

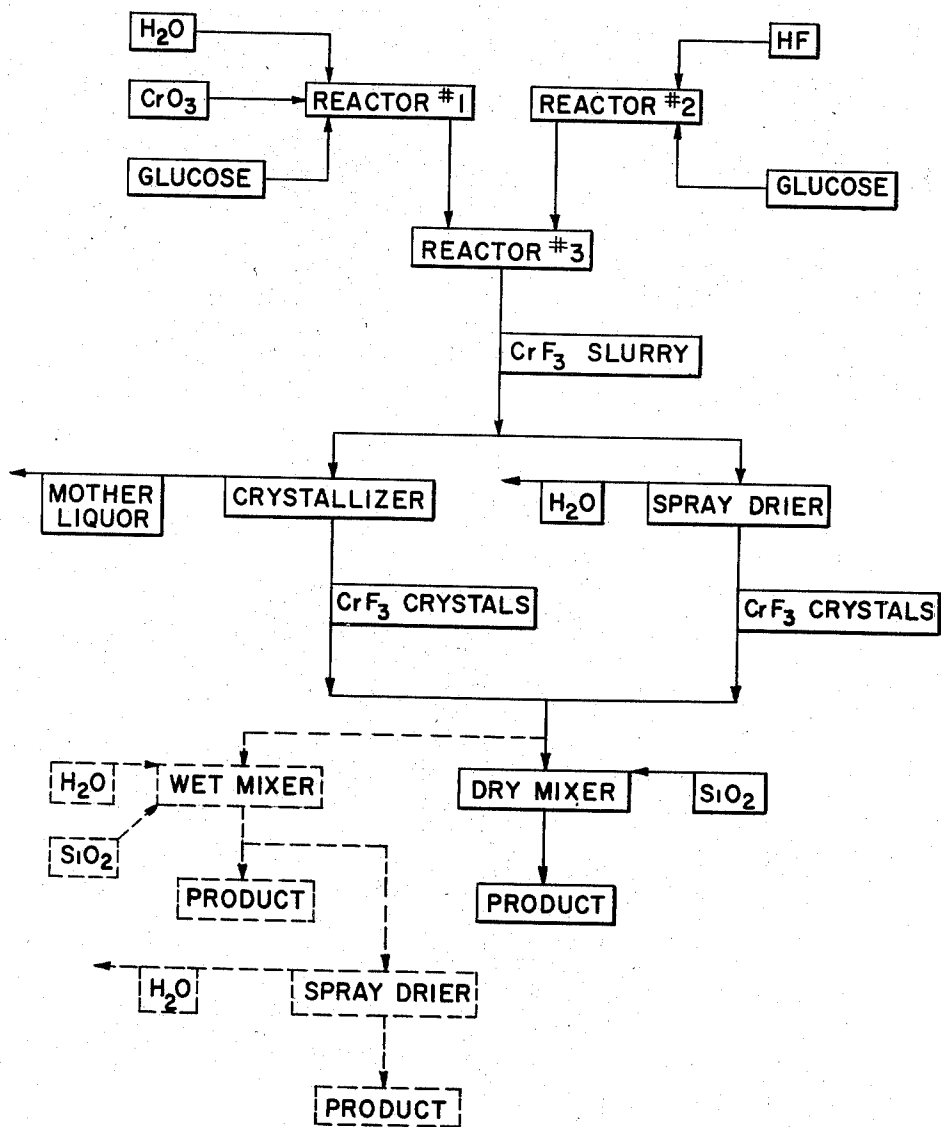
July 1, 1958

R. C. SMITH

2,841,541

CHEMICAL COMPOSITION FOR CHROMIUM PLATING

Filed Oct. 28, 1955



INVENTOR
ROBERT C. SMITH

BY

C.T. Cross

ATTORNEY

1

2,841,541

CHEMICAL COMPOSITION FOR CHROMIUM PLATING

Robert C. Smith, Painesville, Ohio, assignor to Diamond Alkali Company, Cleveland, Ohio, a corporation of Delaware

Application October 28, 1955, Serial No. 543,373

4 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 an aqueous chromium electrolyte, its preparation and use in the electrodeposition 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 inherent necessity of reducing chromium from the hexavalent stage 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 such a "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 has frequently 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.

