, 69% potassium dichromate, 1.1% potassium silicofluoride, and 2.3% strontium sulfate, weight basis. An aqueous solution, No. 3, was prepared with this mixture, and its equilibrium composition at 130° F. is given below.

Two other solid, finely divided mixtures each consisting of chromic anhydride, potassium dichromate, strontium chromate, potassium silicofluoride, and strontium sulfate, were added to water to provide Nos. P–1 and P–2, both of which were prior art commercial solutions having equilibrium compositions at 130° F. as noted in Table 1.

Of these solutions, Nos. 1, 2, and 3 illustrate the invention; in each of them potassium dichromate was present in excess of its solubility, the excess being greatest in No. 1 and least in No. 2; in Nos. P–1 and P–2, the prior art solutions, no excess potassium dichromate was present. All solutions were comparable to the extent that the catalysts were suplied by potassium silicofluoride and strontium sulfate and had saturated, self-regulated concentrations.

Table 1

Soln. No.	1	2	3	P-1	P-2
Temp., ° F.	90	110	130	130	130
Total Dissolved CrO_3, g./l.	205	247	302	225	175
Chromic Anhydride, g./l.	120	120	120	205	155
CrO_3 from Potassium Dichromate, percent of Total	41.4	51.5	60.4	9.1	13.2
Cat. Ratio	124:1	130:1	125:1	84:1	89:1

EXAMPLE 2

The etching action of a bath solution of the invention, corresponding to No. 3 of Example 1, is compared here with that of two prior art bath solutions, corresponding to Nos. P–1 and P–2 of Example 1. All baths were operated at 130° F. In each case, a weighed unetched steel strip, having an exposed area of 6 sq. in. was used as cathode, and a low current density was applied for 1 hour, after which the strip was removed, washed, dried, and weighed to determine the loss in weight. Tests were run throughout the current density range of maximum etch (up to 0.05 a.s.i.) and also up to 0.10 a.s.i. Substantially identical, unetched steel strips were used for all runs. The results are tabulated in Table 2, the loss of weight of the strips being reported as grams per hour of applied current per 6 square inches of metal surface.

Table 2

Soln. No.	Current Density, a.s.i.	Loss of Weight of Metal, g./hr./6 sq. in.
3	0.034	0.0375
	.05	.05
	.05	.0625
	.10	.069
P-1	.015	.344
	.031	.3625
	.05	.356
	.10	.3875
P-2	.0125	.381
	.031	.381
	.05	.256
	.10	.269

As is apparent, the etching produced by solution No. 3 is substantially less than that produced by the other two solutions; at 0.05 a.s.i., for example, the etching was reduced to only 14% to 24% of that in the other solutions.

EXAMPLE 3

This example demonstrates the reduced tendency of the catalyst ratio to change with changes in temperature. Three bath solutions, Nos. 4, P–3 and P–4 were made up each having a total dissolved CrO_3 content of 200 g./l. at 90° F. Solution No. 4 had chromic anhydride and excess amounts of potassium dichromate, strontium sulfate, and potassium silicofluoride; its composition was within the limits of the invention, and it was prepared in a manner similar to Nos. 1, 2 and 3 of Example 1. Nos. P–3 and P–4 were prior art commercially used bath solutions, had excess amounts of strontium sulfate and potassium silicofluoride but not of potassium dichromate, and were prepared from mixtures like those used for Nos. P–1 and P–2 of Example 1. The catalyst ratio was determined for each solution at 90°, 110° and 130° F. and is given in Table 3. The total CrO_3 concentration for Nos. P–3 and P–4 remained at 200 g./l. at each temperature, but that for No. 4 increased to 250 g./l. at 110° and to 300 g./l. at 130°.

Table 3

Temp., ° F.	90	110	130
Cat. Ratio:			
No. 4	124:1	130:1	125:1
No. P-3	134:1	98:1	72:1
No. P-4	240:1	151:1	90:1

It is evident that the ratio for No. 4 was substantially constant throughout the temperature interval while that for the other solutions varied considerably.

