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CHROMIUM ELECTROPLATING

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

It is, therefore, the principal object of the invention to provide a stable additive for an acidc 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.

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.

It has now been found that the highly surface-active compounds of this invention, as exemplified by the compounds of Table I, which carry a fluorinated carbon chain and a sulfonic group are unusually stable even though hydrogen is present in the carbon chains attached to the sulfonic radical, and resist oxidation potentials existing during electrolysis with insoluble anodes in acidic solutions of hexavalent chromium. Heretofore, no 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.

The fluorocarbon sulfonic compounds of this invention are usable in aqueus acidic hexavalent chromium plating baths of conventional composition and have been found to lower the surface tension of such baths to amazingly low values and cause the formation of small as opposed to large bubbles of electrolytically evolved gases. Concurrently, the compounds of this invention apparently impart sufficient surface viscosity to the bubbles which, in combination with their low surface energy, prevents their violent collapse at the surface of the bath. The fluorocarbon sulfonic compounds of this invention can be characterized by the formula hereinafter designated Formula I:

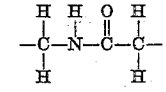
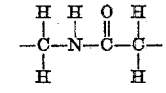
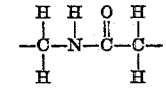
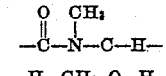
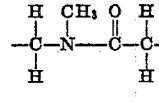
$$R_FMSO_3X$$

where R_F represents a saturated fluorocarbon chain including straight, branched and cyclic fluorocarbon chains of 3 to 12 carbon atoms; M is an aliphatic carbon linkage group containing from 1 to 4 carbon atoms, said carbon atoms carrying hydrogen, oxygen, nitrogen or combinations thereof and positioned between the R_F group and the sulfur of the sulfonic group, and X is a cation. Chlorine or bromine atoms may be present in proximity to the fluorine atoms on the carbon chain so long as a minor number of chlorine or bromine atoms are present relative to the fluorine atoms, for example, less than about 30% of the fluorine atoms. In this case M may contain hydrogen atoms in addition to chlorine or bromine atoms, and moreover the terminal carbon atom, or otherwise stated the carbon atom farthest removed from the sulfonic group, may carry a chlorine or bromine atom. Such chloro or bromo substituted compounds are still stable to the most powerful anodic oxidation. The cation X may represent hydrogen or may be a metallic ion from the groups including the alkali metals, alkaline earth metals, rare earth metals and heavy metals, such as NH_4, Mg, Zn, Ca, Cr, Al, Ni, Cu, Ce, etc. These compounds can be considered to be a special type of anionic surface-active agent, and in the accomplishment of the objects of this invention the anionic radical constitutes the dominant surface-active portion. In comparison to the anionic radical, the cation is relatively unimportant even though additional quantities of certain cations have been observed

to increase the stability of the foam, such as zinc and copper.

Typical representatives of the compounds covered by Formula I which are suitable as additives to hexavalent chromium baths and the optimum concentrations for use in such baths are given in Table I.

TABLE I

No.	R_F	—M—	$-SO_3-$	X	Optimum Conc. in bath, grams/liter
(1).....	$CF_3(CF_2)_n-$ where n=2–11		$-SO_3-$	H, K, NH_4, etc.	0.01–4
(2).....	$CF_3(CF_2)_4-$		$-SO_3-$	H, K, NH_4, etc.	0.2–2
(3).....	$CF_3(CF_2)_5-$		$-SO_3-$	H, K, NH_4, etc.	0.2–2
(4).....	$CF_3(CF_2)_6-$		$-SO_3-$	H, K, NH_4, etc.	0.1–1.5
(5).....	$CF_3(CF_2)_7-$		$-SO_3-$	H, K, NH_4, etc.	4–6
(6).....	$CF_3(CF_2)_4-$		$-SO_3-$	H, K, NH_4, etc.	0.2–2

As may be seen from a study of Formula I and Table I, the R_F group contains not less than 3 and not more than 12 carbon atoms, and M contains from 1 to 4 carbon atoms so that the compounds of this invention may be further characterized as containing from 4 to 16 carbon atoms per sulfonic group. It will be understood that the proportions set forth in Table I represent only optimum concentrations and that somewhat lower concentrations may be employed to advantage and that concentrations up to saturation may be used with good results.

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. For example, to synthesize #2 of Table I, 1,1 dihydroperfluorohexyl amine is obtained by hydrogenation of perfluorocaproic amide or its nitrile, and thereafter reacting the 1,1 dihydroamine with chloroacetylchloride and subsequently replacing the alkyl halide group with the sulfonic radical by treatment with sodium sulfite.