It is, therefore, a principal object of this invention to provide a new and improved catalyst composition which can be prepared from readily available materials and which produces a marked and significant improvement in the quality of chromium electrodeposited and in the operation of a chromium electrolyte containing the catalyst.

A further object of the invention is to provide a chromium plating solution having improved operating characteristics and being capable of use in the electrodeposition of chromium characterized by an improved hardness, brightness, corrosion resistance, and other desirable properties. These and other objects and advantages of the invention will appear more fully from the following description thereof.

THE PRESENT INVENTION

It has been discovered that by employing as an aqueous

2

electrolyte for the electrodeposition of chromium, a solution containing chromium ions, anions of an inorganic acid, and a catalyst of this invention, whether the catalyst is added as a premixed material or formed in situ in the electrolyte, a chromium electrodeposit characterized by excellent corrosion resistance, hardness and brilliance, in addition to other desirable properties is attained. Moreover, improved operating characteristics of a chromium electrolyte also are obtained in using a plating solution embodying this invention.

THE CATALYST OF THIS INVENTION

Generally, the catalyst of this invention comprises a mixture of silicon dioxide and a monovalent fluorine-containing compound. More specifically, the catalyst comprises the product obtained by reacting silicon dioxide with a chromium and fluorine-containing compound, such as chromic fluoride, which is preferred, or other trivalent chromium compounds.

This invention further contemplates the preparation of a catalyst by reacting silicon dioxide with the product obtained by combining a chromium compound, preferably a chromium-containing compound such as chromic acid (CrO_3) with a reducing agent and hydrogen fluoride. Alternatively, the practice of this invention also contemplates reacting silicon dioxide with a trivalent chromium and fluorine-containing compound, notably chromic fluoride, to form a catalyst. In practice, either of these methods may include the mixing of silicon dioxide with either a wet or dry chromium and fluorine-containing material. More specifically, there also is contemplated the addition of silicon dioxide to a chromium and fluorine-containing material, preferably, chromic fluoride or the product obtained by reacting chromic oxide with a reducing agent and hydrogen fluoride, with subsequent spray drying of the thus-formed mixture.

PREPARATION OF A CATALYST OF THIS INVENTION

The preparation of a catalyst embodying this invention conveniently may be accomplished by reacting a chromium compound, preferably a chromium and fluorine-containing trivalent chromium compound, such as chromic fluoride or the reaction product of a reducing agent, hydrogen fluoride, and chromic acid (CrO_3), other chromium oxides, e. g., Cr_2O_3 , or other chromium compounds which will introduce no undesired ions into the final product, e. g., chromium carbonate, bicarbonate, and the like, with silicon dioxide. Sources of the silicon dioxide which desirably is utilized in a finely-divided state, e. g., minus 325 mesh, may, of course, include various silica flours, Ottawa sand, silica gel, and the like.

In its broadest aspects, this invention contemplates that the quality of chromium electrodeposits may be improved by adding to an aqueous chromium electrolyte either separately, or, preferably, as a pre-mixed material, silicon dioxide and a chromium and fluorine-containing compound, especially one in which the chromium is in the trivalent form. It will be appreciated, of course, that in some instances wherein a chromium electrolyte contains trivalent chromium and fluorine, that additions of silicon dioxide per se may be made with advantageous results in accordance with this invention.

Chromic fluoride is a preferred source of chromium and fluoride ion in the practice of this invention. Not only does this material provide the desired chromium in the catalyst but it can furnish chromium ions for replenishment and maintenance of chromium in the electrolyte. Moreover, it supplies the desired chromium without introducing into the electrolyte any undesirable ionic or non-ionic substances which might interfere with plating action. The chromic fluoride employed may either be the

commercially available product or, if desired, may be prepared by reacting a chromium compound, a reducing agent and hydrogen fluoride as indicated hereinbefore.

