United States Patent Office 3,041,257 Patented June 26, 1962

3,041,257

CHROMIUM ELECTROPLATING

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No Drawing. Filed Aug. 25, 1960, Ser. No. 51,770
11 Claims. (Cl. 204—51)

This invention relates to the electrodeposition of chromium from aqueous acidic hexavalent chromium baths and has particular reference to aqueous acidic hexavalent chromium baths comprising a stable additive composition for the bath which is capable of reducing substantially the formation of spray and mist during electrolysis.

It is well known in the art that large quantities of hydrogen are evolved at the cathodes and large quantities of oxygen and ozone are evolved at the insoluble anodes during the electrodeposition of chromium from aqueous acidic hexavalent chromium solutions or baths. An undesirable spray and mist of chromic acid is given off from the bath as the many gas bubbles formed by the relatively large quantities of hydrogen, oxygen and ozone burst violently at the surface of the bath.

The spray and mist that is given off during electrolysis is of considerable volume, and is highly toxic to the workers in and around the area of the spray. Furthermore, the mist is highly corrosive to nearby equipment, and has a deleterious contaminating effect on other plating baths in the vicinity.

Many attempts have been made by those skilled in the art to prevent or to minimize substantially the formation of this highly undesirable spray and mist during the electrodeposition of chromium from aqueous acidic hexavalent chromium solutions. The methods proposed heretofore have not been entirely satisfactory.

This invention is concerned particularly with providing a stable additive composition for acidic hexavalent chromium baths which is capable of minimizing substantially the formation of spray and mist during electrolysis of such baths with insoluble or highly polarized anodes, and to provide a new and improved hexavalent chromium plating bath.

For a complete understanding of this invention, reference is made to the following detailed description.

In accordance with this invention stable additive compositions for aqueous acidic hexavalent chromium electroplating baths have been found that are highly satisfactory in preventing substantially the formation of spray and mist during electrolysis.

Chromium electropolating baths are well known in the art, and basically they comprise chromium trioxide, CrO_3, chromic acid or chromic anhydride, water, and a catalyst. There would be no chromium deposited from the bath without the catalyst. The addition of a suitable catalyst in the ratio of about 1 part by weight to 100 parts by weight of chromic acid produces a satisfactory working solution. The above ratio can be varied to meet different plating conditions. Thus, the ratio has been varied by those skilled in the art from about 1:60 to 1:250.

The catalyst employed in the chromium electroplating bath can be a sulfate, usually introduced into the bath by the addition of sulfuric acid.

Some common formulations are as follows: (i) 33 ounces of chromic acid per gallon of electrolyte and 0.33 ounce of sulfuric acid (98%) per gallon of electrolyte; (ii) 54 ounces of chromic acid per gallon of electrolyte and 0.54 ounce of sulfuric acid (98%) per gallon of electrolyte; and (iii) 40 ounces of chromic acid per gallon of electrolyte and 0.40 ounce of sulfuric acid (98%) gallon of electrolyte.

Chromium electroplating baths can be prepared by supplying CrO_3 in the form of chromic anhydride or in the form of compounds containing cations which do not affect adversely the bath characteristics. Such compounds include the chromates, dichromates, and polychromates of potassium, sodium, magnesium and calcium. The CrO_3 can be added in the form of chromic acid and/or dichromic acid in solution. Where alkali metal cations are present, the bath should not be neutralized in excess of 80% of the dichromate end-point.

Sulfate ions can be added in the form of sulfuric acid as above set forth or as a sulfate salt or salts with a cation that does not affect adversely the characteristics of the bath. Examples of such cations include potassium, sodium, calcium, strontium, magnesium, and chromium.

Silicofluoride ions can be added to the bath to maintain and to regulate the catalyst acid radical content of the bath. Silicofluoride ions can be added in the form of fluosilicic acid. Also, they can be added as silicofluoride salt or salts with a cation that does not affect adversely the bath characteristics such as potassium, sodium, magnesium, and chromium. The silicofluoride ion is usually present in an amount equal to about 1% to 2% of the chromic acid concentration.

The examples below are illustrative of typical bath formulations.

Example I

	Ounces per gallon
Chromic acid (CrO_3)	27 to 67
Strontium sulfate	0.81 to 2.01
Potassium silicofluoride	2.16 to 5.36

Example II

Chromic acid (CrO_3)	40
Sulfuric acid	0.24
Fluosilicic acid	0.40

The stable additive compositions of this invention are soluble in conventional aqueous acidic hexavalent chromium baths and will prevent or minimize effectively the formation of spray and mist. Furthermore, the additive compositions are stable to the extremely powerful oxidizing conditions that exist at the insoluble anodes during the electro-deposition of chromium from such baths.

