July 1, 1958 R. C. SMITH 2,841,540

CHEMICAL COMPOSITION FOR CHROMIUM PLATING

Filed Oct. 28, 1955 4 Sheets-Sheet 1

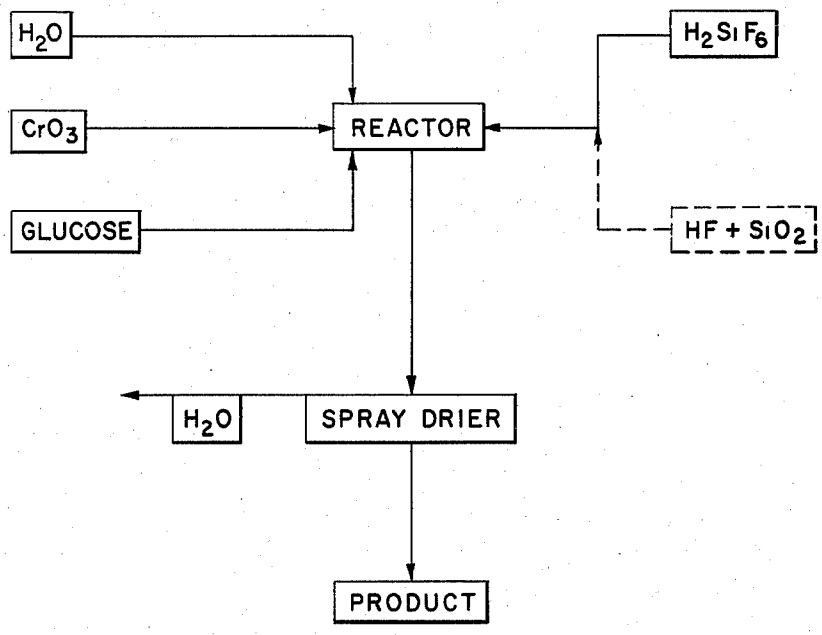


FIG. 1

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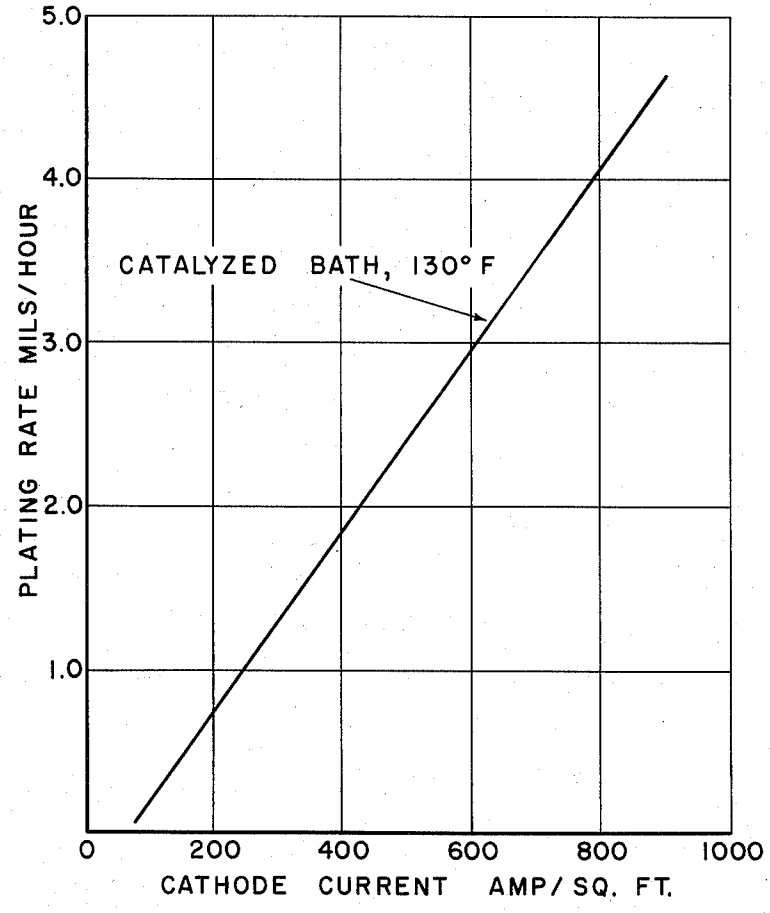