PREPARATION OF CHROMIC FLUORIDE

In accordance with this invention, chromic fluoride may be prepared by first partially reducing chromium trioxide, e. g., as by treating an aqueous solution of chromic acid (chromium trioxide) with a polyhydroxy organic reducing agent such as glucose, the reducing agent being employed in an amount insufficient completely to reduce all of the chromium trioxide to the trivalent form. This partially reduced chromic acid solution (I) then is reacted with (1) further reducing agent and (2) hydrogen fluoride, as by combining the partially reduced chromic acid solution (I) with a second solution (II) comprising a mixture of (1) at least sufficient of the same or a different reducing agent to effect complete reduction of hexavalent chromium in solution (I) to trivalent form, and (2) hydrogen fluoride, preferably in the form of an aqueous hydrofluoric acid solution, in an amount sufficient completely to react with the chromium to form chromic fluoride. The combined solutions (III) which comprise chromic fluoride dissolved and/or slurried in an aqueous medium can, if desired, be employed without further treatment or separation. However, it generally is desirable to separate the chromic fluoride either in the form of finely-divided crystals, via conventional crystallization techniques or, preferably, by spray drying. The thus-obtained chromic fluoride crystals may be employed in the practice of this invention, or separately as a source of chromium ions in an aqueous chromium electrolyte.

STRUCTURE OF THE CATALYST OF THIS INVENTION

The precise composition of a catalyst embodying this invention will depend, of course, upon the relative proportions of silicon dioxide and other reactants employed, as well as the reaction conditions utilized. However, it has been definitely shown that while no accurate chemical structure can be illustrated by formula, a catalyst of this invention has a reproducible and constant chemical composition containing chromium, fluorine, and silicon. A specific composition contains, for example, 27.0% chromium, 26.2% fluorine, and 6.64% silicon; or 27.5% chromium, 26.8% fluorine and 3.96% silicon. Generally, it is preferred to prepare a catalyst containing fluorine to silicon in a weight ratio within the range from 4:1 to 10:1.

PREPARATION OF A CATALYST OF THE INVENTION

Referring now to the accompanying drawing, there is schematically illustrated one method of preparing a catalyst embodying the invention. As shown, water, chromium trioxide, and glucose are combined in a first reactor, while hydrogen fluoride and glucose are combined in the second reactor, these combined mixtures being introduced into a third reactor to form a chromic fluoride slurry. The chromic fluoride crystals may be spray-dried or separated via crystallization to obtain a dry chromic fluoride material. It will be appreciated, of course, that the foregoing steps may be eliminated by employing chromic fluoride from another source.

These chromic fluoride crystals then may be dry mixed with silicon dioxide to form a premixed catalyst of this invention. Alternatively, the crystals may be mixed with water and silicon dioxide added thereto to form an aqueous catalyst embodying the invention. This liquid catalyst may then either be used as such or spray-dried to obtain a granular material.

REACTANTS

The chromium and fluorine-containing compound com-

prising a reactant in the practice of this invention may generally be any trivalent chromium compound or substance reducible to trivalent chromium which does not introduce into an electrolyte any undesired ionic or non-ionic substances. As pointed out hereinbefore, trivalent chromium compounds are preferred especially chromic fluoride.

Generally, the silicon dioxide may comprise any commercially available SiO_2 -containing material, such as sand, preferably of substantially 100% silicon dioxide content, silica flour, silica gel, and the like. The silicon dioxide material desirably is employed in the form of a granular finely-divided substance preferably having a particle size of less than 325 mesh.

REDUCING AGENT

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 ($\text{C}_4\text{H}_8\text{O}_4$)	Erythrose, Threose.
2. Pentoses ($\text{C}_5\text{H}_{10}\text{O}_5$)	Aribinose, Ribose, Cyclose, Xylose, Lyxose.
3. Methylpentoses ($\text{C}_6\text{H}_{12}\text{O}_6$)	Fucose, Styracitol, Rhamnose, Rhodose.
4. Hexoses ($\text{C}_6\text{H}_{12}\text{O}_6$)	Mannose, Cacaoose, Glucose (Dextrose), Galactose, Gulose, Fructose (Levulose), Sorbose.