EXAMPLE 4

The reduced tendency of the catalyst ratio to change with changes in total dissolved CrO_3 concentration is shown here. Three bath solutions, Nos. 5, P–3 and P–5 were used, each having a total dissolved CrO_3 content of 200 g./l. at 90° F. Solution No. 5, illustrating the invention, was prepared similarly to Nos. 1, 2 and 3 of Example 1. Solution No. P–3 corresponds to No. P–3 of Example 3, while No. P–5 was a commercially used bath solution similar to Nos. P–1 and P–2 of Example 1 except for its higher ratio. The catalyst ratio was determined for each solution in the as-prepared state or "low" CrO_3 concentration level, and also after additions of chromic anhydride to produce "medium" and "high" concentrations. The additions are apparent from Table 4, but it may be noted here that for No. 5 the addition to the low concentration solution was 40 g./l. and that to the medium concentration solution was 34 g./l.; for No. P–3 the corresponding additions were 50 g./l. and 50 g./l.; and for No. P–5 the additions were 25 g./l. and 25 g./l. All determinations were made at 110° F. The terms "low," "medium," and "high" are relative, being used for convenience in identifying the concentrations.

Table 4

Soln. No.	Low Concn.		Medium Concn.		High Concn.	
	CrO_3, g./l.	Cat. Ratio	CrO_3, g./l.	Cat. Ratio	CrO_3, g./l.	Cat. Ratio
5	207	129:1	247	130:1	281	132:1
P–3	200	98:1	250	134:1	300	182:1
P–5	175	112:1	200	136:1	225	162:1

As shown, the ratio for No. 5 was substantially constant throughout the additions while that for Nos. P–3 and P–5 varied considerably.

EXAMPLE 5

There is illustrated in this example the manner in which the catalyst ratio may be varied by the addition of soluble strontium or soluble sulfate while still maintaining the bath saturated and self-regulated with respect to the sulfate concentration.

A bath solution was made up containing 120 g./l. chromic anhydride, 200 g./l. potassium dichromate, 5 g./l. potassium silicofluoride, and 10 g./l. strontium sulfate. The last three compounds were present in excess of their solubilities. The solution, which may be designated the original solution (it corresponds to No. 2 of Example 1), was then divided into five equal parts to form solutions Nos. 6, 7, 8, 9, and 10. No. 8 was used as a control, and its composition, determined at 110° F. and noted below in Table 5, represents that of the original solution. To No. 7 there was added 1.0 g./l. of strontium in the form of strontium carbonate, and similarly, 3.0 g./l. of strontium was added to No. 6. To Nos. 9 and 10 were added 0.5 and 1.0 g./l., respectively, of sulfate, added as sodium sulfate. The composition of each solution was determined at 110° F. and is set forth in Table 5.

Table 5

Soln. No.	6	7	8	9	10
Strontium added, g./l.	3.0	1.0			
Sulfate added, g./l.				0.5	1.0
Total Dissolved CrO_3, g./l.	261	258	256	256	256
Total Sulfate, g./l.	0.90	1.44	1.90	2.16	2.49
Silicofluoride, g./l.	0.53	0.57	0.57	0.56	0.57
Catalyst Proportion	0.59	0.40	0.30	0.26	0.23
Catalyst Ratio	221:1	160:1	118:1	105:1	92:1

As is apparent, the ratio increases with the addition of soluble strontium and decreases with addition of soluble sulfate. If the ratios are plotted as ordinates against the strontium additions as abscissas, and if the sulfate additions are expressed stroichiometrically as the negative equivalent of the strontium additions so that a continuous abscissa is present ranging from about minus 1.0 g./l. of added strontium through 0 g./l. and up to 3.0 g./l., it will be found that a continuous curve is obtained. This curve is essentially linear in this range and shows that for each 0.3 g./l. increase or decrease in added strontium, the ratio respectively increases or decreases by approximately 10 units.

EXAMPLE 6

The effect of temperature as well as total dissolved CrO_3 and chromic anhydride concentration, are demonstrated herein. Several solutions of varying chromic anhydride concentration were prepared, equilibrated at 90° F. for several hours, and then analyzed. Similarly, other solutions were prepared and analyzed at progressively higher temperature levels. The analyses of these solutions, numbered from 11 to 28, are shown in Table 6.

Table 6

Soln. No.	Temp., ° F.	C.A., g./l.	Total Dissolved CrO_3, g./l.	CrO_3 from Pot. Dichrom., percent	Sulfate, g./l.	Siloco-Fluoride, g./l.	Cat. Prop.	Cat. Ratio
11	90	50	153	67.4	1.16	0.25	0.22	119
12	90	70	167	58.0	1.27	0.29	0.23	118
13	90	120	205	41.4	1.46	0.37	0.25	124
14	90	170	248	31.5	1.56	0.41	0.26	141
15	90	220	280	21.4	1.68	0.61	0.36	138
16	90	320	380	15.8	1.63	0.58	0.36	192
17	110	120	264	54.5	1.94	0.57	0.29	119
18	110	220	346	36.5	2.09	0.66	0.32	143
19	110	320	445	28.0	2.01	0.69	0.34	188
20	130	120	306	60.8	2.06	0.73	0.36	126
21	130	220	385	43.0	2.26	0.84	0.37	144
22	130	320	479	33.2	2.23	0.90	0.40	178
23	150	120	376	68.2	2.24	1.08	0.48	135
24	150	220	464	52.7	2.48	1.23	0.45	150
25	150	320	555	42.5	2.41	1.17	0.48	185
26	170	120	456	73.5	2.25	1.81	0.80	145
27	170	220	526	58.2	2.56	1.63	0.64	156
28	170	320	605	47.2	2.55	1.76	0.69	177

