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[54] MIST SUPPRESSION IN ELECTROPLATING SOLUTIONS

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[58] **Field of Search** 204/41, 51, 1.01

[56] **References Cited**

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[57] **ABSTRACT**

In accordance with certain of its aspects, this invention relates to novel compositions and to a process for suppressing mist formation in an aqueous composition which comprises incorporating hydrophobic particles having a particle size of 0.002-100 microns into said aqueous compositions. The process is applicable, for example, to chromium electroplating solutions.

8 Claims, No Drawings

MIST SUPPRESSION IN ELECTROPLATING SOLUTIONS

This invention relates to novel suppressant compositions and to the use of such compositions in plating processes. More particularly, this invention relates to compositions which may be used in electrolytic metal plating operations to reduce losses of the plating bath due to fume and/or spray production.

As is well known to those skilled in the art, electroplating baths (such as chromium plating baths) may be characterized by high fume or spray losses. The production of fumes from an electroplating bath may be objectionable from a health viewpoint because of pollution and waste problems. The use of various additives in electroplating bath compositions has not been entirely satisfactory since such additives are usually surfactants. Such surfactants may be expensive and may produce adverse effects upon the electroplated article which is ultimately produced.

Other attempts to reduce fume and spray production have involved the use of floating plastic materials such as ping pong balls in order to reduce the effective surface area which may produce such fumes and sprays. Such attempts, however, have not been entirely satisfactory because it has been found that such floating articles may pick up particles of wax or other foreign materials and deposit such matter upon the surface of the article to be plated either before or after electroplating to produce defects such as streaks, pits, etc.

It is an object of this invention to provide novel compositions useful in electroplating processes. A further object of the invention is to provide novel fume-suppressing compositions which may be used in electroplating processes. Another object of the invention is to provide effective means for controlling losses in electroplating processes due to fume and/or spray production without producing adverse effects upon the plated articles produced.

In accordance with certain of its aspects, this invention relates to novel compositions and to a process for suppressing mist formation in an aqueous composition which comprises incorporating hydrophobic particles having a particle size of 0.002–100 microns into said aqueous composition.

According to one of its aspects, this invention relates to a process for suppressing the production of fumes and mists from an aqueous electroplating bath solution which comprises passing current from an anode to a metal cathode through an aqueous electroplating bath solution containing a metal compound providing metal ions for electroplating metal and including a blended dispersion of hydrophobic particles having a particle size of 0.002–100 microns, to produce a plated article, and removing said plated article from said aqueous electroplating bath solution.

According to another of its aspects, this invention may be employed to control vapor, mist, spray, or bubble formation in other liquids (such as stripping liquors, pickling liquors, anodizing baths, etc.).

The hydrophobic particles which may be used according to the present invention may be composed of inert water repellent material which does not appreciably dissolve in the particular electroplating bath solution in which the production of fumes is to be inhibited or reduced. As used herein, the term "inert" is meant to refer to materials which do not react with the aqueous electroplating bath solutions. Typical hydrophobic polymeric materials which may be used according to the invention include polyfluorinated hydrocarbons, polypropylene, polyvinyl chloride, and polystyrene. Other natural or artificial hydrophobic materials which may be used include talc, wax, alumina, polymers or copolymers of styrene, butadiene, acrylonitrile, vinyl acetate, vinyl chloride, etc.; diatomaceous earth; silicates, e.g. sodium silicate; insoluble carbonates; insoluble carbides; etc., or mixtures of such materials. Silica which has been coated with a polysiloxane (such as polyalkyl polysiloxanes, e.g. characterized by dimethylsiloxy groups or diethylsiloxy groups) is especially useful. Finely divided silica which contains a surface coating of hydrolyzed dimethyl-dichlorosilane is a preferred hydrophobic material for use according to the invention. Typically, the particles employed according to the process of the

invention may be finely divided, naturally occurring or artificially prepared materials. They may be spherical, angular, chunky, ovular, elongated or platelet-shaped. Preferably, the particles may have an average diameter of 0.002–100 microns, typically 0.005–10 microns, and preferably 0.01–1.0 microns.