Other illustrative monosaccharides include methylhexoses ($\text{C}_7\text{H}_{14}\text{O}_7$), heptoses ($\text{C}_7\text{H}_{14}\text{O}_7$), methylheptoses ($\text{C}_8\text{H}_{16}\text{O}_8$), octoses ($\text{C}_8\text{H}_{16}\text{O}_8$), nonoses ($\text{C}_9\text{H}_{18}\text{O}_9$), and decoses ($\text{C}_{10}\text{H}_{20}\text{O}_{10}$).

Other types of sugars which may be employed include di-saccharides such as pentose-hexose ($\text{C}_{11}\text{H}_{20}\text{O}_{10}$), methylpentose-hexose ($\text{C}_{11}\text{H}_{22}\text{O}_{10}$), and hexose-hexose ($\text{C}_{12}\text{H}_{22}\text{O}_{12}$); 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 di-basic 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. In addition to the foregoing organic reducing agents, in some instances inorganic reducing agents such as hydrogen peroxide, sulfur dioxide and the like, also may be employed.

In certain cases, the chromium and fluorine-containing compound may be replaced, either wholly or in part, by another suitable fluoride-containing compound such as NaF, KF, NH_4F , $\text{NH}_4\text{F}\cdot\text{HF}$, BaF_2 and CaF_2 .

In order that those skilled in the art may more completely understand the preparation of catalysts of this

invention and the preferred methods by which these catalysts are prepared, the following specific examples are offered:

Example I

PART A

Into a 5000 ml. round-bottom flask, equipped with an agitator, heating means and a thermometer are introduced 1500 ml. of water and 750 gms. of chromium trioxide. To this solution is gradually added 110 gms. of glucose dissolved in 200 ml. of water to form a first solution. The rate of addition of the glucose is sufficient to maintain vigorous boiling of the reaction mixture. In a separate flask are mixed 697.5 gms. of a 60% by weight hydrofluoric acid solution containing 167.5 gms. of glucose dissolved in 300 ml. of water to form a second solution. The first and second solutions are then combined at a rate which maintains vigorous boiling, the second solution being added to the first solution and external heat applied when necessary to maintain the boiling for a total of about 2 hours. By this procedure, 266.7 gms. of wet chromic fluoride crystals containing 26.1% by weight of chromium are obtained.

PART B

The procedure of part A is repeated and the product combined with the wet crystals of part A. This combined product comprises a chromic fluoride crystal slurry. This slurry is spray-dried using a spray drier having an upper wall temperature of approximately 250–260° F. and an outlet temperature of 210°–220° F. By this procedure 2225 gms. of a chromic fluoride product having an analysis of 29.5% chromium and 29.7% fluorine are obtained.

Example II

PART A

Using the spray-dried product of Example I, part B, a chromic fluoride solution is prepared by adding a portion of such product to water. To the resulting solution is added finely-divided (minus 325 mesh) silicon dioxide in amounts to provide a weight ratio of 12 parts fluorine to 1 part of silica. This combined mixture is spray-dried at a temperature of 250° F. to obtain a product containing 27.0% chromium, 26.2% fluorine and 6.64% silicon in a 97% yield. This product then may be added as a catalyst to an aqueous chromium electrolyte in accordance with the practice of this invention.

PART B

Using the spray-dried product as prepared by the procedure of Example I, part B, a dry mixture of chromic fluoride and finely-divided silicon dioxide (minus 325 mesh) is prepared by adding such silicon dioxide to the chromic fluoride crystals in an amount to provide a fluorine:silica weight ratio of 4:1. There is thus prepared a dry mixture embodying the invention and adapted to the added aqueous chromium electrolyte as a catalyst.

Example III

Using the procedure according to Example I, a quantity of wet chromic fluoride crystals are prepared. These crystals are allowed to air-dry without heating. The analysis of the products obtained comprises 30.8% by weight chromium and 33.8% by weight fluorine. This product may be employed in the preparation of a catalyst embodying the invention by combining it with silicon dioxide as indicated in the preceding example.