These new soluble fluorocarbon sulfonic compounds of Table I as the acids or their salts show an unexpected degree of surface activity in the hexavalent chromium baths. For example, the incorporation of a small quantity of about .2 gram to 1 gram per liter of the compounds designated by the numerals (1), (2), (3) or (4) of Table I greatly minimizes and substantially prevents the formation of fine spray and mist from a chromic acid electroplating bath operating at room temperature. Although an ordinary non-fluorinated aliphatic sulfonic acid having a carbon chain containing at least 8 carbon atoms or an aromatic sulfonic acid having at least an 8 carbon alkyl chain attached to the benzene ring is fairly stable when merely dissolved in acidic hexavalent chromium plating baths, such materials are rapidly and completely oxidized when the plating solution is electrolyzed using insoluble anodes, such as lead, lead-tin, lead-antimony or other lead alloy anodes. In less than four hours of electrolysis, 1 gram per liter of these non-fluorinated sulfonic acids is oxidized away leaving inorganic sulfate as a decomposition product in the bath. The sulfate thus formed alters the usual ratio of chromic acid anhydride (CrO_3) to sulfate and thus interferes with the plating range of the bath unless the excess sulfate is removed by precipitation. It will be apparent that if other "catalyst" radicals are being employed in the bath with or instead of sulfate, such for example, as fluoride or fluosilicate, the formation of excess sulfate ion will correspondly affect the chromic acid anhydride ratio to the catalyst radical with a comparable decrease in the plating range of the bath. Because of the increased difficulties of control of the bath caused by the breakdown in the bath of such non-fluorinated sulfonic acids, their use is undesirable. In contrast, the fluorocarbon sulfonic compounds of the type covered by Formula I when dissolved in the bath, amazingly resist oxidation during electrolysis even when extremely high potentials are employed, and even though hydrogen is present on some carbon atoms in the compound.

In a large proportion of commercial chromium plating, the chromium is applied over an underlayer of nickel. Where nickel is the underlayer, the fluorocarbon sulfonic compounds of this invention tend to render the underlying nickel plate less sensitive to passivation by contact with the chromic acid solution before current is applied. In forming a chromium layer over nickel, it has been found to be desirable in some instances to preliminarily cathodically gas (at low voltage) the nickel plated article as it is immersed in the hexavalent chromium plating bath and before the higher electroplating voltage is applied. Such mild cathodic gassing is accomplished by using voltages below the plating voltage for a short period of time. One suitable condition for such gassing is a potential of 2 to 3 volts maintained for about 5–30 seconds.

In contrast to the fluorocarbon sulfonic compounds of this invention, if a fluorocarbon carboxylic acid, for example, the compounds, perfluorocaproic acid

$$CF_3(CF_2)_4COOH$$

and perfluorocaprylic acid $CF_3(CF_2)_6COOH$ or their salts is added to chromic acid baths used for the electrodeposition of chromium, for example, baths containing

the ratio of 100:1 of CrO_3 to SO_4, there results a darkish or much more dull chromium deposit, that is, there is a marked decrease in brightness of the deposit which can be overcome only by the use of an unusual ratio of CrO_3 to SO_4, for example, 50:1 instead of the usual 100:1.

While operating conditions for the baths of this invention are not critical, it is preferred that the operating temperature not exceed about 55° C.–66° C. because of possible hydrolysis of compounds containing amide linkages, such as Examples 2 and 5 of Table I.

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 I 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
0.3–4 grams/liter 1,1 dihydroperfluorohexyl sulfonic acid
Temperature, 20° C.–30° 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 sulfate ion.

Example II

400 grams/liter chromic acid (CrO_3)
3–4 grams/liter SO_4 ion
0.1–3 grams/liter 1,1 dihydroperfluoroctyl sulfonic acid
Temperature, 20° C.–40° C.
Cathode current density—100–500 amps./sq. ft.

In forming a chromium coating on underlayers of nickel or copper, it is desirable to maintain the ratio of CrO_3 to SO_4 between about 75:1 and 150:1. Where the underlayer is white brass (20% Cu–80% Zn) it has been found that the ratio of CrO_3 to SO_4 may be increased to as high as 200:1.

Example III

400 grams/liter CrO_3
2–3 grams/liter SO_4 ion
1.5 grams/liter H_2SiF_6
0.2–2 grams/liter of $CF_3(CF_2)_4CH_2NHCOCH_2SO_3Na$
Temperature—20° C.–30° C.
Cathode current density 100–400 amps./sq. ft.

Example IV

200–400 grams/liter CrO_3
2–4 grams/liter SO_4 anion
0.5–3 grams/liter 1,1 dihydroperfluorohexyl sulfonic acid
5–15 grams/liter zinc dichromate or zinc oxide or zinc carbonate
Temperature—20° C.–50° C.
Cathode current density—150–300 amps./sq. ft.

In the solutions of this invention, zinc ions, copper ions and mixtures of zinc and copper ions may be advantageously used in concentrations of about 5–20 grams/liter, and when such quantities are employed the stability of the foam is increased.

This application is a continuation-in-part of my prior copending application, Serial No. 334,082, filed January 29, 1953, now abandoned.

