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CHROMIUM PLATING

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15 Claims. (Cl. 204—51)

The present invention relates to the electrodeposition of chromium and more particularly to the electrodeposition of chromium from chromic acid baths which produce a minimum of spray and mist during electrodeposition. This application is a continuation-in-part of U.S. application Serial No. 688,829, filed October 8, 1957, and now abandoned.

The electrodeposition of chromium from aqueous chromic acid baths produces a substantial amount of spray and mist. The bath is exceedingly corrosive and toxic. To minimize the danger and corrosiveness caused by the operation of these baths under conditions producing spray and mist, it is necessary to design special equipment and to provide large ventilation capacity. This corrosive spray and mist is caused by the formation of gas bubbles at the electrodes (oxygen at the anodes and hydrogen at the cathodes). These bubbles are relatively large and when they break at the surface, the electrolyte spatters into very fine droplets which become airborne.

Certain additives having strong wetting characteristics are, and have been, used to reduce mist and spray. However, none of the additives now known are completely successful from a commercial viewpoint. Some are useful for very short periods of time but then rapidly decompose in the highly oxidizing chromic acid baths. Others, although effective in preventing spray and mist, are strongly adsorbed on the cathodes resulting in electrodeposits that have poor adhesion and that are pitted. The most successful additives are the fluorinated long chain hydrocarbons which are very expensive.

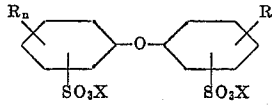
It is an objective of this invention to provide a process for electroplating chromium from chromic acid baths with concomitant production of a minimum of spray and mist.

It is another object of this invention to provide a composition of matter which when incorporated in chromic acid baths minimizes the production of spray and mist during electrodeposition.

The invention also contemplates the use of chromic acid baths from which chromium may be electrodeposited with a minimum of mist and spray at the surface.

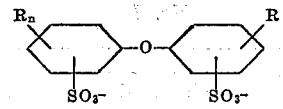
I have now discovered that when chromium is electrodeposited from a chromic acid bath in which is incorporated a small but effective amount of a sulfonated alkyl diphenyl oxide, the electrodeposition is carried out with the production of an amount of spray and mist which is substantially less than that produced with baths that do not include this additive.

The sulfonated alkyl oxide added to the bath has the following general formula:



wherein R is an alkyl group having from 6 to 18 carbon atoms in the chain and X is a cation, and *n* has a value of

0 or 1. The cation, X, is selected from hydrogen, ammonium and metals, and excludes metalloids which are converted in the chromic acid bath to acid radical anions which have a deleterious effect on the bath or on the electrodeposited chromium. Illustrative metals include sodium, potassium, lithium, trivalent chromium, calcium, barium, magnesium, nickel, iron, and copper. The preferred compounds are the sulfonated salts of sodium, potassium, lithium or ammonium. The operative alkyl groups, R, includes the hexyl, octyl, nonyl, dodecyl and octadecyl groups. The octyl, nonyl and dodecyl groups are preferred. Chromic acid baths are highly acid and strongly ionizing in nature. The sulfonated alkyl diphenyl oxide in the bath is believed to exist in the form of the acid radical, having the formula:



The sulfonated alkyl dipenhyl oxide as produced and utilized is a mixture of the various substituted products. The sulfonic acid salt group is believed primarily substituted in the position ortho to the oxygen-substituted carbon, whereas the alkyl chain is primarily substituted in the para position. The additive as commercially produced and utilized may also be a mixture of mono- and dialkyl substituted products. A preferred additive is a mixture of the disulfonated salts of monododecyl diphenyl oxide and didodecyl diphenyl oxide. The disodium and dipotassium salts are preferred.

It have discovered that when as little as 0.005 g./l. (gram per liter) of sulfonated alkyl diphenyl oxide is added to a chromic acid bath in the chromium plating process, the amount of mist and spray is very substantially reduced. Although these additives are stable in chromic acid baths, they do decompose to a slight extent and over a period of time are "used up," to which drag-out contributes. The minimum initial amount added to the bath is to a large extent governed by the contemplated replenishment rate. It is also in part governed by cost considerations and by the actual construction of the plating tanks. Baths containing this additive have a stable foam blanket on the surface. It is desirable that this blanket should be stable and of substantial, yet not too great, thickness, which could be dangerous because of the large amount of entrapped oxygen and hydrogen. For this reason the geometry of the plating system affects the desired concentration of additive as it will affect the thickness of the foam blanket for a given volume of bath. It is not contemplated that more than about 5 g./l. of the additive will be used. I prefer to use baths which contain about 0.01 g./l. and 0.25 g./l. in the bath.