The stable additive composition of this invention comprises specific non-ionic wetting agents alone or in admixture with certain alkyl aromatic sulfonates to be detailed more fully hereinafter. The non-ionic wetting agents or surfactants are selected from the group consisting of (1) polymers of ethylene oxide having an average molecular weight of from about 1,300 to 1,800, (2) a cogeneric mixture of conjugated polyoxypropylene-polyoxyethylene compounds containing in their structure oxypropylene groups, oxyethylene groups and an organic radical derived from an organic compound containing a plurality of reactive hydrogen atoms, the compounds being characterized in that all of the oxypropylene groups are present in polyoxypropylene chains that are attached to the organic radical at the site of a reactive hydrogen atom to thereby constitute a polyoxypropylene polymer, the oxyethylene groups are attached to the polyoxypropylene polymer in polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymer in the mixture is within the range of from about 1,500 to 1,800, as determined by hydroxyl number, and the oxyethylene groups present constitute from about 80% to 95% by weight of the mixture, and (3) mixtures of (1) and (2).

Nonionic wetting agent (2) above can be represented by the structural formula

$$HO(C_2H_4O)_X(C_3H_6O)_Y(C_2H_4O)_ZH$$

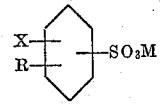
wherein Y represents an integer sufficient to provide a molecular weight of polyoxypropylene of from 1500 to 1800, and X and Z are in integers the total of which is sufficient to provide oxyethylene groups in an amount equal to from about 80% to 95% by weight of the total weight of the molecule.

Compounds of the types above described under (2) are available commercially under the proprietary designation "Pluronic."

It has been determined also, according to the present invention, that substantial reduction of the undesired chromic acid spray can be accomplished by adding to the bath an admixture of from 10 to 90 parts by weight of the above enumerated nonionic wetting agents (1), (2), and (3) and from 90 to 10 parts by weight of an alkyl aromatic sulfonic acid compound of the benzene series containing at least 7 carbon atoms in an alkyl group.

While the specific nonionic wetting agents (1), (2), and (3) enumerated above are effective in reducing substantially the chromic acid spray, it is preferred to employ the admixture as set forth hereinbelow as it is even more effective. The preferred admixture will comprise from 40 to 60 parts by weight of nonionic wetting agent (1), (2), or (3) and from 60 to 40 parts by weight of alkyl aromatic sulfonic acid compound of the benzene series containing at least 7 carbon atoms in an alkyl group.

Alkyl aromatic sulfonic acid compounds of the benzene series containing at least 7 carbon atoms in an alkyl group can be represented by the formula



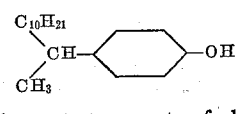
in which X represents hydrogen; a hydroxyl group; a lower alkyl group such as methyl, ethyl, propyl, isopropyl, and n-butyl; an alkoxy group such as methoxy, ethoxy, benzyloxy and the like; an aryloxy group such as phenoxy and methylphenoxy; or a carboxyl group. R represents an alkyl hydrocarbon radical (saturated or unsaturated) containing 7 or more (preferably 10 to 19) carbon atoms, and M represents hydrogen or a metal, or an ammonium or an organic ammonium radical. For convenience this class of compounds will be referred to hereinafter as "alkyl aromatic sulfonates of the benzene series."

Reference is made to U.S. Patent 2,195,409 for a more detailed description of alkyl aromatic sulfonates of the benzene series, specific examples thereof, and methods of preparing the same.

The following specific example is given by way of illustration. All parts are by weight unless otherwise designated.

Example III

One hundred parts of commercial lauryl alcohol (obtained by hydrogenation of fatty acids from cocoanut oil), 100 parts of phenol, and 100 parts of anhydrous zinc chloride are mixed and refluxed at 190° C. to 200° C. with agitation for about 16 hours. The condensation product is washed with water until substantially free of water-soluble products, and the resulting oil is fractionally distilled in vacuo. The fraction of the distillate collected as a faint yellow to water-white oil between 210° C. to 230° C. at 13 mm. mercury pressure consists mainly of lauryl phenols of which the probable formula of the main constituent is



One houndred twenty-two parts of chlorosulfonic acid are added to 270 parts of the resulting oil which is held at a temperature below 10° C., then sulfonation is continued at room temperature for 2 hours. The sulfonation mixture is drowned in four times its weight of a mixture of ice and water and a solution of sodium hydroxide is added while keeping the temperature below 35° C. until the product is neutral (pH=7.0). The neutralized solution is evaporated to dryness to provide an alkyl aromatic sulfonate of the benzene series suitable for use in this invention.