Besides the relationships apparent from the graph, several others of broad applicability involving dissolved bath ingredients, temperature, and other factors may be noted in connection with Example 6.

As the temperature increases, the total catalyst concentration increases, including both the sulfate and silicofluoride. Through the temperature range of 90 to 170° F., total catalyst may increase from about 1.5 to about 4.5 g./l., sulfate increases from about 1.16 to 2.60 g./l., silicofluoride from about 0.25 to 1.81 g./l., and the silicofluoride-sulfate proportion from 0.22 to 0.80.

With increasing total dissolved CrO_3 from 150 to 605 g./l., or to the higher concentration of 800 g./l., total catalyst, sulfate, silicofluoride, and the silicofluoride-sulfate proportion gradually increase within the general limits noted in the preceding paragraph.

As chromic anhydride increases in the range noted in Table 6, or in the wider range of 50 to 500 g./l., total catalyst increases gradually until the anhydride has a value of about 320–350 g./l. and beyond that tends to remain constant or decline a little. Sulfate and silicofluoride each increases to an anhydride value of about 220–350 g./l. and then each decreases, the silicofluoride increase and decrease tending to be more gradual than sulfate. The silicofluoride-sulfate proportion tends to be fairly constant. The general limits of these various catalyst quantities are as noted above.

Catalyst ratio generally increases with increasing total dissolved CrO_3 concentration, and as indicated in Table 6, the increase in ratio tends to be greater at the lower temperatures. At a given temperature, the ratio increases with chromic anhydride and with total dissolved CrO_3. At a chromic anhydride concentration level of 120 g./l., the ratio increases with temperature, and this is true at a concentration level of 220 g./l., the ratio values for both levels varying between 119:1 and 156:1, which, as indicated, represents a substantially constant ratio from a plating point of view; at 320 g./l. the ratio decreases from 192:1 to 177:1 as temperature increases; it is thus apparent that intermediate the 220 and 320 g./l. levels the ratio is exactly constant as temperature increases. Such exact constancy of ratio with increasing temperature is unique as well as useful.

The preferred ratios have been described above as extending up to about 140:1; these ratios are not only well adapted for barrel plating but also they favor the plating of crack-free deposits, and porous chromium deposits. In some cases a ratio as high as 200:1 is useful, as for plating chromium on copper, for example; and ratios up to about 250:1 are applicable with some basis metals such as copper, brass, or zinc. In general the useful ratios are those below 250:1, and as will be understood, the baths described herein will be made up and operated at such ratios. At the other end, ratios of about 100:1 and up are practical, as are those below about 100:1, obtainable by addition of a soluble sulfate-containing compound as described.

The baths not only have the advantages of prior baths of self-regulated catalyst contents, such as good current efficiency and plating speed, wide plating range, good covering power, activating effect in plating over passive nickel, leveling action, and smooth deposits, but they also provide control of the CrO_3 and suppressor potassium contents owing to the presence of excess potassium dichromate. The control of the catalyst, CrO_3 and suppressor potassium concentrations is inherent because as long as excess ingredients are present, these concentrations are self-regulated by virtue of the solubility characteristics of the ingredients. The baths are simple in composition, thus at a given temperature there are only two variable component concentrations, water and chromic anhydride; and they are simple in operation, behaving much like a solution of one ingredient in their stability to temperature and concentration changes, because from a chromium plating point of view, apart from the temperature variable, there is only one composition variable, the chromic anhydride.

The baths are quite appropriate for barrel plating, where drag-out is a special problem, because of the insensitivity of the bath composition to temperature and concentration changes. The usefulness of the baths in applications where drag-in is present has been noted; drag-in may occur in several ways, as in plating processes that include a sulfuric acid treatment, or where the parts to be plated are of a type characterized by high drag-in. A somewhat reduced spray loss is realized by the use of excess amounts of potassium dichromate. An advantageous application of the mixture used to prepare the baths is as an addition agent for certain existing baths to help produce brighter and clearer plate, particularly in low current density plating ranges.

In the light of the foregoing description, the following is claimed:

1. An improved method of electrodepositing chromium on a metal article by means of an aqueous CrO_3-containing, catalyst-containing, chromium plating bath, said method being characterized by having a CrO_3/catalyst ratio in said bath which has a substantially reduced tendency to change with changes in CrO_3 and catalyst concentrations and temperatures, which comprises essentially: passing current from an anode to said article as a cathode immersed in said bath at a temperature of 90 to 140° F.; said bath containing a total of dissolved CrO_3 of about 150 to about 380 g./l., strontium sulfate and potassium silicofluoride as catalyst-supplying compounds each in an amount sufficient to saturate said bath with dissolved catalytic sulfate and silicofluoride, respectively, and to provide therein an undissolved residue of each compound, and potassium dichromate as a non-catalytic, silicofluoride-suppressing, CrO_3- and potassium-supplying compound; said potassium dichromate being present in an amount in excess of its solubility in the bath and providing: (1) an undissolved residue thereof in said bath, (2) a portion of said total dissolved CrO_3 equal to about 30 to about 77 by weight of said total, and (3) an amount of dissolved potassium to suppress the concentration of the dissolved silicofluoride; the concentration of said portion of dissolved CrO_3 being self-regulated owing to the presence of said undissolved residue of potassium dichromate, said suppressed silicofluoride concentration being self-regulated owing to the presence of said undissolved residue of potassium silicofluoride, said dissolved potassium concentration being self-regulated by virtue of the presence of said undissolved residues of potassium silicofluoride and potassium dichromate, and said dissolved sulfate concentration being self-regulated owing to the presence of said undissolved residue of strontium sulfate; 70 to 170 g./l. of said total dissolved CrO_3 being supplied as chromic anhydride; the relationship between said temperature, said chromic anhydride, said total and said portion of dissolved CrO_3 being variable in the manner defined by the area EFGHE of the graph shown in the accompanying drawing; and the ratio of total dissolved CrO_3 to the sum of dissolved sulfate plus ½ the dissolved silicofluoride being in the range of 115:1 to 140:1.

2. The method of claim 1 wherein said dissolved suppressed silicofluoride concentration is about 0.30 to about 1.20 g./l., said dissolved sulfate concentration is about 1.25 to about 2.40 g./l., and wherein the proportion of dissolved suppressed silicofluoride to dissolved sulfate is in the range of 0.22 to 0.55 and increases in said range with increasing temperature.

3. The method of claim 1 wherein said CrO_3/catalyst ratio is decreased below 115:1 by adding a soluble sulfate compound to the bath in an amount to maintain the total dissolved sulfate concentration both saturated and self-regulated, said soluble sulfate compound having a greater solubility in the bath than said strontium sulfate.

4. The method of claim 1 wherein said CrO_3/catalyst ratio is increased above 140:1 by adding a soluble strontium compound to the bath to suppress the dissolved sulfate concentration, the amount of said soluble strontium compound being such as to maintain the total dissolved sulfate concentration both saturated and self-regulated, said soluble strontium compound having a greater solubility in the bath than said strontium sulfate.

5. The method of claim 1 wherein said bath is free of compounds acting to alter the concentration of dissolved sulfate.

6. An improved method of electrodepositing chromium on a metal article by means of an aqueous CrO_3-contain-

ing, catalyst-containing, chromium plating bath, said method being characterized by having a CrO_3/catalyst ratio in said bath which has a substantially reduced tendency to change with changes in CrO_3 concentration and temperature, which comprises essentially passing current from an anode to said article as a cathode immersed in said bath at a temperature between room temperature and the boiling point of the bath solution; said bath containing dissolved CrO_3 and, strontium sulfate and potassium silicofluoride as catalyst-supplying compounds each in an amount sufficient to saturate said bath with dissolved catalytic sulfate and silicofluoride respectively and to provide therein an undissolved residue of each compound, and potassium dichromate as a non-catalytic, silicofluoride-suppressing, CrO_3- and potassium-supplying compound; said potassium dichromate being present in an amount: (1) in excess of its solubility in the bath thereby providing an undissolved residue thereof in the bath, (2) to provide dissolved potassium for suppressing said dissolved silicofluoride saturation concentration, and (3) to provide a portion of said dissolved CrO_3 in the bath; said dissolved potassium and suppressed silicofluoride concentrations being self-regulated by virtue of the presence of said undissolved residues of potassium dichromate and potassium silicofluoride, said portion of dissolved CrO_3 being self-regulated owing to the presence of said undissolved residue of potassium dichromate, and said dissolved sulfate concentration being self-regulated owing to the presence of said undissolved residue of strontium sulfate; the balance of said dissolved CrO_3 being supplied as chromic anhydride.