The sulfonated alkyl diphenyl oxides are solid materials and are preferably added to the bath in the form of an aqueous solution. When such solutions are stored, an undesirable mold is formed. I have discovered that stable aqueous solutions of the sulfonated alkyl diphenyl oxide may be prepared by incorporating a sodium or potassium salt of chromic acid in the solution. Preferably between about one g./l. to five g./l. of potassium or sodium chromate or dichromate are used. The addition of these stablized solutions to chromic acid baths is the preferred method of preparing chromic acid baths which produce a minimum of spray and mist during the electrodeposition of chromium.

It has been found that the sulfonated alkyl diphenyl oxides are effective in reducing spray and mist in the various types of chromic acid baths. These include baths containing sulfate catalyst, and also those containing mixed catalysts. It is effective in low concen-

tration baths, such as those containing 180 to 250 g./l. of chromic acid, as well as medium and high concentration baths containing as much as 550 to 600 g./l. of chromic acid. These baths are operated under conventional process conditions. The chromium electroplating baths referred to herein are the conventional hexavalent chromium baths comprised largely of chromic acid. Although these baths are commonly referred to as being formed from chromic acid, they are more correctly noted as being formed from chromic anhydride or equivalent material.

For the purpose of further illustrating the advantages of the present invention, the following illustrative examples are included:

Chromium electrodeposition was carried out in a standard cell by electrolysis using insoluble lead anodes and plating on the cathode. Standard conditions were used unless otherwise specified.

No. 1

CrO_3	g./l.	250
SO_4 (as Na_2SO_4)	g./l.	2.5
The sodium salt of sulfonated dodecyl diphenyl oxide	g./l.	0.25
Temperature	° F.	110

C.D.—1 a.s.i.

No. 2

CrO_3	g./l.	325
SO_4	g./l.	3.25
The sodium salt of sulfonated dodecyl diphenyl oxide	g./l.	1.0
Temperature	° F.	120

C.D.—1.5 a.s.i.

No. 3

CrO_3	g./l.	400
SO_4	g./l.	4.0
The sodium salt of sulfonated dodecyl diphenyl oxide	g./l.	5.0
Temperature	° F.	105

C.D.—0.75 a.s.i.

No. 4

CrO_3	g./l.	250
SO_4	g./l.	2.5
The sodium salt of sulfonated dodecyl diphenyl oxide	g./l.	0.5
Temperature	° F.	130

C.D.—2.5 a.s.i.

No. 5

CrO_3	g./l. 400
K_2SiF_6	In excess of saturation
$SrSO_4$	In excess of saturation

C.D.—1 a.s.i.

The sodium salt of sulfonated dodecyl diphenyl oxide

(*a*) 2 g./l.	Temperature, ° F.	110
(*b*) 0.25 g./l.	do	110
(*c*) 0.25 g./l.	do	130
(*d*) 0.025 g./l.	do	**110**
(*e*) 0.025 g./l.	do	130

No. 6

CrO_3	g./l. 250
K_2SiF_6	In excess of saturation
$SrSO_4$	In excess of saturation
$K_2Cr_2O_7$	g./l. 10
$SrCrO_4$	g./l. 5

C.D.—1 a.s.i.

The sodium salt of sulfonated dodecyl diphenyl oxide

(*a*) 1 g./l.	Temperature, ° F.	130
(*b*) 0.25 g./l.	do	110
(*c*) 0.25 g./l.	do	130
(*d*) 0.025 g./l.	do	110
(*e*) 0.025 g./l.	do	130
(*f*) 0.01 g./l.	do	125

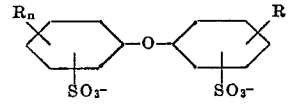
The additive used in the noted tests was a mixture of the disodium salts of monododecyl diphenyl oxide disulfonate and didodecyl diphenyl oxide disulfonate (4:1 ratio). The potassium salts are as effective, as are the homologous alkyl substituted compounds.

The baths made up and operated as specified in the examples have relatively thin stable foam blankets at the surface and exhibit a substantial reduction of the amount of mist and spray when compared to similar baths used as controls. Service tests illustrated that the baths were effective for relatively long periods of time without replenishment and that the baths could be maintained in excellent condition by periodic additions of the additive. An unusual feature of the baths containing very small amounts of the sulfonated alkyl diphenyl oxides is that they effectively operate with a minimum of spray and mist and yet, many of the baths have such a small concentration of the additive that there is little discernable lowering of surface tension. Life tests run over relatively long periods of time did not indicate any buildup of harmful decomposition products.