The amount of stable additive composition of this invention that is added to the chromium electroplating bath will be sufficient to provide a bath surface tension of at least 55 dynes per cm.^{2} at 25° C. It has been determined that the stable additive composition of this invention, whether it comprise the above defined nonionic wetting agents alone or the nonionic wetting agents in admixture with the alkyl aromatic sulfonates of the benzene series, can be added in amount of from about .015 to .40 ounce per gallon of electrolyte. It is within the skill of those versed in the art to determine the amount of additive composition required to provide a bath surface tension of at least 55 dynes per cm.^{2} at 25° C., or at least an amount sufficient to retard substantially the liberation of chromic acid fumes or spray from the bath.

The non-ionic wetting agents alone provide for substantial reduction of the surface tension of the chromium electroplating bath and is satisfactory for most baths. However, for baths of higher chromic acid concentration it is preferred to employ the admixture of non-ionic wetting agent acid alkyl aromatic sulfonates as above defined as the surface tension of the bath is more effectively controlled thereby eliminating substantially any undesired chromic acid spray.

The examples that follow are illustrative of this invention.

Example IV

To a chromic acid bath containing 54 ounces of CrO_3 per gallon of aqueous solution and a ratio of HSO_4:CrO_3 within the range of 1:100 there is added .20 ounce per gallon of a non-ionic wetting agent consisting of a cogeneric mixture of conjugated poloxypropylene-polyoxyethylene compounds containing in their structure oxyproylene groups, oxyethylene groups and an organic radical derived from an organic compound containing a plurality of reactive hydrogen atoms, the compounds being characterized in that all of the oxypropylene groups are present in polyoxypropylene chains that are attached to the organic radical at the site of the reactive hydrogen atom to thereby constitute a polyoxypropylene polymer, the oxyethylene groups are attached to the polyoxypropylene polymer in polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymer in the mixture is about 1500 to 1800 as determined by hydroxyl number, and the oxyethylene groups present constitute about 80% by weight of the mixture. During operation of this bath, substantially no chromic acid spray or mist is noted.

Example V

A chromium plating bath is prepared as described in Example IV above except that 40 ounces of CrO_3 are employed per gallon of solution and .20 ounce per gallon of a polymer of ethylene oxide having a molecular weight of about 1500. Excellent results are obtained in plating various types of objects in this bath and there is substantially no chromic acid spray or mist noted.

To the chromium plating bath of Example II there is added about .30 ounce per gallon of a stable additive composition consisting of, by weight, 50 parts of the nonionic wetting agent used in Example IV and 50 parts of the alkyl aromatic sulfonate of the benzene series of Example III. Good plating results are obtained and no objectionable chromic acid spray is noted.

The operating conditions for the bath of this invention are the same as those employed for the baths without the addition of the stable additive composition of this invention. Thus, operating temperatures of from about 100°

C. to 160° C. can be employed, and current densities of from about 100 to 500 amperes per square foot are satisfactory.

A significant reduction in the spray and mist formed during electrodeposition of chromium from aqueous acidic hexavalent chromium baths is apparent when the additive composition of this invention is employed. Further the additive compositions of this invention are very stable. That is they do not decompose in the chromium bath and lose their effectiveness.

It is to be understood that the above description of this invention is illustrative only and not in limitation thereof.

We claim as our invention:

1. A chromic acid plating bath for the electrodeposition of chromium comprising an aqueous acidic hexavalent chromium solution containing a non-ionic wetting agent selected from the group consisting of (1) polymers of ethylene oxide having an average molecular weight of from 1300 to 1800, (2) a cogeneric mixture of conjugated polyoxypropylene-polyoxyethylene compounds containing in their structure oxypropylene groups, oxyethylene groups and an organic radical derived from an organic compound containing a plurality of reactive hydrogen atoms, the compounds being characterized in that all of the oxypropylene groups are present in polyoxypropylene chains that are attached to the organic radical at the site of a reactive hydrogen atom to thereby constitute a polyoxypropylene polymer, the oxyethylene groups are attached to the polyoxypropylene polymer in polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymer in the mixture being from about 1500 to 1800 as determined by hydroxyl number, and the oxyethylene groups present constitute from about 80% to 95% by weight of the mixture, and (3) mixtures of (1) and (2), said non-ionic wetting agent being present in an amount sufficient to retard substantially the liberation of chromic acid fumes from said bath.

2. A chromic acid plating bath for the electrodeposition of chromium comprising an aqueous acidic hexavalent chromium solution containing a stable additive composition comprising (A) from 10 to 90 parts by weight of a non-ionic wetting agent selected from the group consisting of (1) polymers of ethylene oxide having an average molecular weight of from 1300 to 1800, (2) a cogeneric mixture of conjugated polyoxypropylene-polyoxyethylene compounds containing in their structure oxypropylene groups, oxyethylene groups and an organic radical derived from an organic compound containing a plurality of reactive hydrogen atoms, the compounds being characterized in that all of the oxypropylene groups are present in polyoxypropylene chains that are attached to the organic radical at the site of the reactive hydrogen atom to thereby constitute a polyoxypropylene polymer, the oxyethylene groups are attached to the polyoxypropylene polymer in polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymer in the mixture being from about 1500 to 1800 as determined by hydroxyl number, and the oxyethylene groups present constitute from about 80% to 95% by weight of the mixture and (3) mixtures of (1) and (2), and (B) from 90 parts to 10 parts by weight of an alkyl aromatic sulfonic acid compound of the benzene series containing at least 7 carbon atoms in an alkyl group, said stable additive composition being present in an amount sufficient to retard substantially the liberation of chromic acid fumes from said bath.

3. A chromic acid plating bath for the electrodeposition of chromium comprising an aqueous acidic hexavalent chromium solution containing a stable additive composition comprising (A) from 40 to 60 parts by weight of a non-ionic wetting agent selected from the group consisting of (1) polymers of ethylene oxide having an average molecular weight of from 1300 to 1800, (2) a cogeneric mixture of conjugated polyoxypropylene-polyoxyethylene compounds containing in their structure oxypropylene groups, oxyethylene groups and an organic radical derived from an organic compound containing a plurality of reactive hydrogen atoms, the compounds being characterized in that all of the oxypropylene groups are present in polyoxypropylene chains that are attached to the organic radical at the site of the reactive hydrogen atom to thereby constitute a polyoxypropylene polymer, the oxyethylene groups are attached to the polyoxypropylene polymer in polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymer in the mixture being from about 1500 to 1800 as determined by hydroxyl number, and the oxyethylene groups present constitute from about 80% to 95% by weight of the mixture, and (3) mixtures of (1) and (2), and (B) from 60 parts to 40 parts by weight of an alkyl aromatic sulfonic acid compound of the benzene series containing at least 7 carbon atoms in an alkyl group, said stable additive composition being present in an amount sufficient to retard substantially the liberation of chromic acid fumes from said bath.

4. The method of chromium plating which comprises electrodepositing chromium from a chromic acid plating bath comprising a non-ionic wetting agent selected from the group consisting of (1) polymers of ethylene oxide having an average molecular weight of from 1300 to 1800, (2) a cogeneric mixture of conjugated polyoxypropylene-polyoxyethylene compounds containing in their structure oxypropylene groups, oxyethylene groups and an organic radical derived from an organic compound containing a plurality of reactive hydrogen atoms, the compounds being characterized in that all of the oxypropylene groups are present in polyoxypropylene chains that are attached to the organic radical at the site of the reactive hydrogen atom to thereby constitute a polyoxypropylene polymer, the oxyethylene groups are attached to the polyoxypropylene polymer in polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymers in the mixture is from about 1500 to 1800 as determined by hydroxyl number, and the oxyethylene groups present constitute from about 80% to 95% by weight of the mixture, and (3) mixtures of (1) and (2), said nonionic wetting agent being present in an amount sufficient to retard substantially the liberation of chromic acid fumes from said bath.

5. The method of chromium plating which comprises electrodepositing chromium from a chromic acid plating bath comprising a stable additive composition comprising (A) from 10 to 90 parts by weight of a non-ionic wetting agent selected from the group consisting of (1) polymers of ethylene oxide having an average molecular weight of from about 1300 to 1800, (2) a cogeneric mixture of conjugated polyoxypropylene-polyoxyethylene compounds containing in their structure oxypropylene groups, oxyethylene groups and an organic radical derived from an organic compound containing a plurality of reactive hydrogen atoms, the compounds being characterized in that all of the oxypropylene groups are present in polyoxypropylene chains that are attached to the organic radical at the site of a reactive hydrogen atom to thereby constitute a polyoxypropylene polymer, the oxyethylene groups are attached to the polyoxypropylene polymer in polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymer in the mixture being within the range of from about 1500 to 1800 as determined by hydroxyl number, and the oxyethylene groups present constitute from about 80% to 95% by weight of the mixture, and (3) mixtures of (1) and (2), and (B) from 90 parts to 10 parts by weight of an alkyl aromatic sulfonic acid compound of the benzene series containing at least 7 carbon atoms in an alkyl group, said stable additive composition being present in an amount sufficient to retard substantially the liberation of chromic acid fumes from said bath.

6. The method of chromium plating which comprises electrodepositing chromium from a chromic acid plating

bath comprising a stable additive composition comprising (A) from 40 to 60 parts by weight of a non-ionic wetting agent selected from the group consisting of (1) polymers of ethylene oxide having an average molecular weight of from about 1300 to 1800, (2) a cogeneric mixture of conjugated polyoxypropylene-polyoxyethylene compounds containing in their structure oxypropylene groups, oxyethylene groups and an organic radical derived from an organic compound containing a plurality of reactive hydrogen atoms, the compounds being characterized in that all of the oxypropylene groups are present in polyoxypropylene chains that are attached to the organic radical at the site of a reactive hydrogen atom to thereby constitute a polyoxypropylene polymer, the oxyethylene groups are attached to the polyoxypropylene polymer in polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymer in the mixture being within the range of from about 1500 to 1800 as determined by hydroxyl number, and the oxyethylene groups present constitute from about 80% to 95% by weight of the mixture, and (3) mixtures of (1) and (2), and (B) from 60 parts to 40 parts by weight of an alkyl aromatic sulfonic acid compound of the benzene series containing at least 7 carbon atoms in an alkyl group, said stable additive composition being present in an amount sufficient to retard substantially the liberation of chromic acid fumes from said bath.

7. A chromic acid plating bath for the electro-deposition of chromium comprising an aqueous solution of from about 33 ounces to 54 ounces per gallon of CrO_3, an amount of H_2SO_4 sufficient to provide a weight ratio of H_2SO_4:CrO_3 of 1:250 to 1:60 and a quantity of non-ionic wetting agent selected from the group consisting of (1) polymers of ethylene oxide having an average molecular weight of from about 1300 to 1800, (2) a cogeneric mixture of conjugated polyoxypropylene-polyoxyethylene compound containing in their structure oxypropylene groups, oxyethylene groups and an organic radical derived from an organic compound containing a plurality of reactive hydrogen atoms, the compound being characterized in that all of the oxypropylene groups are present in polyoxypropylene chains that are attached to the organic radical at the site of a reactive hydrogen atom to thereby constitute a polyoxypropylene polymer, the oxyethylene groups are attached to the polyoxypropylene polymer in polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymers in the mixture is from about 1500 to 1800 as determined by hydroxyl number, and the oxyethylene groups present constitute from about 80% to 95% by weight of the mixture, and (3) mixtures of (1) and (2) said non-ionic wetting agent being present in an amount sufficient to retard substantially the liberation of chromic acid fumes from said bath.

8. A chromic acid plating bath for the electrodeposition of chromium comprising an aqueous solution of from about 33 ounces to 54 ounces per gallon of CrO_3, an amount of H_2SO_4 sufficient to provide a ratio of H_2SO_4:CrO_3 of 1:250 to 1:60 and a quantity of a stable additive composition comprising (A) from 10 to 90 parts by weight of non-ionic wetting agent selected from the group consisting of (1) polymers of ethylene oxide having an average molecular weight of from about 1300 to 1800, (2) a cogeneric mixture of conjugated polyoxypropylene-polyoxyethylene compounds containing in their structure oxypropylene groups, oxyethylene groups and an organic radical derived from an organic compound containing a plurality of reactive hydrogen atoms, the compound being characterized in that all of the oxypropylene groups are present in polyoxypropylene chains that are attached to the organic radical at the site of the reactive hydrogen atom to thereby constitute a polyoxypropylene polymer, the oxyethylene groups are attached to the polyoxypropylene polymer in polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymers in the mixture being from about 1500 to 1800 as determined by hydroxyl number, and the oxyethylene groups present constitute from about 80% to 95% by weight of the mixture, and (3) mixtures of (1) and (2), and (B) from 90 parts to 10 parts by weight of an alkyl aromatic sulfonic acid compound of the benzene series containing at least 7 carbon atoms in an alkyl group said stable additive composition being present in an amount sufficient to retard substantially the liberation of chromic acid fumes and spray from said bath.

