

1

2,750,335

CHROMIUM ELECTRODEPOSITION

Henry Brown, Huntington Woods, and Donald R. Millage, St. Clair Shores, Mich., assignors to The Udylyte Research Corporation, Detroit, Mich., a corporation of Michigan

No Drawing. Application July 17, 1953,
Serial No. 368,836

5 Claims. (Cl. 204—51)

This invention relates to improvements in the electrodeposition of chromium from aqueous acidic hexavalent chromium baths, and more particularly concerns new exceedingly stable additives for such baths which are capable of substantially reducing the formation of spray and mist during electrolysis.

The electrodeposition of chromium from aqueous acidic hexavalent chromium solutions takes place, as is well known, with the evolution of relatively large quantities of hydrogen at the cathode and of oxygen and ozone at the insoluble anodes. The undesirable spray and mist of chromic acid results from the violent bursting of the multitudinous gas bubbles of high surface energy which are released by the electrolysis. The spray and mist resulting from this bubble bursting is of considerable volume because of the high current densities used in the plating, the low efficiency of chromium deposition and the use of insoluble anodes. Due to the corrosiveness and high toxicity to the workers of this spray and mist and its well known deleterious contaminating effect on other plating baths such as nickel, copper, cadmium and zinc, it is necessary in large scale production to employ powerful ventilation to continuously remove the same as it is formed. For example, to carry away the mist formed in a 2,000 gallon tank installation requires an exhaust of as much as 10,000 cubic feet per minute to enable safe continuous production. The use of powerful ventilation is expensive not only from the standpoint of the initial installation cost and upkeep maintenance, but also because of the abstraction of the heated air in winter. Moreover, not all of the spray and mist is removed from the area of the plating tank even when powerful ventilation is employed and this is especially true on wide plating tanks. In the usual installation, a certain amount of chromic acid mist does contaminate the air, especially when stray air currents pass over the tank during electrodeposition. From the standpoint of toxicity, the maximum safe concentration of chromium trioxide is now considered to be 0.1 milligram per cubic meter of inhaled air. In addition to the disadvantages connected with adequate ventilation, there is the further disadvantage of the loss of chromic acid in the exhausted air which may amount to about 30% of the chromic acid which is used in the electrodeposition. The amount of chromic acid thus exhausted, together with that which is carried out on the surface of the articles themselves,

2

actually represents more chromic acid than that which is used up in the formation of the chromium coating.

The problems arising as the result of the formation of chromic acid spray and mist in commercial chromium plating, were recognized almost from the very inception of chromium plating and various attempts have been made to prevent or to greatly minimize the formation of this spray and mist. As examples of attempted solutions, it has been suggested to form blankets on the surface of the bath by the use of various oils, floating objects such as plastic pieces, and various wetting agents especially non-ionic wetting agents. None of these attempts have been found to be eminently satisfactory, and all have left much to be desired. For example, non-ionic wetting agents are rapidly oxidized at the anode, and floating plastic pieces are too readily displaced when articles are placed in and taken out of the bath. Heretofore, no ordinary compound which is soluble in a conventional aqueous acidic hexavalent chromium bath has been found that will prevent or effectively minimize the formation of spray and mist and yet be stable to the extremely powerful oxidizing conditions existing at the insoluble anodes during the electrodeposition of chromium from such baths.

It is, therefore, the principal object of the invention to provide a stable additive for an acidic hexavalent chromium bath which greatly minimizes the formation of spray and mist during electrolysis of such baths with insoluble or highly polarized anodes.

Another important object of this invention is to provide improved acidic hexavalent chromium baths and a method for chromium plating which substantially eliminates the necessity for the use of expensive ventilating procedures currently employed.

Another object is to provide an additive for an aqueous acidic hexavalent chromium bath which is capable of producing chromium deposits of increased brightness which persists with increasing thickness of the deposits.

It has now been found that these and related objects are accomplished when certain cationic surface-active compounds characterized as 1,1 dihydro fluorocarbon amines or their salts are added to aqueous acidic hexavalent chromium baths of the type conventionally used in chromium electroplating.

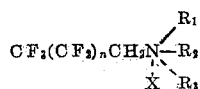
Broadly the amines which are suitable for the purposes of this invention comprise the primary, secondary, tertiary and quaternary 1,1 dihydro fluorocarbon amines containing a saturated fluorocarbon chain of from 3 to 7 carbon atoms, and the salts of the primary, secondary and tertiary amines. Preferred salts are the chromic acid or dichromate salts. Typical examples of these 1,1 dihydro fluorocarbon amines and the optimum concentrations for use in otherwise conventional hexavalent chromium baths are given in Table I. It is to be understood that the proportions set forth in Table I represent only the optimum concentrations, and that benefit is received with somewhat lower concentrations and that concentrations up to saturation may be used with good results. Preferably quantities approaching saturation should be employed for maximum reduction of spray and maximum brightness of plate.