What is claimed is:

1. 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 R_FMSO_3X, where R_F represents a saturated fluorocarbon chain of 3 to 12 carbon atoms, M is a carbon linkage group containing from 1 to 4 carbon atoms and positioned between the R_F group and the sulfur of the sulfonic group, the carbon atoms in said linkage group carrying at least one element selected from the group consisting of hydrogen, oxygen and nitrogen and X is a cation, said compound containing in the R_F substituent a number of atoms selected from the group consisting of chlorine and bromine which number is minor relative to the number of fluorine atoms present in said R_F substituent said compound being added in sufficient amount to substantially decrease formation of spray and mist.

2. A method of electrodepositing chromium wherein the formation of spray and mist is substantially decreased which comprises electrolyzing an aqueous acidic hexavalent chromium solution containing at least about .01 gram/liter of a compound having the formula R_FMSO_3X, where R_F represents a saturated fluorocarbon chain of 3 to 12 carbon atoms, M is a carbon linkage group containing from 1 to 4 carbon atoms and positioned between the R_F group and the sulfur of the sulfonic group, the carbon atoms in said linkage group carrying at least one element selected from the group consisting of hydrogen, oxygen and nitrogen, and X is a cation, said compound containing in the R_F substituent a number of atoms selected from the group consisting of chlorine and bromine which number is minor relative to the number of fluorine atoms present in said R_F substituent.

3. A method of electrodepositing chromium over nickel which comprises the steps of incorporating in an aqueous acidic hexavalent chromium bath at least about .01 gram/liter of a compound having the formula R_FMSO_3X, where R_F represents a saturated fluorocarbon chain of 3 to 12 carbon atoms, M is a carbon linkage group containing from 1 to 4 carbon atoms and positioned between the R_F group and the sulfur of the sulfonic group, the carbon atoms in said linkage group carrying at least one element selected from the group consisting of hydrogen, oxygen and nitrogen, and X is a cation, said compound containing in the R_F substituent a number of atoms selected from the group consisting of chlorine and bromine which number is minor relative to the number of fluorine atoms present in said R_F substituent immersing a nickel coated article in the said bath, cathodically gassing said article by applying a voltage to the bath less than that normally applied for plating, and thereafter electroplating chromium from said bath.

4. A method of electrodepositing chromium which comprises the steps of adding to an aqueous acidic hexavalent chromium solution at least about .01 gram/liter of a compound having the formula R_FMSO_3X, where R_F represents a saturated fluorocarbon chain of 3 to 12 carbon atoms, M is a carbon linkage group containing from 1 to 4 carbon atoms and positioned between the R_F group and the sulfur of the sulfonic group, the carbon atoms in said linkage group carrying at least one element selected from the group consisting of hydrogen, oxygen and nitrogen and X is a cation, said compound containing in the R_F substituent a number of atoms selected from the group consisting of chlorine and bromine which number is minor relative to the number of fluorine atoms present in said R_F substituent and about 5 to 20 grams/liter of a metallic ion selected from the group consisting of zinc, copper, and mixtures thereof, and electroplating chromium from the solution.

5. A method of electrodepositing chromium wherein the formation of spray and mist is substantially decreased, comprising the steps of electrolyzing an aqueous acidic hexavalent chromium solution containing at least about .01 gram/liter of a compound having the formula R_FMSO_3X, where R_F represents a saturated fluorocarbon chain of 3 to 12 carbon atoms, M is a carbon linkage

group containing from 1 to 4 carbon atoms and positioned between the R_F group and the sulfur of the sulfonic group, the carbon atoms in said linkage group carrying at least one element selected from the group consisting of hydrogen, oxygen and nitrogen and X is a cation said compound containing in the R_F substituent a number of atoms selected from the group consisting of chlorine and bromine which number is minor relative to the number of fluorine atoms present in said R_F substituent and regulating the thickness of the foam blanket which is formed by passing ammonia vapors over the said foam blanket.

6. A bath for the electrodeposition of chromium comprising an aqueous acidic hexavalent chromium solution containing a compound having the formula R_FMSO_3X, where R_F represents a saturated fluorocarbon chain of 3 to 12 carbon atoms, M is a carbon linkage group containing from 1 to 4 carbon atoms and positioned between the R_F group and the sulfur of the sulfonic group, the carbon atoms in said linkage group carrying at least one element selected from the group consisting of hydrogen, oxygen, and nitrogen, and X is a cation, said compound containing in the R_F substituent a number of atoms selected from the group consisting of chlorine and bromine which number is minor relative to the number of fluorine atoms present in said R_F substituent said compound being present in sufficient amount to substantially decrease formation of spray and mist.

7. A bath for the electrodeposition of chromium comprising an aqueous acidic hexavalent chromium solution containing at least about .01 gram/liter of a compound having the formula R_FMSO_3X, where R_F represents a saturated fluorocarbon chain of 3 to 12 carbon atoms, M is a carbon linkage group containing from 1 to 4 carbon atoms and positioned between the R_F group and the sulfur of the sulfonic group, the carbon atoms in said linkage group carrying at least one element selected from the group consisting of hydrogen, oxygen, and nitrogen, and X is a cation, said compound containing in the R_F substituent a number of atoms selected from the group consisting of chlorine and bromine which number is minor relative to the number of fluorine atoms present in said R_F substituent.

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