9. A chromic acid plating bath for the electrodeposition of chromium comprising an aqueous solution of from about 33 ounces to 54 ounces per gallon of CrO_3, an amount of H_2SO_4 sufficient to provide a ratio of H_2SO_4:CrO_3 of 1:250 to 1:60 and a quantity of a stable additive composition comprising (A) from 40 to 60 parts by weight of a non-ionic wetting agent selected from the group consisting of (1) polymers of ethylene oxide having an average molecular weight of from about 1300 to 1800, (2) a cogeneric mixture of conjugated polyoxypropylene-polyoxyethylene compounds containing in their structure oxypropylene groups, oxyethylene groups and an organic radical derived from an organic compound containing a plurality of reactive hydrogen atoms, the compound being characterized in that all of the oxypropylene groups are present in polyoxypropylene chains that are attached to the organic radical at the site of the reactive hydrogen atom to thereby constitute a polyoxypropylene polymer, the oxyethylene groups are attached to the polyoxypropylene polymer in polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymers in the mixture being from about 1500 to 1800 as determined by hydroxyl number, and the oxyethylene groups present constitute from about 80% to 95% by weight of the mixture, and (3) mixtures of (1) and (2), and (B) from 60 parts to 40 parts by weight of an alkyl aromatic sulfonic acid compound of the benzene series containing at least 7 carbon atoms in an alkyl group said stable additive composition present in an amount sufficient to retard substantially the liberation of chromic acid fumes and spray from said bath.

10. A stable additive composition for addition to chromic acid plating baths whereby the liberation of chromic acid fumes from said baths during use is retarded substantially comprising (A) from 10 to 90 parts by weight of a non-ionic wetting agent selected from the group consisting of (1) polymers of ethylene oxide having an average molecular weight of from 1300 to 1800, (2) a cogeneric mixture of conjugated polyoxypropylene-polyoxyethylene compounds containing in their structure oxypropylene groups, oxyethylene groups and an organic radical derived from an organic compound containing a plurality of reactive hydrogen atoms, the compounds being characterized in that all of the oxypropylene groups are present in polyoxypropylene chains that are attached to the organic radical at the site of the reactive hydrogen atom to thereby constitute a polyoxypropylene polymer, the oxyethylene groups are attached to the polyoxypropylene polymer in polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymer in the mixture being from about 1500 to 1800 as determined by hydroxyl number, and the oxyethylene groups present constitute from about 80% to 95% by weight of the mixture, and (3) mixtures of (1) and (2), and (B) from 90 parts to 10 parts by weight of an alkyl aromatic sulfonic acid compound of the benzene series containing at least 7 carbon atoms in an alkyl group, said stable additive composition being present in an amount sufficient to retard substantially the liberation of chromic acid fumes from said bath.

11. A stable additive composition for addition to chromic acid plating baths whereby the liberation of

chromic acid fumes from said baths during use is retarded substantially comprising (A) from 40 to 60 parts by weight of a non-ionic wetting agent selected from the group consisting of (1) polymers of ethylene oxide having an average molecular weight of from 1300 to 1800, (2) a cogeneric mixture of conjugated polyoxypropylene-polyoxyethylene compounds containing in their structure oxypropylene groups, oxyethylene groups and an organic radical derived from an organic compound containing a plurality of reactive hydrogen atoms, the compounds being characterized in that all of the oxypropylene groups are present in polyoxypropylene chains that are attached to the organic radical at the site of the reactive hydrogen atom to thereby constitute a polyoxypropylene polymer, the oxyethylene groups are attached to the polyoxypropylene polymer in polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymer in the mixture being from about 1500 to 1800 as determined by hydroxyl number, and the oxyethylene groups present

constitute from about 80% to 95% by weight of the mixture, and (3) mixtures of (1) and (2), and (B) from 60 parts to 40 parts by weight of an alkyl aromatic sulfonic acid compound of the benzene series containing at least 7 carbon atoms in an alkyl group, said stable additive composition being present in an amount sufficient to retard substantially the liberation of chromic acid fumes from said bath.

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