Example IV

Into a 5000 ml. 3-necked round-bottom flask equipped with an agitator, thermometer and heating means are introduced 500 ml. of water and 250 gms. of chromium trioxide. To this solution is added, with agitation, 67 ml. of a glucose solution (92.5 gms. of glucose in 167 ml. of water) and 71.0 gms. of silicon dioxide (finely-

divided Ottawa sand). In a separate container are combined 231.0 gms. of a 60.4% by weight hydrofluoric acid solution, and 100 ml. of the same type glucose solution described above. These solutions are then combined. After all of the hydrofluoric acid-glucose mixture is introduced, agitation is continued for 10 minutes. This solution is then spray-dried. Analysis of the resultant product, obtained in a 93.1% yield, indicates the composition of 27.5% by weight chromium, 26.8% by weight fluorine, 3.96% by weight silicon.

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

Catalysts prepared in accordance with this invention may generally be employed in a variety of aqueous 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 condition for producing brilliant, decorative plates is not necessarily identical with those desirably employed in forming a hard or engineering plate.

Application of a catalyst of this invention generally may be regulated based upon the fluoride ion 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 a given 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 lower concentration than those set forth below, advantages in improved throwing power and covering power generally will be realized. Similarly, concentrations higher than those set forth below also may be employed. In such instance, an improved efficiency 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 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 and 2.25 gms. per liter. These values reflect the preferred practice when the sulfate ion concentration in the bath is approximately 1.0 gms. per liter.

In electrodepositing 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 concentrations are contemplated for use in a conventional aqueous chromium electrolyte containing a sulfate ion concentration of approximately 1.5 gms. per liter.

As the foregoing concentration ranges indicate, the practice of this invention preferably involves replacing a portion of the inorganic acid content, such as the sulfuric acids of a conventional chromium plating solution, with a catalyst of this invention. In a preferred practice, the sulfate ion concentration is reduced by an amount equal to the quantity of plating catalysts employed.

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 generally may 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 antimony, 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, are well-known to the art.

Specifically, to illustrate the practice of this invention using the hereinbefore described catalysts in chromium plating, the following examples are provided.

Example V

PART A

Into a 3-necked, 5000 ml. round-bottom flask equipped with a thermometer, agitation and heating means are introduced 600 ml. of water with 300 gms. of chromium trioxide. To this solution is added 56 gms. of glucose in 90 ml. of water. In a separate flask, the same amount of an identical glucose solution is added to 279 gms. of a 60% by weight hydrofluoric acid solution. This hydrofluoric acid-glucose solution is then added gradually to the chromium trioxide solution, the rate of addition being such as to maintain the reaction mixture at a boil. The addition is completed in about 1 1/4 hours. After the solutions are combined, 85.2 gms. of silicon dioxide (finely-ground Ottawa sand) is added. The resultant mixture is then spray dried using a spray drier having an upper wall temperature of 245-270° F. and a feed rate of about 130 ml. per minute. There is obtained by this procedure 549.5 gms. of product having an analysis of 27.0% chromium, 26.2% fluorine and 6.64% silicon.

PART B

The catalyst prepared according to the procedure of part A is then employed in preparing a chromium plating solution containing 250 gms. per liter of chromium trioxide, 1.5 gms. per liter of sulfuric acid, and 11.4 gms. per liter of catalyst. A similar bath is prepared containing the same amounts of chromium trioxide and sulfuric acid but containing 13.4 gms. per liter of catalyst. These solutions are then electrolyzed at 130° F. at 300 amps. per sq. ft. using bronze cathode rods and a copper coulometer in series with the baths. Baths 1 and 2 (11.4 gms. per liter and 13.4 gms. per liter respectively),

are allowed to stand overnight before electrolysis. The results of such electrolysis are as follows:

Bath No.	Time (Minutes)	Temp. (° F.)	Current (Amps.)	Efficiency
1-----	60	130	5	21.8% (Bright deposit).
2-----	60	130	5	21.4% (Bright deposit).

As the foregoing data indicates, a bright deposit is obtained together with an excellent cathode current efficiency by the practice of this invention.

Example VI

PART A

In a dry mixer are combined 168.5 gms. of chromic fluoride solids and 14.6 gms. of silicon dioxide (minus 325 mesh). These materials, employed in amounts to provide a fluorine:silica ratio of 8:1, the chromic fluoride solids, comprising 32.0% chromium and 32.3% fluorine, are blended thoroughly. The calculated composition of the resultant mixture is 29.4% chromium, 29.7% fluorine and 3.71% silica.

