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CHROMIUM PLATING

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This invention relates to improvements in the electrodeposition of chromium from aqueous acidic hexavalent chromium baths, and more particularly concerns exceptionally stable additives for such baths which are capable of substantially reducing the amount of spray and mist which is normally formed 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.

The important objects of the present invention are to provide a stable additive for acidic hexavalent chromium baths which is capable of minimizing the formation of spray and mist during electrolysis of such baths with insoluble or highly polarized anodes; to improve the operating efficiency of hexavalent chromium baths; to provide an improved and simplified method for chromium plating which greatly reduces the over-all cost of chromium electro-deposition and to provide a new and improved hexavalent chromium plating bath.

In accordance with the present invention, it has now been found that fluorocarbon sulfonic compounds which contain a terminal or omega hydrogen in the fluorocarbon radical, are exceptionally useful in reducing the formation

of spray and mist during the electrolysis of a hexavalent chromium plating bath. For example, if a 1,1-dihydrofluorocarbon sulfonic acid containing a terminal or omega hydrogen in the fluorocarbon radical is used in an acidic hexavalent chromium plating bath, the surface tension of the bath is not lowered to the same extent, at any given concentration of sulfonic acid compound, as it is when the terminal hydrogen is replaced by fluorine as in the compounds disclosed in copending applications, Serial No. 334,081 and Serial No. 334,082, filed on January 29, 1953. However, the prevention of mist and spray from the rapidly collapsing bubbles of hydrogen and oxygen evolved at the cathodes and anodes respectively, is dependent not only on the lowering of the surface tension of the bath but also on the stability of the bubble film or foam. Even though the surface tension of the bath is greatly decreased by the presence of a suitable material, that factor itself is insufficient and it is necessary for continuous and economic operation that the foam blanket be of certain stability and not subject to too rapid decomposition. It is believed that the increased stability of the foam blanket of the present invention is at least partially dependent upon the viscosity of the bubble film which is imparted by the improved additive of this invention.

The compounds which are suitable as additives to acidic hexavalent chromium plating baths for the purposes of this invention may be represented by the formula designated Formula A:

$$H(CF_2 \cdot CF_2)_x(CH_2)_yZM$$

where X is 2–15, Y is 1–3, M is a cation and Z is a radical selected from the group consisting of —SO_3— and —OSO_3—. These compounds have been found to completely prevent mist and spray in warm chromic acid plating baths and are stable to the electrolytic oxidation which occurs at the lead or lead-alloy-anodes during electrodeposition of chromium. The compounds of this invention may be added in the form of the free acid or a salt which may contain any of a wide variety of ions including sodium, potassium, lithium, ammonium, calcium, strontium, magnesium, ferric ion, trivalent chromium ion, aluminum ion, zinc, nickel, copper, pyridinium, etc.

Some of the additives of this invention may be prepared by telomerization of tetrafluoroethylene and methyl alcohol or methyl chloride, for example, as is generally disclosed in United States Letters Patent No. 2,559,628 and No. 2,559,629. The products of this process may then be converted into the additives of this invention by ordinary methods of preparative organic chemistry, that is, the 1,1-dihydrohalides or alcohols are thus converted into the sulfonic or sulfate compounds of this invention. In general, by this method of preparation, X is an average value and thus mixtures where X is a value in the range of 2 to 10 may be present. However, fractions may be separated where X is a value in the range of 3 to 7 or 5 to 7.

The 1,1-dihydro, 1,1,2,2-tetrahydro compounds (compounds in accordance with Formula A where Y is 1 and 2 respectively) and also the hexahydro compounds (where Y is 3) can be used, although the preferred compounds are those represented by Formula A when Y is 1. With compounds having an average X value of 2 to 10, the concentration which can be advantageously employed may vary between about 0.01 gram/liter and 10 grams/liter. Although, in general, no further benefits are obtained from the use of concentrations above about 4 grams/liter, concentrations up to saturation may be employed without deleterious effects on the chromium plate obtained, while concurrently obtaining complete suppression of mist and spray.

With the warmer operated chromium plating baths (for example, 50°–90° C.) the longer chain compounds are preferred, that is, those with X averaging at least 4. Furthermore, in the operation of warm baths the sulfonic group is preferred over the sulfate group because of the tendency for hydrolysis and breakdown of the latter sulfated compounds. The sulfates, in general, however, are more soluble in the bath (especially in the hot baths) and longer chain compounds can be used, for example, where X is higher than 15. However, in most operations the sulfonic acid compound is preferred because of its greater stability in the bath and X may be as high as 10 or 15 and still have some solubility in the bath, especially when the bath is operated hot. Moreover, when mixtures are used, i. e., when X is 2 to 10 or 2 to 15 the shorter chain members help solubilize the longer chain members.

In the examples given below illustrating typical operating baths and some of the compounds represented by Formula A, the value given for X represents an average value. It is to be understood that the particular additives set forth in the examples may be replaced by other compounds represented by Formula A and used in the typical baths set forth in quantities within the broad range above set forth.

Example I

150–400 grams/liter CrO_3 (chromic acid anhydride)
1–6 grams/liter sulfate
0.05–3 grams/liter $H(CF_2.CF_2)_6CH_2SO_3H$
Temperature, 20° to 80° C.
Cathode current density, 10–50 amps/sq. dm. (approximately 100–500 amps/sq. ft.)

The sulfate ion may be replaced completely or partially by other catalysts such as the fluoride ion, the fluorosilicate ion or mixtures thereof. The proportion of fluoride or the fluosilicate ion which is most advantageously employed is merely that proportion which provides a substantially equivalent catalytic effect to that which is provided by the 1–6 grams/liter of the sulfate ion.

Example II

200–400 grams/liter CrO_3
2–6 grams/liter sulfate or equivalent, as fluoride or fluosilicate
5–80 grams/liter sodium dichromate
.05–3 grams/liter $H(CF_2 \cdot CF_2)_7CH_2OSO_3Na$
Temperature, 20°–80° C.
Cathode current density, 10–50 amps/sq. dm.

Example III

200–400 grams/liter CrO_3
1–6 grams/liter SO_4
0.05–3 grams/liter $H(CF_2 \cdot CF_2)_5C_2H_4SO_3Na$
Temperature, 20°–90° C.
Cathode current density, 10–50 amps/sq. dm.

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:

$$H(CF_2 \cdot CF_2)_x(CH_2)_yZM$$

where Z is a radical selected from the group consisting of —SO_3— and —OSO_3—, M is a cation, X is 2 to 10 and Y is 1 to 3, said compound being present in sufficient amount to substantially decrease the formation of spray and mist.

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

$$H(CF_2 \cdot CF_2)_x(CH_2)_yZM$$

where Z is —SO_3—, M is a cation, X is 2 to 10 and Y is 1, said compound being present in sufficient amount to substantially decrease the formation of spray and mist.

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

$$H(CF_2 \cdot CF_2)_x(CH_2)_yZM$$

where Z is —SO_3—, M is a cation, X is 3 to 7 and Y is 1, said compound being present in sufficient amount to substantially decrease the formation of spray and mist.

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

$$H(CF_2 \cdot CF_2)_x(CH_2)_yZM$$

where Z is —SO_3—, M is a cation, X is 2 to 10 and Y is 2, said compound being present in sufficient amount to substantially decrease the formation of spray and mist.

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

$$H(CF_2 \cdot CF_2)_x(CH_2)_yZM$$

where Z is —OSO_3—, M is a cation, X is 2 to 10 and Y is 1, said compound being present in sufficient amount to substantially decrease the formation of spray and mist.

6. A process for electrodepositing chromium which comprises the step of electrolyzing an aqueous acidic hexavalent chromium solution containing a compound having the formula:

$$H(CF_2 \cdot CF_2)_x(CH_2)_yZM$$

where Z is a radical selected from the group consisting of —SO_3— and —OSO_3—, M is a cation, X is 2 to 10 and Y is 1 to 3, said compound being present in sufficient amount to substantially decrease the formation of spray and mist.

7. A process for electrodepositing chromium which comprises the step of electrolyzing an aqueous acidic hexavalent chromium solution containing a compound having the formula:

$$H(CF_2 \cdot CF_2)_x(CH_2)_yZM$$

where Z is —SO_3—, M is a cation, X is 2 to 10 and Y is 1, said compound being present in sufficient amount to substantially decrease the formation of spray and mist.

8. A process for electrodepositing chromium which comprises the step of electrolyzing an aqueous acidic hexavalent chromium solution containing a compound having the formula:

$$H(CF_2 \cdot CF_2)_x(CH_2)_yZM$$

where Z is —SO_3—, M is a cation, X is 3 to 7 and Y is 1, said compound being present in sufficient amount to substantially decrease the formation of spray and mist.

9. A process for electrodepositing chromium which comprises the step of electrolyzing an aqueous acidic hexavalent chromium solution containing a compound having the formula:

$$H(CF_2 \cdot CF_2)_x(CH_2)_yZM$$

where Z is —SO_3—, M is a cation, X is 2 to 10 and Y is 2, said compound being present in sufficient amount to substantially decrease the formation of spray and mist.

10. A process for electrodepositing chromium which comprises the step of electrolyzing an aqueous acidic hexavalent chromium solution containing a compound having the formula:

$$H(CF_2 \cdot CF_2)_x(CH_2)_yZM$$

where Z is —OSO_3—, M is a cation, X is 2 to 10 and Y is 1, said compound being present in sufficient amount to substantially decrease the formation of spray and mist.

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