FIG. 2

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CHEMICAL COMPOSITION FOR CHROMIUM PLATING

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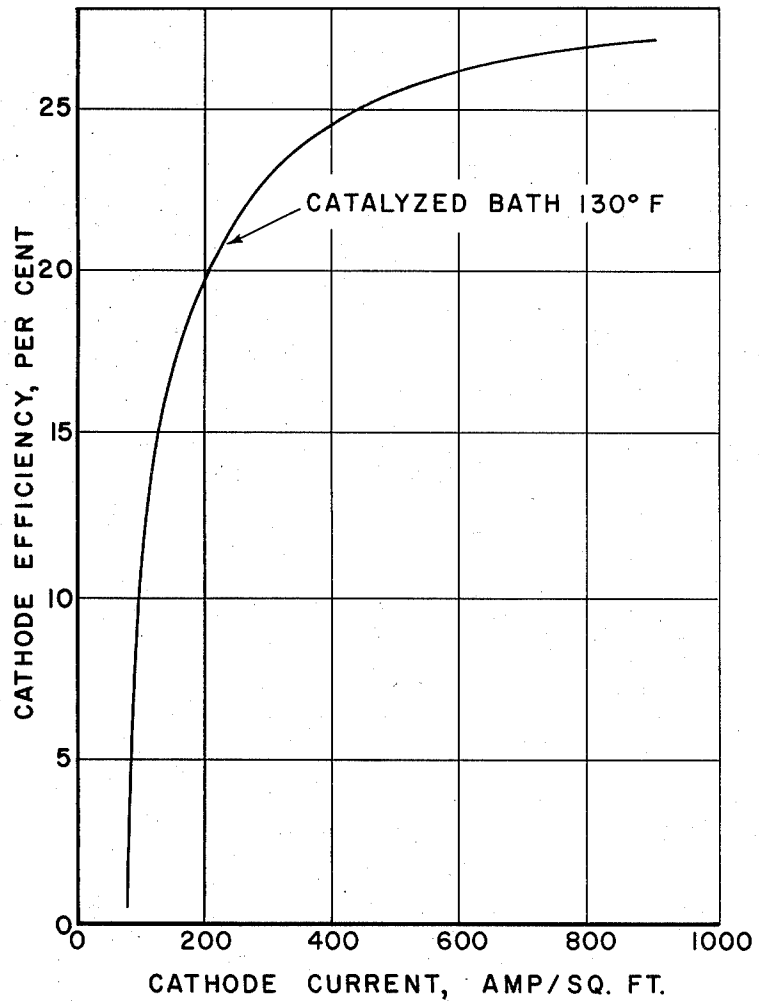


FIG. 3

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CHEMICAL COMPOSITION FOR CHROMIUM PLATING

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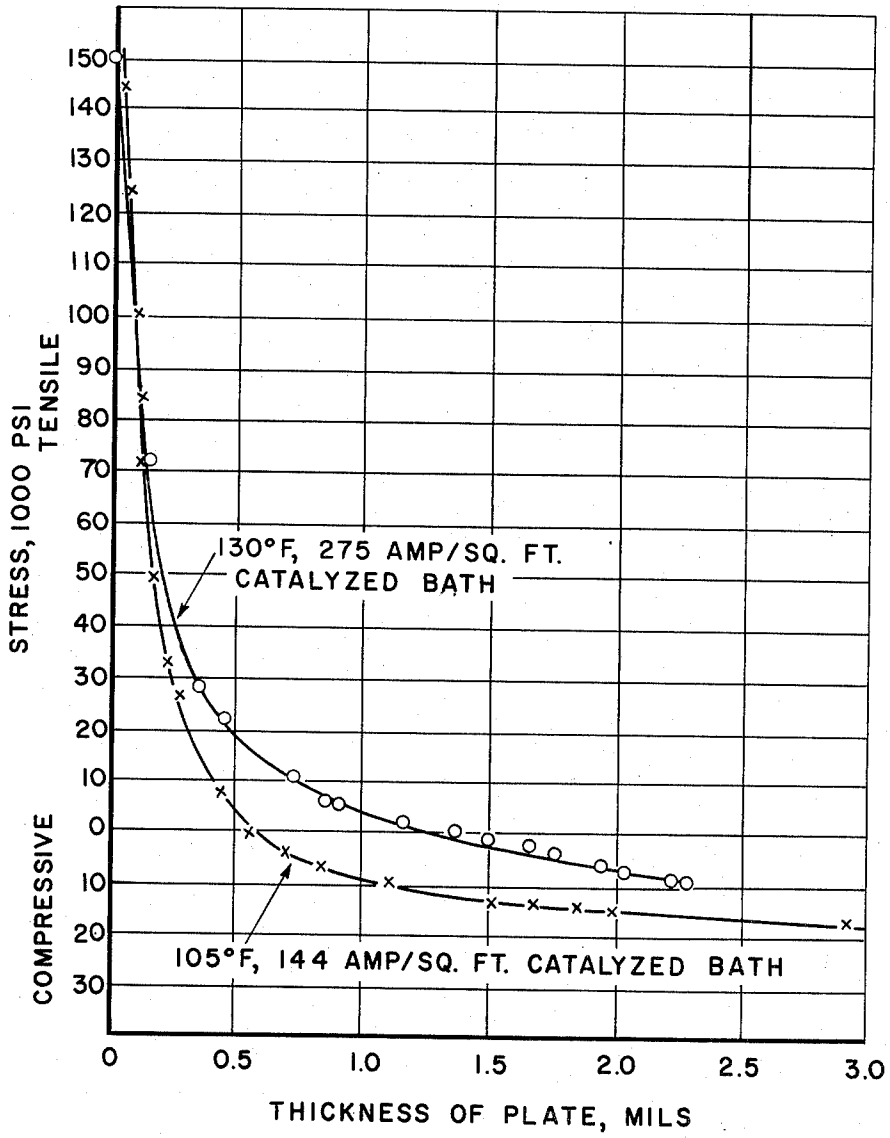


FIG. 4

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United States Patent Office 2,841,540 Patented July 1, 1958

2,841,540

CHEMICAL COMPOSITION FOR CHROMIUM PLATING

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Application October 28, 1955, Serial No. 543,354

11 Claims. (Cl. 204—51)

This invention relates to improvements in the electrodeposition of chromium and more particularly relates to a new and improved catalyst for addition to an aqueous chromium electrolyte and to the preparation and use of such a catalyst in the electro-deposition of chromium.

THE PRIOR ART

Although numerous chromium plating baths have heretofore been proposed and used, in many instances chromium remains as one of the most difficult metals to electrodeposit satisfactorily. This difficulty is due, in part at least, to the necessity of reducing chromium from the hexavalent state to the free metal. In an effort to improve the efficiency of chromium plating, aqueous chromium electrolytes have been proposed and used wherein chromium is present in a trivalent form. Although chromium can be electrodeposited from a so-called "trivalent bath" with a lower current consumption than is required in electrodeposition from a hexavalent chromium bath, the quality of the electrodeposits in many cases, up to this time, has not been entirely satisfactory.

Moreover, as in the case of plating from prior chromium baths, the deposited chromium frequently has been characterized by a dull appearance and rather poor adherence unless precautions are taken in controlling a number of variables, such as temperature, current density, agitation, and concentration of reagents, within relatively narrow limits which frequently are difficult to maintain in practice.

Up to this time, chromium has generally been deposited from a so-called "conventional bath" which consists of chromic acid (CrO_3) and sulfuric acid, these materials being present in amounts to provide a chromic acid: sulfate ratio from about 50:1 to about 150:1. Accordingly, the expression "conventional bath," as used hereinafter, is intended to refer to such an electrolyte and, in most instances, refers specifically to an aqueous solution consisting of chromic acid and sulfuric acid present in amounts to provide a chromic acid:sulfate ratio of about 100:1.

While conventional chromium plating solutions have long been employed in the electroplating industry and, at times, produce satisfactory electrodeposits, these baths generally have been characterized by relatively poor throwing power, low plating speed and low current efficiency, and have required rather close control to produce bright and adherent chromium electrodeposits.

OBJECTS OF THIS INVENTION

It is, therefore, a principal object of this invention to avoid the difficulties heretofore encountered in the electro-deposition of chromium and to provide an improved chromium plating solution.

It is a further object of this invention to provide a new and improved catalyst for an aqueous chromium electrolyte from which chromium electrodeposits characterized by improved brightness, smoothness, and other desirable properties can readily be obtained.

A further object of the invention is to provide a chromium electrolyte having improved throwing power, covering power, current efficiency, and other desirable properties.

It is a still further object of this invention to provide a chromium plating solution and catalyst therefor from which chromium electrodeposits of increased hardness may be obtained.

A still further object of this invention is to provide a chromium plating catalyst which may be added to conventional chromium plating baths to improve both the operating characteristics and the quality of the chromium electrodeposited therefrom.

These and other objects and advantages of the invention will appear more fully from the following description thereof.

Referring now briefly to the accompanying drawings which will be discussed in detail hereinafter:

Fig. 1 schematically illustrates the preparation of a catalyst in accordance with this invention;

Fig. 2 is a graph illustrating the plating rate at varying current densities obtained by the practice of this invention:

Fig. 3 is a graph illustrating the cathode efficiencies at varying current densities obtained by the practice of the present invention; and

Fig. 4 is a graph demonstrating the stress characteristics of chromium electrodeposited in accordance with the practice of this invention.

THE PRESENT INVENTION

It has now been discovered that by employing, as an aqueous electrolyte for chromium electrodeposition, a solution containing, in combination (1) chromium ions, (2) anions of an inorganic acid, and (3) a catalyst of this invention, a chromium electrodeposit characterized by improved corrosion resistance, hardness, and brightness, in addition to other desirable properties, is obtained. Moreover, electrodeposition from the foregoing plating solution is characterized by improved throwing power, current efficiency, and covering power over wider temperature and current density ranges than heretofore generally believed practicable.