PART B

Using the product of part A, there are prepared chromium plating solutions each comprising 250 gms. per liter of chromic acid and 1.5 gms. per liter sulfuric acid and a quantity of a catalyst of this invention. Chromium is electrodeposited from these electrolytes for one hour at 130° F. and 300 amps. per sq. ft. using 1/4" diameter bronze rods (3" plating length) as cathodes. A copper coulometer is connected in series with the baths. The baths are allowed to stand overnight before electrolysis is begun. The results are tabulated below as follows:

Bath No.	Catalyst Content (gms./liter)	Time (Minutes)	Temp. (° F.)	Current (Amperes)	Efficiency
1-----	8.4	60	130	5	21.7% (Very bright and smooth deposit).
2-----	10.0	60	130	5	21.8% (Very bright and smooth deposit).
3-----	11.7	60	130	5	21.9% (Very bright and smooth deposit).

Example VII

Further to illustrate the practice of the present invention, a chromium plating bath is made up by combining the following: 250 gms. per liter of chromium trioxide, 1.5 gms. per liter sulfuric acid, 10.1 gms. per liter of chromium fluoride, and 1.07 gms. per liter of silicon dioxide (Ottawa silica flour) thereby providing a solution containing 0.5 gm. per liter of silica and a fluoride of 3.0 gms. per liter. Using this bath, a series of bronze rods employed as cathodes were electroplated with chromium at a temperature of 130° F., for 60 minutes using a current of 5 amps. The resultant chromium electrodeposit was bright and smooth.

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 invention as defined by the appended claims.

What is claimed is:

1. A composition of matter comprising the reaction product obtained by chemically reacting a trivalent chromium compound, silicon dioxide and a fluorine-containing compound, the proportions of these elements in the reaction product being about 27% chromium, about 26% fluorine and about 4% to 7% silicon.

2. A composition of matter comprising the reaction product obtained by chemically reacting a trivalent chromium compound, silicon dioxide and a fluorine-containing compound, the proportions of those elements in the reaction product being about 27% chromium, about 26% fluorine and silicon in an amount within a fluorine:silicon weight ratio of about 4 to 10:1.

3. In the method of electrodepositing chromium which comprises passing an electrical current from an anode to a cathode through an aqueous electrolyte containing chromium ions, and ions of an inorganic acid, the improvement which includes adding to said aqueous electrolyte an amount of the composition defined by claim 1 sufficient to provide in said aqueous electrolyte a fluorine content from about 0.5 to 7.0 grams per liter.

4. In the method of electrodepositing chromium which comprises passing an electrical current from an anode to a cathode through an aqueous electrolyte containing chromium ions and ions of an inorganic acid, the improvement which includes adding to said aqueous electrolyte an amount of composition defined by claim 2

sufficient to provide in said aqueous electrolyte a fluorine content from about 0.5 to 7.0 grams per liter.

References Cited in the file of this patent

UNITED STATES PATENTS

Re. 16,598	Hambuechen	Apr. 19, 1927
1,749,443	Proctor	Mar. 4, 1930
1,815,081	Sohn et al.	July 21, 1931
1,844,751	Fink et al.	Feb. 9, 1932
1,928,284	Fink et al.	Sept. 26, 1933
2,640,021	Passal	May 26, 1953

FOREIGN PATENTS

617,292	Great Britain	Feb. 3, 1949
---------	---------------	--------------

OTHER REFERENCES

- Gilman: Inorganic Reactions, 1930, p. 222.
 Talipov et al.: Chemical Abstracts, vol. 48 (February 1954), pp. 1869-1870.
 Mellor: Comprehensive Treatise on Inorg. Chem., vol. 6, page 956.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,841,541

July 1, 1958

Robert C. Smith

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

Column 4, line 39, second line of the footnote to the table headed, "MONOSACCHARIDES", for " $C_7K_{14}O_7$ " read -- ($C_7H_{14}O_7$) --; column 10, line 2, for "litter" read -- liter --.

Signed and sealed this 21st day of October 1958.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents