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CHROMIUM PLATING ELECTROLYTE AND METHOD FOR PREVENTING MIST THEREIN

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U.S. Cl. 204—51 10 Claims
Int. Cl. C23b 5/06; B01k 1/00

This invention relates to the prevention of mist and spray in acidic hexavalent electroplating baths. More particularly, it relates to the use of certain surface-active solfobetaines in chromium plating baths to suppress the evolution of the poisonous mist and spray of chromic acid from such baths. The baths of this invention are particularly useful in applications where chromium is deposited in thicknesses appreciably greater than those used in decorative chromium plate, i.e., in the so-called hard chromium plating wherein a chromium plate of greater than about 0.2 mil is used for engineering purposes to obtain a hard surface for wear resistance or for low friction, etc.

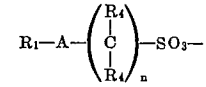
There is no question that outstanding surface-active agents for suppressing mist and spray from decorative chromium plating baths are the perfluoroalkane sulfonic acids as described in U.S. 2,750,334. Such compounds are remarkably effective and are completely stable to the powerful anodic oxidation conditions prevailing during the chromium plating. However, in studies of thick chromium plating of various steel surfaces it was found that in those cases wherein the basis metal contained fine pits, these perfluoro alkane sulfonic acids actually promote pitting at these sites in the thick chromium plate. If these surface-active agents are not used in the chromium plating bath, the original small pits in the steel surface are filled in and closed, or practically closed up by the chromium plate, whereas, in the presence of the perfluoro sulfonic surface-active agents, the original pits are enlarged in the chromium plate (see Tech. Proceedings American Electroplaters' Soc., vol. 45, p. 118).

The reason for the development of pitting in thick chromium plate at the site of small surface pits in the basis metal is not well understood, but the phenomenon is not restricted solely to the perfluoro alkane sulfonic acids. For example, we have found that sodium lauryl sulfate or lauryl sulfonic acid added to the plain chromium plating bath also promote pit enlargement in the thick chromium plate.

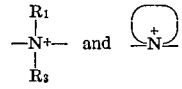
While the perfluoro alkane sulfonic acids such as perfluoro para ethyl cyclohexyl sulfonic acid and perfluoro n-octyl sulfonic acid tend to promote the pit enlargement effect described above, they nevertheless differ in the degree of enlargement they cause. The perfluoro n-octyl sulfonic causes less pit enlargement, less flaring out, than perfluoro p-ethyl cyclohexyl sulfonic acid, and this is especially noticeable with very small pits of about 2 or 3 mils diameters in the base metal, which are often not flared out.

After further studies, we have now found that surface-active agents based on a structure illustrated by the formula below are remarkably effective in suppressing spray and mist and do not have the disadvantage of promoting the enlargement of surface pits in the subsequent chromium plate as do the perfluoro alkane sulfonic acids. The present compounds allow, or even help, normally bridging or filling-in and closing of small pits in the basis meta. The degree of filling-in will depend on the size of the surface pits and the thickness of the applied chromium plate.

The surface-active compounds contemplated by this invention are of the following formula:



where R_2 is an alkyl group containing 12–22 carbon atoms inclusive; each of R_4 is selected from the group consisting of hydrogen, hydroxy, chloro, and methyl and ethyl radicals; n is an integer from 1 to 5 inclusive; and A is an organic radical selected from the group consisting of



where R_1 and R_3 are selected from the group consisting of hydrogen and alkyl and cycloalkyl groups containing 1–18 carbon atoms wherein the sum of carbon atoms in R_1 and R_3 is no more than 18, and where



is a heterocyclic radical wherein only nitrogen and carbon atoms are joined in a 5 or 6 membered ring. It is understood that hydrocarbon groups R_1, R_2, R_3 and the heterocyclic radical



may also be substituted with groups such as —NO_2, —NH_2 —CN, halogen, etc.

The compounds described above are sulfobetaines of N-alkane-sulfonic acids, i.e., inner sulfonic acid salts of long chain primary, secondary, or tertiary amines, or inner sulfonic acid salts of N-alkyl heterocyclic compounds. The compounds are sometimes known by other nomenclature, and for example may be referred to as alkane sultones of the various amines or heterocyclics, e.g., the propane sultone of stearyl dimethyl amine or the propane sultone of 1-stearyl piperidine. Such compounds are quaternary wetting agents, are internally neutralized, and are compatible with anionics such as fluoroalkane sulfonic acids and phosphonic acids as well as the cationic 1,1-dihydroperfluoro hexyl amine.

The compounds of this invention are known compounds and may be prepared by conventional techniques, see for example British Patent 764,340 or Ann. 565, 22, 1949. As examples, an alkane sultone such as propane sultone is reacted with an alkyl amine such as lauryl amine in methanol at about 35° C. to obtain the sulfobetaine of 3-laurylamine propanesulfonic acid, or propane sultone is reacted with an N-alkyl heterocyclic such as 1-lauryl piperidine at about 120° C. to obtain the sulfobetaine of 3-(1-lauryl piperidine) propanesulfonic acid.

The more effective compounds of the invention are generally those wherein R_2 is a straight chain alkyl group of 16–20 carbon, and n is 3 or 4. When A in the above formula is an amine nucleus, R_1 and R_3 are preferably hydrogen or methyl groups, most preferably the latter. When A is a heterocyclic radical, preferably it contains 1 or 2 nitrogen atoms and is the residue of 5 or 6 membered heterocyclic compound originally containing at least one secondary nitrogen atom as exemplified by pyrrole, piperidine, pyrrolidine, piperazine, pyrazole, pyrazine, etc. Especially preferred of the heterocyclic quaternaries is propane sultone of 1-stearyl piperidine.

The most preferred compound is the sulfobetaine of N,N-dimethyl-3-stearylamino propanesulfonic acid. This compound is preferred because of its great stability and relatively high solubility in water and in acidic hexavalent

chromium plating solutions. It is much more soluble in water and in the chromic acid bath than the compound where R_2 is an 18 carbon straight alkyl chain and R_1 and R_3 are hydrogen and the hydrogen ion, respectively. However, even those amine sulfonic acids which are less soluble give good results in the acidic chromium plating because concentrations as low as about 5 to 10 mg./liter are adequate, and while the sodium, ammonium, etc. salts of these free acids are more soluble, the compounds, of course, are present as the free acid, or the sulfobetaine form in the acidic chromium plating baths.

The above described surface-active compounds can also be used in decortaive (thin) chromium plating operations, either alone or in conjunction with more expensive, highly fluorinated, surface-active agents such as perfluoro alkane sulfonic or fluoro-alkane phosphonic acids. When used in combination, less of the fluoro-alkane surface-active agents will drag-out as films as the chromium plated work is withdrawn from the bath.

When the sulfobetaines of this invention are used for thick (hard chrome) application, they should be used in the absence of the perfluoro alkane sulfonic acids. The presence of the perfluoro alkane sulfonic acid would, as described above, promote the pit enlargement effect. On the other hand, certain compounds such as 1,1 di-hydro perfluoro hexylamine, $(CF_3(CF_2)_4CH_2NH_2)$ do not cause pit enlargement, but they are not as effective as the sulfobetaines in the filling in of the surface pits with thicker chromium plating.

The preferred perfluoro alkane sulfonic acids to be used in conjunction with the sulfobetaines in decorative plating are the ring types such as perfluoro p-ethyl cyclohexyl sulfonic acids, perfluoro cyclohexyl ethane omega sulfonic acid and similar perfluoro alkane sulfonic acids that have similar surface tension properties. However, the straight chain type such as perfluoro n-octyl sulfonic acid also gives good conjunctive results. Instead of perfluoro alkane sulfonic acids, fluoro-alkane phosphonic acids (e.g. $H(CF_2CF_2)_nPO(OH)_2$ where n is 1 to 5) may be used together with the surface-active sulfobetaine compounds for purposes of decorative chromium plating.

The surface-active sulfobetaines of this invention can be used in all types of acidic hexavalent chromium plating baths, dilute or concentrated, and containing catalyst radicals besides sulfate, such as fluoride, silicofluoride (fluosilicate), fluoborate, fluoaluminate, fluotitanate, fluozirconate, trichloroacetic, monochloroacetic, monochloropropionic, or mixtures of these catalyst radicals.

The acidic hexavalent chromium plating baths may be made up from straight chromic acid anhydride or chromic acid, or from mixtures with dichromates, chromates, and polychromates. It is generally preferred to use straight chromic acid or chromic acid anhydride. The presence of cations besides hydrogen such as Na, K, Li, NH_4, Mg, Sr, Zn, Cu, Co, Al, Ca, pyridinium etc. are not detrimental but in general they are best kept in minor concentration.

Using a preferred compound of this invention such as the sulfobetaine of N,N-dimethyl-stearylamine propane sulfonic acid, it is possible to suppress to a very great extent the mist and spray from the chromium plating baths operated at about 105° F. with as little as 2 mg./liter of such compounds. With baths operated at about 120° F., it is preferred to use slightly higher concentrations such as 3 to 5 mg./liter. When using compounds with shorter alkyl chains, i.e., R_2 in the foregoing formula contains 12 carbon atoms, concentrations as high as 0.3 and 0.5 gram/liter may be optimum. The surface-activity of these compounds is manifested not only by an appreciable lowering of the surface-tension of the chromic acid solutions but also by formulation of a blanket of foam on the surface of the chromium plating bath during electrolysis, and it is this foam blanket that is most effective for the complete suppression of mist and spray during the electrolysis. When R_2 is a stearyl group, the foam blanket forms very readily with very low concentrations and does not collapse very readily when the current is turned off. Thus, while the long chain compounds require more careful control of concentration to avoid over-foaming, nevertheless, only trace concentrations (5 mg./liter) are needed to suppress mist and sprays.

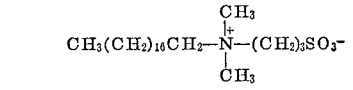
When the sulfobetaines of this invention are used together with a fluoroalkane surface-active agent in decorative chromium plating baths, it is possible to use, for example, 2 to 3 milligrams/liter of the sulfobetaine of N,N-dimethyl-stearylamino propanesulfonic acid with as little as 5 to 10 mg./l. of perfluoro p-ethyl cyclohexyl sulfonic acid (or the K, Na, Mg, etc. salts) to completely suppress mist and spray. Similar small additions need be made only once per 8 hours of continuous plating, or half such additions per 4 hours of continuous electrolysis.

Following are listed several representative examples of acidic hexavalent chromium plating baths employing the surface-active sulfobetaines for the suppression of mist and spray during electrolysis.

EXAMPLE I

(Hard chrome)

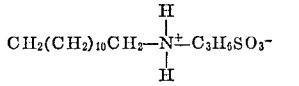
150 g./l. CrO_3
CrO_3/SO_4 ratio equal to about 100 to 1
0.3 to 0.5 g./l. of fluosilicic acid
Temperature of about 120° F.
Cathode current densities of 100 to 250 amps/sq. ft.
0.002 to 0.006 gram/liter of



sulfobetaine of N,N-dimethyl-3-stearylamino propanesulfonic acid

EXAMPLE II

140–250 g./l. CrO_3
1.5–3 g./l. H_2SO_4
Temperature of 70° to 120° F.
Cathode current densities of 100 to 300 amps/sq. ft.
0.3 to 0.5 gram/liter of



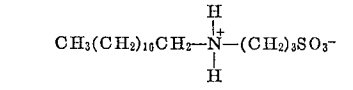
0.1 gram/liter of $CF_3(CF_2)_4CH_2NH_2$

EXAMPLE III

100–150 g./l. CrO_3
100 g./l. $Na_2Cr_2O_7$ or $K_2Cr_2O_7$
2–3 g./l. sulfate anion
Temperature of 70° to 130° F.
Cathode current densities of 100 to 300 amps/sq. ft.
0.1–0.2 gram/liter perfluoro p-ethyl cyclohexyl sulfonic acid (Na or K salt)
0.002–0.005 g./l. sulfobetaine of N,N-dimethyl-stearylamine butanesulfonic acid

EXAMPLE IV

200–250 g./l. CrO_3
2 to 2.5 g./l. sulfate anion
Temperature of 100° to 105° F.
Cathode current densities of 100 to 250 amps/sq. ft.
0.002 to 0.008 g./l. of

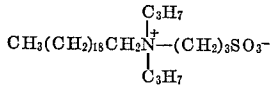


0.005–0.1 g./l. of $H(CF_2CF_2)_nPO(OH)_2$ where n is 1 to 5

EXAMPLE V

150–400 g./l. CrO_3
Saturation concentration of $SrSO_4$, and 0.5 g./l. H_2SiF_6

Temperature of 70° to 130° F.
Cathode current densities of 100 to 300 amps/sq. ft.
0.1–0.6 g./l. perfluoro p-ethyl cyclohexyl sulfonic acid
0.005–0.02 g./l. perfluoro n-octyl sulfonic acid (or Na, K, etc. salts)
0.005 g./l. of



EXAMPLE VI

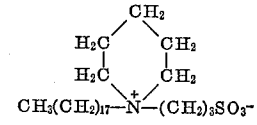
150–250 g./l. CrO_3
Saturation concentration of $SrSO_4$
Temperature of 100°–115° F.
Cathode current density of 200 amps/sq. ft.
0.004 to 0.02 g./l. of the sulfobetaine of N,N-dimethyl-3-stearylamine propanesulfonic acid

EXAMPLE VII

150–250 g./l. CrO_3
CrO_3/SO_4 ratio equal to about 100 to 1 to 150 to 1
0 to 0.5 g./l. fluosilicic acid
Temperature of about 120° F.
Cathode current densities of 100 to 250 amps/sq. ft.
0.002 to 0.006 g./l. of the sulfobetaine of N,N-dimethyl-3-stearylamino propanesulfonic acid
0.003 to 0.01 g./l. of perfluoro n-octyl sulfonic acid

EXAMPLE VIII

150 g./l. CrO_3
CrO_3/SO_4 ratio equal to about 100 to 1 to 150 to 1
0.3 to 0.5 g./l. of fluosilicic acid
Temperature of about 120° F.
Cathode current densities of 100 to 250 amps/sq. ft.
0.002 to 0.006 of



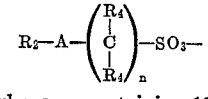
i.e., sulfobetaine of 3-(1-stearyl piperidine) propanesulfonic acid

EXAMPLE IX

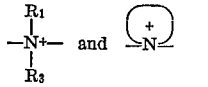
1.5–3 g./l. H_2SO_4
Temperature of 70° to 120° F.
Cathode current densities of 100 to 300 amps/sq. ft.
0.3 to 0.5 gram/liter of the sulfobetaine of 3-(1-lauryl piperazine) propanesulfonic acid
0.1 g./l. of $CF_3(CF_2)_4CH_2NH_2$
140–250 g./l. CrO_3

We claim:

1. An aqueous acidic hexavalent chromium electroplating bath containing dissolved therein cromic acid and from 0.002 to about 0.5 gram/liter of a surface-active compound of the formula

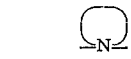


where R_2 is an alkyl group containing 12–22 carbon atoms inclusive; each of R_4 is selected from the group consisting of hydrogen, hydroxy, chloro, and methyl and ethyl radicals; n is an integer from 1 to 5 inclusive; and A is an organic radical selected from the group consisting of



where R_1 and R_3 are selected from the group consisting of hydrogen and alkyl and cycloalkyl groups containing

1–18 carbon atoms wherein the sum of carbon atoms in R_1 and R_3 is no more than 18, and where



is a heterocyclic radical wherein only nitrogen and carbon atoms are joined in a 5 or 6 membered ring.

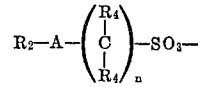
2. A bath in accordance with claim **1** containing a surface active compound wherein R_2 is an alkyl group containing 16–20 carbons, R_4 is hydrogen, and n is the integer 3 or 4.

3. A bath in accordance with claim **1** wherein said surface-active compound is the sulfobentaine of N,N-dimethyl-3-stearylamino propanesulfonic acid.

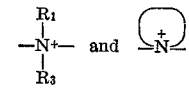
4. A bath in accordance with claim **1** wherein said surface-active compound is the sulfobentaine of N,N-dimethyl-stearylamino butanesulfonic acid.

5. A bath in accordance with claim **1** wherein said surface-active compound is the sulfobentaine of 3-(1-stearyl piperidine) propanesulfonic acid.

6. In a method to suppress mist and spray from aqueous acid hexavalent chromium plating baths, the improvement which comprises the addition to said bath of from 0.002 to about 0.5 gram/liter of a surface-active compound represented by the formula



where R_2 is an alkyl group containing 12–22 carbon atoms inclusive; each of R_4 is selected from the group consisting of hydrogen, hydroxy, chloro, and methyl and ethyl radicals; n is an integer from 1 to 5 inclusive; and A is an organic radical selected from the group consisting of



where R_1 and R_3 are selected from the group consisting of hydrogen and alkyl and cycloalkyl groups containing 1–18 carbon atoms wherein the sum of carbon atoms in R_1 and R_3 is no more than 18, and where



is a heterocyclic radical wherein only nitrogen and carbon atoms are joined in a 5 to 6 membered ring.

7. A method in accordance with claim **6** wherein R_2 is an alkyl group containing 16–20 carbons, R_4 is hydrogen, and n is the integer 3 or 4.

8. A method in accordance with claim **6** wherein said surface-active compound is sulfobetaine of N,N-dimethyl-3-stearylamino propanesulfonic acid.

9. A method in accordance with claim **6** wherein said surface-active compound is the sulfobetaine of N,N-dimethyl-stearylamino butanesulfonic acid.

10. A method in accordance with claim **6** wherein said surface-active compound is the sulfobetaine of 3-(1-stearyl piperidine) propanesulfonic acid.

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U.S. Cl. X.R.

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