THE CATALYST OF THIS INVENTION

The catalyst of this invention may be added to a conventional chromium electrolyte, at times preferably, although not necessarily, in lieu of a portion of the inorganic acid previously employed, or to another chromium electrolyte, comprises the product obtained by combining and reacting (1) a chromium compound, preferably a chromium oxide, such as CrO_3 (chromic acid) (2) an organic reducing agent, and (3) at least one substance selected from the group consisting of (*a*) fluosilicic acid and (*b*) the reaction product of hydrogen fluoride, preferably an aqueous hydrofluoric acid solution with silicon dioxide.

STRUCTURE OF THE CATALYST

The precise composition of the catalyst embodying the invention will, of course, vary somewhat, depending on the relative proportions of organic reducing agent, chromic acid and fluosilicic acid, or hydrogen fluoride-silicon dioxide reaction product, employed, as well as the temperatures, reaction times, and other process conditions utilized. Moreover, the resultant catalyst has not thus far been found subject to characterization as a precise chemical structure but has been established as a reproducible complex material containing silicon, chromium and fluorine.

As indicated above, while the catalyst composition will vary somewhat, depending on several factors,

catalysts embodying this invention generally may be termed as complex silicon-chromium-fluorine-containing materials wherein these constituents are present in amounts within the following ranges, the numbers indicating proportions in terms of percent by weight of the total catalyst:

Chromium	23–28
Silicon	2.5–7.75
Fluorine	24–36

Illustrative of specific catalyst compositions in accordance with this invention wherein the quantities are expressed in terms of percent by weight of the total catalyst, are the following:

Catalyst No.	Chromium	Silicon	Fluorine
1	26.8	6.36	30.2
2	28.2	6.45	35.0
3	27.4	5.8	31.9
4	27.5	5.73	32.4
5	25.5	4.17	30.6
6	26.1	5.16	33.0
7	23.5	4.23	25.7
8	23.2	2.58	27.5
9	24.7	4.88	31.6
10	24.7	5.24	32.3
11	23.9	6.40	28.9
12	23.9	3.94	30.3
13	23.0	3.00	36.4
14	24.6	7.58	32.4
15	23.6	7.20	33.1
16	23.6	4.99	29.5
17	28.0	7.23	33.6
18	23.7	7.12	23.9
19	27.0	4.89	26.7
20	23.0	7.75	31.7
21	22.9	7.42	30.1
22	23.3	6.54	27.1
23	23.9	5.97	25.5
24	26.3	4.14	24.9
25	27.2	4.83	27.7
26	28.0	4.58	25.1
27	27.2	4.47	25.1

PREPARATION OF A CATALYST OF THE INVENTION

Referring now to the accompanying drawing, Fig. 1 illustrates the generally preferred method of producing a catalyst of this invention.

As there shown, suitable amounts of water, chromium trioxide and an organic reducing agent, such as glucose, are introduced into a reactor along with the proper amount of fluosilicic acid or, alternatively, the reaction product of hydrogen fluoride and silicon dioxide. From this reactor there is obtained a catalyst-water slurry which preferably, as indicated, is spray-dried to remove water and to obtain a finely-divided granular product.

Generally, as indicated, the preparation of a catalyst embodying this invention involves combining (1) chromium trioxide (chromic acid), (2) fluosilicic acid, and (3) an organic reducing agent, portions of the organic reducing agent preferably, although not necessarily, being separately pre-mixed with the chromium trioxide and fluosilicic acid, respectively, these separate materials then being combined to obtain a catalyst-water mixture which may either be employed as such or, preferably, spray-dried to obtain a dry, granular material.

More specifically, a preferred method of preparing a catalyst of this invention comprises combining chromium trioxide with water and a reducing agent in an amount insufficient completely to reduce all of the hexavalent chromium to the trivalent form, thus forming a first solution. A second solution is then prepared by combining fluosilicic acid, the commercially available acid, or, if desired, the product prepared by reacting hydrogen fluoride and silicon dioxide, the latter preferably being in a finely-divided state, with sufficient of the same or a different reducing agent to effect complete reduction of the chromium trioxide originally present in the first solution.

This second solution is then combined with the first solution in any suitable reactor, typically glass-lined, provided with agitation and heating means. As indicated above, the thus-formed catalyst-water mixture may, in certain applications, be employed without further treatment. However, in most cases it is desirable to obtain a dry granular product which advantageously can be accomplished by spray-drying the liquid catalyst mixture at an elevated temperature to obtain a finely-divided material.

Considering the reactants and processing conditions in some detail, attention is directed first to the chromium compound employed. For a number of reasons, chromic acid (CrO_3) is the preferred chromium compound used in preparing a catalyst of this invention. However, other chromium oxides also may be used, e. g., Cr_2O_3. At times, other chromium compounds which do not introduce undesired ions into a chromium electrolyte also may be used, e. g., chromium carbonate, chromium bicarbonate, and the like.

Glucose, the preferred reducing agent is, of course, but one of several organic reducing agents which can be employed. The expression "organic reducing agent," as used in the specification and claims, is intended to include various oxidizable organic substances, e. g., polyhydroxy organic compounds, capable of reducing hexavalent chromium in solution. Suitable organic reducing agents include mono- and poly-saccharides, especially the so-called "reducing sugars," i. e. mono- and/or disaccharides, such as the following:

MONOSACCHARIDES

Type	Specific Compounds
1. Tetroses ($C_4H_8O_4$)	Erythrose, Threose.
2. Pentoses ($C_5H_{10}O_5$)	Arabinose, Ribose, Cyclose, Xylose, Lyxose.
3. Methylpentoses ($C_6H_{12}O_5$)	Fucose, Styracitol, Rhamnose, Rhodeose.
4. Hexoses ($C_6H_{12}O_6$)	Mannose, Cocaose, Glucose (dextrose), Galactose, Gulose, Fructose (Levulose), Sorbose.

Other illustrative monosaccharides include Methylhexoses ($C_7H_{14}O_6$), Heptoses ($C_7H_{14}O_7$), Methylheptoses ($C_8H_{16}O_7$), Octoses ($C_8H_{16}O_8$), Nonoses ($C_9H_{18}O_9$), and Decoses ($C_{10}H_{20}O_{10}$).

Other types of sugars which may be employed include di-saccharides such as pentose-hexose ($C_{11}H_{20}O_{10}$), methylpentose-hexose ($C_{11}H_{22}O_{10}$) and hexose-hexose ($C_{12}H_{22}O_{12}$); trisaccharides, such as 2 methylpentoses-hexoses and 3 hexoses, as well as tetrasaccharides, e. g., 4 hexoses.

Other suitable organic reducing agents include various polyhydroxy compounds, such as glycerine, various alcohols, gelatin, wood flour or sawdust, organic acids, especially mono- and/or dibasic acids such as oxalic, maleic, tartaric, acetic, formic, citric, glycollic and succinic acids; esters, such as alkyl formates, acetates, propionates, butyrates, and the like. Those skilled in the art will realize, of course, that various other organic reducing agents also may be employed. The preferred polyhydroxy organic reducing agent in the practice of this invention is glucose, both because of its low cost and its ready availability.

It will be appreciated that the organic reducing agent need not always be of the highest purity. In most, if not all, instances, commercially available compounds of the foregoing types are suitable. At times, even relatively impure materials, such as blackstrap molasses or other form of molasses, tanner's sugar, i. e., unrefined corn sugar, bagasse, fruit pulp, and the like, may satisfactorily be used.

The fluosilicic acid (H_2SiF_6) reactant may comprise a commercially available acid, such as a 30% by weight fluosilicic acid solution, which is preferred. Equivalent amounts of fluosilicic acid may be supplied in other ways as by the alternative method of using the reaction product of hydrogen fluoride and silicon dioxide. When the latter technique is employed, it is desirable to utilize an aqueous hydrogen fluoride solution, such as a 60.4% hydrogen

fluoride solution, and to react this solution with silicon dioxide in the form of a finely-divided material (preferably minus 325 mesh), silica gel, sand, silica flour or similar materials.

While the proportions of reactants can be varied somewhat, it has been found desirable to employ enough organic reducing agent at least sufficient completely to reduce all of the hexavalent chromium originally present in the chromium-containing reactant employed in preparing the catalyst. The ratio of chromic acid, or other chromium-containing compounds, to fluosilicic acid may vary. However, as a practical matter, it is preferred to employ as small amounts as possible of fluosilicic acid, or the reaction product of hydrogen fluoride and silicon dioxide, with the chromic acid, while still obtaining an economically complete reaction. Generally, a large excess of fluosilicic acid can be employed without deleteriously affecting the catalyst activity. However, it has been discovered that the bulk density of a spray-dried catalyst varies inversely with the amount of fluosilicic acid employed. Accordingly, insofar as possible, while still maintaining economically complete reaction, it generally is desirable to utilize a minimum fluosilicic acid/chromium oxide ratio in order to achieve a high bulk density.

In order that those skilled in the art may more completely understand the preparation of catalysts of this invention and the methods by which they are prepared, the following specific examples are offered:

Example I

Into a 5000 ml. round-bottom flask, equipped with an agitator and heating means, are introduced 450 ml. of water and 450 gms. of chromium trioxide. To this solution is added 57 gms. of glucose dissolved in 110 ml. of water. The glucose solution is added gradually until the solution boils and then more rapidly in order to maintain the reaction mixture at a boiling temperature.

To a second flask are added 84 gms. of glucose dissolved in 165 ml. of water, and 1800 ml. of 30% by weight fluosilicic acid. This glucose-fluosilicic acid mixture is then added to the chromium-containing solution and external heat applied as necessary to maintain the mixture at boiling temperature for a total of about two hours, until all of the hexavalent chromium originally present is reduced to trivalent chromium.

The thus-obtained reaction product is filtered to remove formed silicon dioxide and is spray-dried at a temperature of approximately 250° F. to obtain 857 gms. of product. The analysis of the product indicates a composition, in terms of percent by weight, of 24.0% chromium, 36.2% fluorine and 5.86% silicon.

Example II

Into a 3000 ml. round bottom-flask, equipped with an agitator and heating means, are introduced 500 ml. of water and 250 gms. of chromic acid. To this solution is added 35 gms. of glucose in 59 ml. of water. The glucose solution is added slowly until the reaction mixture is hot and then more rapidly to keep the reaction mixture boiling.

In a separate flask, 65 gms. of glucose in 108 ml. of water is mixed with 438 ml. of a 30% by weight fluosilicic acid solution. The fluosilicic acid-glucose solution is then added to the chromium-containing solution rapidly enough to keep the reaction mixture at a boil. After the addition is completed, external heat is applied as necessary to maintain the boiling for approximately two hours until the chromium is all reduced to trivalent chromium.

The resultant mixture then is spray-dried at about 250° F. without removal of formed silicon dioxide. There is thus obtained 531 gms. of finely-divided catalyst.

Example III

To illustrate the preparation of a catalyst of this invention using the reaction product of hydrogen fluoride and silicon dioxide, there is introduced into a round-bottom flask, provided with an agitator and heating means, 74.3 gms. of water and 20.1 gms. of minus 325 mesh silicon dioxide (silica gel). To this mixture is added slowly over a period of about one-half hour 66.6 gms. of a 60.5% by weight hydrofluoric acid solution. At the end of the hydrofluoric acid addition a clear solution is obtained, which solution may be employed as a reactant in lieu of the commercially available fluosilicic acid in the procedures of Examples I and II.

Example IV

To illustrate the high bulk density products obtainable in accordance with the preferred practice of this invention, the following data is obtained by repeating the procedure of Example I, using varying ratios of fluosilicic acid:chromium trioxide.

Ml. of 30% by Wgt. Fluosilicic Acid per gram of Chromic Acid	Bulk Density of Product (g./ml.)
5	0.034
4	0.088
3	0.12
2.5	0.20
2	0.38
1.85	0.95

As the foregoing data indicates, the bulk density generally is inversely proportional to the amount of fluosilicic acid employed. Hence, in most instances, it is desirable to employ a reduced amount of fluosilicic acid, the above indicated 1.85 ml. of 30% fluosilicic acid per gm. of chromic acid being the preferred ratio.

APPLICATION OF A CATALYST OF THIS INVENTION IN THE ELECTRODEPOSITION OF CHROMIUM

Catalysts prepared in accordance with this invention generally may be employed in a variety of chromium electrolytes with advantageous results. However, as those skilled in the art will realize, it often is difficult categorically to specify the precise quantities of catalysts or bath constituents for use in all types of chromium plating. For example, it is well-known that the plating conditions for producing brilliant, decorative plates are not necessarily identical with those desirably employed in forming a hard, non-decorative or so-called "engineering plate."

Application of a catalyst of this invention generally may be regulated based upon the fluoride ion concentration, i. e., F— concentration it provides in a chromium electrolyte; this concentration, in combination with a regulated sulfate ion concentration, generally being an accurate and readily determinable index as to the operability and efficiency of an aqueous electrolyte operated in accordance with this invention. The fluoride ion concentration in solution may readily be determined by various means as by the technique disclosed by H. H. Willard and O. B. Winter, in an article appearing in "Industrial and Engineering Chemistry," Analytical Edition, No. 5, page 7 (1933).

It will be appreciated that the following preferred concentration ranges, in combination with predetermined sulfate ion concentrations, are not to be construed as limiting the amounts of catalyst which advantageously may be employed. In general, amounts less than those below listed can be employed, although at times some sacrifice in plating efficiency and brightness may be involved. However, using a concentration less than those set forth below provides improved throwing power and covering power. Similarly, concentrations greater than those set forth below also may be employed. In such instances, an improved efficienty generally being obtained at the expense of covering power and throwing power.

As those skilled in the art will realize, in certain applications a desired increase in plating efficiency may well dictate the use of a higher concentration. On the contrary, another application and the necessity of obtaining maximum throwing power may well indicate the use of a lower concentration than those set forth below.

Generally, catalysts of this invention may advantageously be used in amounts to provide a fluorine content in an electrolyte of from about 0.5 to 7.0 gms. per liter. In most instances, the silicon:fluorine ratio of a catalyst should be at least 0.0835:1.0, i. e., at least one part by weight of silicon to each 12 parts by weight of fluorine. Optimum results are obtained when, in addition to these concentrations, the catalyst embodies a chromium to fluorine weight ratio within the range from 0.75:1.0 to 1.0:1.25, a 1.0:1.0 ratio being preferred at present.

Preferred catalyst concentrations (in terms of fluoride ion concentration) for decorative plating are within the range from 1.5 to 2.5 gms. per liter, an optimum concentration being between 2.0 to 2.25 gms. per liter. These values reflect the preferred practice and provide optimum results when the sulfate ion concentration in the bath is approximately 1.0 gm. per liter.

In electrodepositiong a hard chromium deposit of the type frequently termed "hard chrome" or "engineering" plating, a preferred fluoride ion concentration is within the range from 2.5 to 3.5 gms. per liter, an optimum value being 3.0 gms. per liter. These values indicate the preferred practice and provide optimum results when the sulfate ion concentration is approximately 1.5 gms. per liter.

The concentration of the chromium ion-providing compound, generally CrO_3, in the electrolyte preferably may vary between 150 and 450 gms. per liter, although excellent results are obtained when the chromic acid content is between 100 and 600 gms. per liter. The quantity of inorganic acid employed, such as sulfuric, nitric, or hydrochloric, preferably sulfuric, also may be varied although preferably within the range from about 0.5 gms. per liter to 2.0 gms. per liter.

PLATING CONDITIONS

Plating solutions embodying the present invention may generally be used to electrodeposit improved coatings of chromium on any conventional cathode material, such as steel, iron, copper, nickel and/or various alloys of these or other metals such as aluminum, magnesium and their alloys. Although a preferred anode material is a lead-containing material, such as an alloy of lead and tin, other anode materials also may be employed, as are well-known to the art.

To illustrate specific plating conditions and plating bath constituent concentrations, together with temperature and current densities which provide excellent electrodeposits, attention is directed to the following examples, wherein such information is tabulated.

Example V

Concentrations and Plating Conditions	Decorative Plating	Engineering Plating
Chromic Acid Concentration (g./l.)	150–250	250
Sulfuric acid concentration (g./l.)	1.0 to 1.5	1.0 to 1.5
CrO_3:H_2SO_4 ratio	165—250:1.0	165 to 250:1.0
Catalyst [1] concentration (g./l.)	5 to 11	11 to 15
Temperature (°F.)	105	130
Current Density (amp./sq. ft.)	125	300

[1] 24.7% chromium, 31.6% fluorine, and 4.88% silicon.

Example VI

To illustrate the excellent results obtained in the quality of chromium electrodeposited and in operating characteristics of a chromium electrolyte embodying the invention, a series of plating runs are conducted employing as a chromium electrolyte an aqueous solution consisting of 250 gms. per liter of chromic acid, 1.5 gms. per liter of sulfuric acid, and 10.0 gms. per liter of a catalyst having an analysis of 31.6% by weight fluorine, 24.7% by weight chromium, and 4.88% by weight silicon. The results of such experiments are set forth below:

PART A.—PLATING RATE

Reference is made to Fig. 2 which graphically indicates the plating rate in terms of mils of chromium deposited/hour using the above bath and catalyst at varying cathode current densities. As shown, an excellent plating rate is provided over a widely varying range of cathode current densities.

PART B.—PLATING EFFICIENCY

Reference is made to Fig. 3 which shows the excellent cathode efficiencies varying with current density in electrode-position from the above bath at 130° F.

PART C.—HARDNESS OF CHROMIUM ELECTRODEPOSITS

Knoop hardness values of chromium electrodeposits from above bath are as follows:

Basis Metal	Thickness of Cr Plate (mils)	Current Density (amp./sq. ft.)	Knoop Hardness Number	
			100 Grams, 570×	500 Grams, 130×
Steel [a]	5.3	310	1,090	[b] 811
Do	6.1	620	1,034	[b] 846
Do	6.2	900	1,003	[b] 819
Do	5.5	310	1,098	[b] 850
Do	6.4	620	1,094	[b] 821
Do	6.4	900	1,075	[b] 801
Brass	8	300	1,098	[b] 874

[a] The steel was hardened to 58—60 Rc.
[b] Hardness measured on polished cross sections. Other measurements were made on the polished surface parallel to the surface of the basis metal.

PART D.—CORROSION PROTECTION

Using the procedure of ASTM Method No. B–117–49T, steel panels coated with 4 mils. of chromium electrodeposited from the above bath were subjected to salt spray fog at a density of 0.6 ml. per 80 square centimeters per hour at a temperature of 93° to 95° F. for 168 hours. Such panels were completely free from rust except at the edges.

PART E.—STRESS OF ELECTRODEPOSITED CHROMIUM

Reference is made to Fig. 4 which illustrates that the above bath when operated either at 105° or at 130° F. provides a chromium electrodeposit characterized by compressive stress even at relatively low thicknesses.

Example VII

PART A

To a 5000 ml. three-necked round-bottom flask equipped with agitation and heating means, are introduced 231.0 gms. of 60.4% hydrofluoric acid solution and 71.0 gms. of silicon dioxide (Ottawa sand flour). This mixture is allowed to stand overnight. To the resultant mixture is then added 500 ml. of water, 250 gms. of chromic acid and 37 gms. of glucose in 67 ml. of water. To the thus-formed solution there is then gradually added, at a rate sufficient to maintain the reaction mixture at a boil, 55.5 gms. of glucose in 100 ml. of solution. The thus-obtained solution is spray dried using a spray drier maintained at 450° F. having an upper wall temperature of 250° F., an outlet temperature of 210° F., at a feed rate of 100 ml. per minute.

PART B

Using the catalyst spray dried in accordance with part A, three chromium plating solutions are prepared. These

solutions, hereinafter termed Nos. 1, 2, and 3 respectively, have the following composition:

	No. 1, gms. per liter	No. 2, gms. per liter	No. 3, gms. per liter
Chromic Acid	250	250	250
Sulfuric Acid	1	1	1
Catalyst	4.2	6.3	8.4

The above baths are prepared and allowed to stand for two hours before electrolysis is begun. Using such baths, electrodeposition of chromium therefrom is carried out at a temperature of 130° F. and a current density of 300 amps per square foot. Using a conventional Hull Cell testing procedure, the following results are obtained:

Bath	Time, Minutes	Temp., ° F.	Current Amps.	Remarks
1	5	110	5	Bright Cr deposit for 3" from left.
2	5	110	5	Bright Cr deposit for 1¾" from left.
3	5	110	5	Bright Cr deposit for 1⅝" from left.

PART C

To illustrate the efficiency of baths embodying the present invention, bronze rods are polished and cleaned and electroplated with chromium from the above bath No. 3, a copper coulometer being used in series with the bath. Using the bath at 130° F. with a current of 5 amperes, for a period of 60 minutes in electrodeposition, a chromium deposit weighing 0.3590 gm. was obtained. This weight reflects a plating efficiency of 20.9%.

It is to be understood that although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited, since changes and alterations therein may be made which are within the full intended scope of this inveniton as defined by the appended claims.

What is claimed is:

1. The reaction product obtained by chemically reacting a chromium compound, an organic reducing agent and fluosilicic acid in amounts sufficient to yield a material containing about 23 to 28% chromium, 2.5 to 7.75% silicon and 24–36% fluorine.

2. The reaction product according to claim 1 wherein the chemical reaction is carried out using sufficient reducing agent to effect the reduction of all chromium to the trivalent form.

3. A reaction product according to claim 1 which is obtained by combining a hexavalent chromium compound with water and a reducing agent in an amount insufficient completely to reduce all of the hexavalent chromium to the trivalent form, thus forming a first solution and adding

thereto fluosilicic acid and a reducing agent in an amount sufficient to effect complete reduction of the chromium to trivalent form.

4. The reaction product according to claim 3 wherein the material is spray dried to obtain a finely-divided material.

5. A reaction product comprising 23–28% chromium, 2.5 to 7.75% silicon, and 24–36% fluorine obtained by chemically reacting a hexavalent chromium compound, fluosilicic acid and an organic reducing agent at an elevated temperature until all of the hexavalent chromium originally present is completely reduced to trivalent chromium.

6. The reaction product according to claim 5 wherein the material is spray dried to obtain a finely-divided product.

7. In the process of electrodepositing chromium from an aqueous electrolyte containing chromium ions, and ions of an inorganic acid, the improvement which includes incorporating into said electrolyte an amount of the product defined by claim 1 such that the fluorine content of said electrolyte is from about 0.5 to 7.0 grams per liter.

8. In the process of claim 7 the improvement which includes incorporating in said electrolyte the product defined by claim 2.

9. In the process of claim 7 the improvement which includes incorporating in said electrolyte the product defined by claim 3.

10. In the process of claim 7, the improvement which includes incorporating in said electrolyte the product defined by claim 4.

11. In the process of electrodepositing chromium from an aqueous electrolyte containing chromium ions, and ions of an inorganic acid, the improvement which includes incorporating into said electrolyte an amount of the product defined by claim 5 such that the flourine content of said electrolyte is from about 0.5 to 7.0 grams per liter.

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