3
TABLE I

	1,1 Dihydro fluorocarbon Amines	Optimum Conc., grams/liter
(1)-----	$\text{CF}_3(\text{CF}_2)_2\text{CH}_2\text{NH}_2$	4-12
(2)-----	$\text{CF}_3(\text{CF}_2)_4\text{CH}_2\text{NH}_2$	0.5-3
(3)-----	$\text{CF}_3(\text{CF}_2)_6\text{CH}_2\text{NH}_2$	0.3-1.5
(4)-----	$\text{CF}_3(\text{CF}_2)_4\text{CH}_2\text{N} \begin{array}{l} \text{H} \\ \diagup \\ \text{CH}_3 \end{array}$	0.5-2
(5)-----	$\text{CF}_3(\text{CF}_2)_4\text{CH}_2\text{N} \begin{array}{l} \text{CH}_3 \\ \diagup \\ \text{CH}_3 \end{array}$	0.5-2
(6)-----	$\text{CF}_3(\text{CF}_2)_4\text{CH}_2\text{N} \begin{array}{l} \text{C}_2\text{H}_5 \\ \diagup \\ \text{H} \end{array}$	0.5-2
(7)-----	$\text{CF}_3(\text{CF}_2)_4\text{CH}_2\text{N} \begin{array}{l} \text{CH}_2\text{CH}_3 \\ \diagup \\ \text{Cl} \end{array} \begin{array}{l} \text{CH}_3 \\ \diagdown \end{array}$	0.05-0.5
(8)-----	$\text{CF}_3(\text{CF}_2)_4\text{CH}_2\text{N} \begin{array}{l} \text{CH}_2\text{COOH} \\ \diagup \\ \text{Br} \end{array} \begin{array}{l} \text{CH}_3 \\ \diagdown \end{array}$	0.1-0.5
(9)-----	$\text{CF}_3(\text{CF}_2)_4\text{CH}_2\text{N} \begin{array}{l} \text{CH}_3 \\ \diagup \\ \text{CH}_3\text{SO}_4 \end{array} \begin{array}{l} \text{CH}_3 \\ \diagdown \end{array}$	0.1-1.5
(10)-----	$\text{CF}_3(\text{CF}_2)_4\text{CH}_2\text{N} \begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{Br} \end{array} \begin{array}{c} \text{CH}_3 \\ \diagdown \end{array}$	0.1-1
(11)-----	$\text{CF}_3(\text{CF}_2)_4\text{CH}_2\text{N} \begin{array}{l} \text{C}_2\text{H}_5 \\ \diagup \\ \text{I} \end{array} \begin{array}{l} \text{C}_2\text{H}_5 \\ \diagdown \end{array}$	0.5-4

The 1,1 dihydro fluorocarbon amines of Table I can be represented by the general formula:

Formula A



where $n=2-6$ and R_1 , R_2 and R_3 are hydrogen or carbon atoms carrying hydrogen, and the sum of the carbon atoms of $\text{R}_1+\text{R}_2+\text{R}_3$ being not more than six, and X is an anion. Preferably X is sulfate, acid sulfate, methiosulfate, fluoride or dichromate.

The surface-active cationic portion of the compounds is the dominant portion in the accomplishment of the invention, and the anionic portion is usually dichromate or chromate once the compound is dissolved in the acidic hexavalent chromium baths. It is to be understood that the basic 1,1 dihydro fluorocarbon amine (that is, the amine without the dotted line attachments to N of R_2 and X) may be the form in which the material is added to the bath. For example, 1,1 dihydro perfluorohexylamine may be added as such. However, once dissolved in the acidic bath, it forms a salt with the chromic acid or dichromates of the bath. This salt formation with the primary amines is also true, of course, with the secondary and tertiary amines.

The presence in the chromium plating baths of halide ions other than fluoride, are not in general as desirable as dichromate, chromate or sulfate, acid sulfate or methiosulfate. Also the presence of organic acids such as formic, acetic, etc. are not generally desirable when insoluble

lead or lead-alloy anodes are used because of their anodic attack on these anodes.

The additives of this invention can be made from fluorocarbon carboxylic acids made by the process as disclosed in U. S. Patent 2,519,983. With such carboxylic acids, amides or nitriles as starting compounds, the various members listed in Table I may be synthesized by conventional methods employed in organic chemistry.

In addition to greatly reducing the formation of spray and mist, the incorporation of the 1,1 dihydro fluorocarbon amine compounds of this invention, for example, 1,1 dihydro perfluorohexylamine in conventional hexavalent chromium plating baths has been found to enable the plating of thicker bright chromium deposits over a bright surface before dulling of the chromium sets in. This advantage has been found to exist in comparison to a conventional hexavalent chromium plating bath or a conventional hexavalent chromium plating bath which has been modified by the incorporation of a fluorocarbon sulfonic compound. This can be readily seen in chromium plates of 0.05 to 1 mil thickness. The thicker chromium plate increases the corrosion protection of nickel, or of nickel, nickel-cobalt, nickel-iron covered ferrous surfaces by decreasing the porosity of the chromium plate. For example, steel that is plated with 1-1.5 mils of bright nickel and over-laid with 0.08 to 0.12 mils of chromium, provides greatly superior corrosion protection in industrial atmospheres than is afforded when the over-layer of chromium has a conventional thickness of only .01-.03 mil.

With the 1,1 dihydro fluorocarbon amines, no excessive trivalent chromium ions are formed in the cathodic processes.

In contrast to the relatively short chain fluorocarbon amines of this invention, ordinary amines such as n-octyl amine or n-dimethyl n-octyl amine do not prevent spray or mist, and it is necessary to use n-decyl amine or longer chain amines to prevent spray and mist from the acidic hexavalent chromium plating baths. However, these ordinary surface-active amines are rapidly oxidized anodically in an amount of about .1-1 gram/liter in about 4 hours, thus destroying their surface-active properties.

The examples given below set forth formulations of operative chromium plating baths useful for decorative or engineering purposes. It will be understood that other compounds covered by Formula A and exemplified by the compounds of Table I may be used in these typical formulations in the place of the particular examples given. Additionally, it is to be understood that mixtures of the compounds of this invention may be employed as well as the single compounds.

Example I

150-250 grams/liter chromic acid (CrO_3)

1.5-3 grams/liter SO_4 ion

2 grams/liter 1,1 dihydro perfluorohexyl amine (Example 2 of Table I)

Temperature $20^\circ\text{C}.$ - $30^\circ\text{C}.$

Cathode current density—100-300 amps./sq. ft. (approximately 10-30 amps./sq. dm.)

In the formulation of Example I, catalysts other than the sulfate ion may be employed, such for example as the fluoride ion or the fluosilicate ion or mixtures thereof. The proportion of fluoride or fluosilicate ion employed is an amount which provides an equivalent catalytic effect to that which is provided by the 1.5-3 grams/liter of the sulfite ion.

Example II

200-400 grams/liter CrO_3

2-4 grams/liter SO_4 anion

1 gram/liter 1,1 dihydro perfluorohexyl trimethyl amine methiosulfate (Example 9 of Table I)

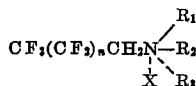
Temperature $20^\circ\text{C}.$ - $50^\circ\text{C}.$

Cathode current density—150-300 amps./sq. ft.

5

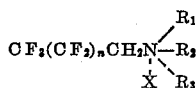
What is claimed is:

1. A bath for the electrodeposition of chromium comprising an aqueous acidic hexavalent chromium solution containing a compound having the formula:



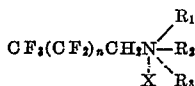
where $n=2$ to 6, R_1 , R_2 , and R_3 are selected from the group consisting of hydrogen and hydrocarbons, the sum of the carbon atoms of $\text{R}_1+\text{R}_2+\text{R}_3$ being not more than 6, and X is an anion, said compound being present in sufficient amount to substantially decrease formation of spray and mist.

2. A bath for the electrodeposition of chromium comprising an aqueous acidic hexavalent chromium solution containing at least about 0.05 gram per liter of a compound having the formula:



where $n=2$ to 6, R_1 , R_2 , and R_3 are selected from the group consisting of hydrogen and hydrocarbons, the sum of the carbon atoms of $\text{R}_1+\text{R}_2+\text{R}_3$ being not more than 6, and X is an anion.

3. In a process of electrodepositing chromium from aqueous acidic hexavalent chromium solutions, the improvement which consists in adding to the solution a compound having the formula:

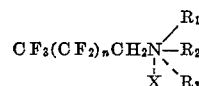


where $n=2$ to 6, R_1 , R_2 , and R_3 are selected from the group consisting of hydrogen and hydrocarbons, the sum

6

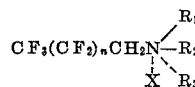
of the carbon atoms of $\text{R}_1+\text{R}_2+\text{R}_3$ being not more than 6, and X is an anion, said compound being added in sufficient amount to substantially decrease formation of spray and mist.

4. A method of electrodepositing chromium which comprises the steps of adding to an aqueous acidic hexavalent chromium solution at least about 0.05 gram/liter of a compound having the formula:



where $n=2$ to 6, R_1 , R_2 , and R_3 are selected from the group consisting of hydrogen and hydrocarbons, the sum of the carbon atoms of $\text{R}_1+\text{R}_2+\text{R}_3$ being not more than 6, and X is an anion, and electroplating chromium from the solution.

5. In a bath for the electrodeposition of chromium comprising an aqueous acidic solution of hexavalent chromium, an additive in an amount of at least about 0.05 gram/liter, said additive consisting of a compound having the formula:



where $n=2$ to 6, R_1 , R_2 , and R_3 are selected from the group consisting of hydrogen and hydrocarbons, the sum of the carbon atoms of $\text{R}_1+\text{R}_2+\text{R}_3$ being not more than 6, and X is an anion.

References Cited in the file of this patent

UNITED STATES PATENTS

2,519,983	Simons	Aug. 22, 1950
2,655,471	Chester	Oct. 13, 1953