The chromium deposits produced under standard conditions were bright and meet the usual commercial standards. The sulfonated alkyl diphenyl oxides are compatible in the baths with the other usual bath components and additives, including other additives used as anti-misting agents. Pilot plant studies of baths containing the sulfonated alkyl diphenyl oxides disclose that over a period of time substantially less chromic acid had to be replaced in the bath. This is attributable to the decrease in spray and mist, both of which contribute to large chromic acid losses in baths without an anti-misting additive. In light of the foregoing description, the following is claimed:

1. An improved bath for the electrodeposition of chromium comprising an aqueous acid chromium plating solution and as an anti-misting additive, a small amount sufficient to substantially decrease mist in said bath of a disulfonated alkyl diphenyl oxide.

2. An improved bath for the electrodeposition of chromium comprising an aqueous chromic acid chromium plating solution and as an anti-misting additive, at least 0.005 g./l. of at least one compound having the general formula



wherein R is an alkyl group having 6 to 18 carbon atoms, and *n* is an integer having a value from 0 to 1.

3. A bath as set forth in claim No. 2, containing between 0.1 g./l. and 0.25 g./l. of the additive.

4. A bath as set forth in claim No. 3 in which R is selected from the class consisting of octyl, nonyl and dodecyl.

5. A bath as set forth in claim No. 2 in which the anti-misting additive is added in the form of the disodium salt of disulfonated monododecyl diphenyl oxide.

6. A bath as set forth in claim No. 2, in which the anti-misting additive is added in the form of the potassium salt of disulfonated monododecyl diphenyl oxide.

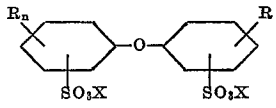
7. A bath as set forth in claim No. 2, in which R is an octyl group.

8. A bath as set forth in claim No. 2, in which R is a nonyl group.

9. In a process for electrodepositing chromium metal

with a minimum of spray and mist the improvement which comprises electroplating chromium from an aqueous chromic acid bath to which has been added a small amount sufficient to substantially decrease mist in said bath of disulfonated alkyl diphenyl oxide.

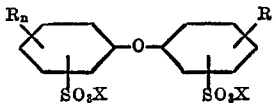
10. In a process for electrodepositing chromium metal with a minimum of spray and mist the improvement which comprises electroplating chromium from an aqueous chromic acid bath to which has been added at least 0.005 g./l. of at least one compound having the general formula



wherein R is an alkyl group having 6 to 18 carbon atoms, *n* is an integer having a value from 0 to 1, and X is a cation selected from the class consisting of hydrogen, ammonium, and a metal.

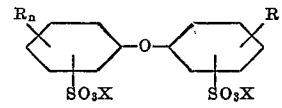
11. A liquid anti-misting additive for minimizing the formation of mist and spray from aqueous chromic acid baths during electrolysis comprising an aqueous solution of a disulfonated alkyl diphenyl oxide stabilized to prevent mold formation with an alkali salt of a chromic acid selected from the class consisting of chromic and dichromic acids in sufficient amount to effect said stabilization.

12. A liquid anti-misting additive for minimizing the formation of mist and spray from aqueous chromic acid baths during electrolysis comprising an aqueous solution of at least one compound having the general formula



wherein R is an alkyl group having 6 to 18 carbon atoms, *n* is an integer having a value from 0 to 1, and X is a cation selected from the class consisting of hydrogen, ammonium, and a metal, stabilized with between 1 g./l. and 5 g./l. of a chromate salt of a metal selected from the class consisting of sodium and potassium.

13. A liquid anti-misting additive for minimizing the formation of mist and spray from aqueous chromic acid baths during electrolysis comprising an aqueous solution of at least one compound having the structural formula



in which R is a dodecyl group, *n* is an integer having a value from 0 to 1, and X is sodium, stabilized to prevent mold formation with an alkali metal chromate in sufficient amount to effect said stabilization.

14. The composition of matter of claim No. 13 in which the alkyl diphenyl oxide additive comprises a mixture of the disodium salt of monododecyl diphenyl oxide disulfonate and didodecyl diphenyl oxide disulfonate in a ratio of about 4 to 1.

15. An improved bath for the electrodeposition of chromium comprising an aqueous chromic acid chromium plating solution and, as an anti-misting additive, a small amount sufficient to substantially decrease mist in said bath of octadecyldiphenyl oxide sulfonate.

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