7. The method of claim 6 wherein said CrO_3/catalyst ratio is decreased by adding a soluble sulfate compound to the bath in an amount to maintain the total dissolved sulfate concentration both saturated and self-regulated, said soluble sulfate compound having a greater solubility in the bath than said strontium sulfate.

8. The method of claim 6 wherein said CrO_3/catalyst ratio is increased by adding a soluble strontium compound to the bath to suppress the dissolved sulfate concentration, the amount of said soluble strontium compound being such as to maintain the total dissolved sulfate concentration both saturated and self-regulated, said soluble strontium compound having a greater solubility in the bath than said strontium sulfate.

9. An improved method of electrodepositing chromium on a metal article by means of an aqueous CrO_3-containing, chromium plating bath, which comprises essentially: passing current from an anode to said article as a cathode immersed in said bath at a temperature of 90 to 170° F.; said bath containing a total of dissolved CrO_3 of about 150 to about 700 g./l., strontium sulfate and potassium silicofluoride as catalyst-supplying compounds each in an amount sufficient to saturate said bath with dissolved catalytic sulfate and silicofluoride, respectively, and to provide therein an undissolved residue of each compound, and potassium dichromate; said potassium dichromate being present in an amount in excess of its solubility in the bath and providing: (1) an undissolved residue thereof in said bath, (2) a portion of said total dissolved CrO_3 equal to about 10 to about 90% by weight of said total, and (3) an amount of dissolved potassium to suppress the concentration of the dissolved silicofluoride; said suppressed silicofluoride and dissolved potassium concentrations being self-regulated by virtue of the presence of said undissolved residues of potassium silicofluoride and potassium dichromate, the concentration of said portion of dissolved CrO_3 being self-regulated owing to the presence of said undissolved residue of potassium dichromate, and said dissolved sulfate concentration being self-regulated owing to the presence of said undissolved residue of strontium sulfate; 50 to 500 g./l. of said total dissolved CrO_3 being supplied as chromic anhydride; the relationship between the temperature, the total and said portion of dissolved CrO_3, and the chromic anhydride being variable in the manner defined by the area ABCDA of the graph shown in the accompanying drawing; and the ratio of total dissolved CrO_3 to the sum of dissolved sulfate plus ½ the dissolved silicofluoride being below about 250:1.

10. An improved method of electrodepositing chromium on a metal article by means of an aqueous CrO_3-containing, chromium plating bath, which comprises essentially: passing current from an anode to said article as a cathode immersed in said bath at a temperature of 90° F. to the boiling point of the bath solution; said bath containing a total of dissolved CrO_3 of about 150 to about 800 g./l., strontium sulfate and potassium silicofluoride as catalyst-supplying compounds each in an amount sufficient to saturate said bath with dissolved catalytic sulfate and silicofluoride, respectively, and to provide therein an undissolved residue of each compound, and potassium dichromate; said potassium dichromate being present in an amount in excess of its solubility in the bath and providing an undissolved residue thereof in said bath and a portion of said total dissolved CrO_3 equal to about 10 to about 99% by weight of said total, said potassium dichromate also providing dissolved potassium to suppress the saturation concentration of the dissolved silicofluoride; the concentrations of said dissolved sulfate, said portion of dissolved CrO_3, said suppressed silicofluoride, and said dissolved potassium being self-regulated; the balance of said total dissolved CrO_3 being supplied as chromic anhydride; said temperature, said total and said portion of dissolved CrO_3, and said chromic anhydride varying substantially in the manner defined by the area ABCDKJA of the graph shown in the accompanying drawing; and the ratio of total dissolved CrO_3 to the sum of dissolved sulfate plus ½ the dissolved silicofluoride being below about 250:1.

11. The method of claim 10 wherein said CrO_3/catalyst ratio is varied by adding to the bath a compound more soluble therein than said strontium sulfate and containing a soluble ionic component of strontium sulfate, the amount of said compound being such as to maintain the total dissolved sulfate concentration of the bath both saturated and self-regulated.

12. The method of claim 11 wherein said CrO_3/catalyst ratio is decreased by adding a soluble sulfate compound to the bath to increase the total dissolved sulfate concentration.

13. The method of claim 11 wherein said CrO_3/catalyst ratio is increased by adding a soluble strontium compound to the bath to suppress the dissolved sulfate concentration.

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