The density of such particles should be such as to allow the particles to remain dispersed in the aqueous electroplating bath composition and, preferably, to float upon the surface of said aqueous electroplating bath composition or remain in dispersion at the gas-liquid interface of said aqueous electroplating bath composition. Thus, coated hydrophobic particles may be employed which have a density which would ordinarily not permit said particles to remain in dispersion, providing that the coating (which may be obtained by chemical or physical means) permits the particles to remain in the vicinity of the gas-liquid interface during the electroplating operation.

Suitable hydrophobic materials which may be used in accordance with the invention are characterized as materials which when thoroughly blended in a 5 percent (volume-volume) aqueous sulfuric acid solution, followed by bubbling air or other non-reactive gas into said dispersion for a period of 30 minutes and permitting the resulting mixture to settle for 30 minutes, produces a two-phase system wherein the upper phase contains hydrophobic particles at the gas-liquid interface, and the lower phase is substantially free of said particles. The particles which separate at the gas-liquid interface may be noted to have formed a complex structure in which the gas or air has been entrained in a cellular or foam-like structure with essentially none of the aerated particles appearing in the lower liquid phase of the dispersion after said 30 minute settling time. In particular, the hydrophobic materials which are used according to the invention are such that when 1 gram of said hydrophobic material is blended with 400 ml of an aqueous solution of 5 percent (volume-volume) sulfuric acid in a typical laboratory blender (such as a "Waring" brand blender) at low speed for 3 minutes a dispersion is formed which may be broken by bubbling a gas (typically air) through said dispersion using a 1-ml straight pipette as a gas wand for 30 minutes, followed by a settling time of 30 minutes to produce a two-phase system. After settling, the hydrophobic materials useful in the present invention form an upper phase which covers the surface of the lower liquid phase containing the 5 percent aqueous sulfuric acid. The upper phase contains hydrophobic particles in complex, porous structures wherein the hydrophobic particles are entrained with the gas forming irregular bubbles or cells of liquid, said irregular bubbles or cells surrounding the hydrophobic particles. The hydrophobic particles are thus essentially removed from the aqueous sulfuric acid solution when the air or other gas is thoroughly mixed with the initial dispersion formed by blending the hydrophobic particles with the aqueous sulfuric acid. Other materials which are not suitable for use according to the invention (such as hydrophilic particles) may be found to form an initial dispersion when blended with an aqueous sulfuric acid, but do not separate into two phases when contacted with a finally divided stream of gas.

Typical electroplating baths which may be treated in accordance with the present invention may include chromium electroplating baths; tin electroplating baths; zinc electroplating baths; etc.

The compositions and processes of the invention have been found to be particularly effective in chromium plating bath processes. In chromium plating operations it is well known that the fumes and sprays produced during the electroplating process may be particularly corrosive and may cause significant losses of plating material in the course of the electroplating process.

It has been found particularly advantageous to incorporate finely divided particulate hydrophobic particles having an average particle size of 0.002–100 microns in diameter into a portion of the bath composition using a high speed blender to

obtain a preliminary dispersion of the foam-suppressing particles in concentrated form. Typically, the concentration of finely divided particulate particles in such preliminary dispersions may be 10–400 g/l. The preliminary dispersion so prepared may then be incorporated into the plating bath composition in order to provide a concentration of about 0.14 grams of hydrophobic particles per square decimeter of aqueous electroplating bath composition having a gas-liquid interface through which fumes or mists of bath composition would normally escape.

A particular advantage of the invention is that the small size and hydrophobic character of the particles may result in preferential sorption into the gas-liquid interface of the bubbles which may be formed at the electrodes. This action of the hydrophobic particles interferes with the spattering of such bubbles which form at the electrodes and tends to reduce and inhibit the formation of mists or sprays by reduction of said spattering effects. In addition, it has been found that a stable, thin, cell-like structure containing said particles may be formed upon the surface of the electroplating bath so that a fine pellicle remains everywhere on the surface of the electroplating bath unless the surface is being constantly and severely agitated. This pellicle further acts to prevent spattering and fuming. Thus, according to the present invention, the conditions of high surface tension characteristics of a normal electroplating bath are preferred and the presence of surfactants which may lower the surface tension is not advantageous.

The following examples are submitted for the purpose of illustration only and are not to be construed as limiting the scope of the invention in any way.

EXAMPLE 1

Preparation of Concentrated Dispersion

A thixotropic dispersion of hydrophobic silica was prepared by blending the following for 1 minute using a laboratory "-Waring" blender:

100 ml of water

24.0 grams chromic acid (CrO_3)

4.8 grams hydrophobic silica (available from Degussa Corp., designated Aerosil R–972 brand hydrophobic silica); particle diameter of 0.01–0.04 microns.

The final volume of the resulting blend was about 200 ml. A 1-liter sample of this dispersion is sufficient for initially charging an electroplating bath contained in a tank having a surface area exposed to the atmosphere of about 170 square decimeters. The dispersion may be prepared by the use of any high-shear blending equipment or similar apparatus.

EXAMPLE 2

Four 1-liter beakers containing 1 liter each of the following chromium plating solution were prepared:

Chromic Acid	g/l	125	250	250	400
Sulfate	g/l	1.25	1.25	1.25	2.0
Fluosilicate	g/l	–	2.50	–	4.0
Fluoride	g/l	–	–	0.50	–

Two electrodes were immersed in each of the four 1-liter samples of chromium plating solution and a current of 10 amperes was passed through the solution. Gas bubbles were observed to form in each of the four beakers. To each beaker was added an amount of the concentrated dispersion from Example 1 sufficient to provide a hydrophobic silica concentration in each of the 1-liter samples of chromium electroplating solution of 0.1 gram per square decimeter of solution exposed to the atmosphere (i.e. 0.1 g/dm²). The fuming and spattering was almost immediately observed to decrease. A stable foam-like coating was observed to form upon the surface of each of the electrolyzed samples of chromium electroplating solution.

EXAMPLE 3

Using the chromium electroplating baths described in Example 2, various articles containing metal surfaces (such as panels, rods, window crank handles, etc.) were chromium plated both with and without the addition of portions of the concentrated mist suppressing dispersion of Example 1. The quality of the chromium plate on each of the chromium-plated parts from each of the baths which contained the mist suppressing composition was then determined and compared with the quality of the chromium plate on parts which were plated in chromium electroplating baths without the mist suppressing dispersion of Example 1. The results are summarized in Table I.

TABLE I

	Concentration [1] (g./dm.²)	Quality of plated article	Mist suppression
Article plated:			
(a)	0.00	Excellent	Severe foaming and spattering.
(b)	0.04	do	Spattering suppressed.
(c)	0.4	do	Do.
(d)	4.0	do	Do.

[1] Hydrophobic silica per square decimeter of gas-liquid interface of aqueous plating solution.

As can be readily observed from the results of Table I, parts plated in chromium electroplating baths containing effective amounts of the mist suppressing compositions of the invention were found to be of excellent quality with no adverse streaking, pitting, or other defects observed in the final chromium-plated articles.

EXAMPLE 4

Duplicate 1-liter samples of the chromium plating baths of Example 2 were prepared using the procedure of Example 1. Sufficient concentrated mist suppressant dispersion was added to the first 1-liter sample of the chromium plating bath to provide a concentration of 0.1 gram of hydrophobic silica per square decimeter of gas-bath liquid interface. The second 1-liter sample of chromium electroplating solution was not treated with mist suppressant. Electrodes were inserted into each sample and the solutions were electrolyzed at 10 amperes for a time period of 8 hours at a solution temperature of 55° C. After 6 hours, the volume of the untreated chromium electroplating sample had decreased from 1,000 ml to approximately 940 ml, whereas the volume of the treated 1-liter sample of chromium electroplating solution was found to be decreased to about 980 ml. From these results it can be seen that fume and spray losses were significantly decreased according to the process of the invention by the use of the hydrophobic mist-suppressing composition of the invention.

EXAMPLE 5

A 300-ml sample of a solution used for metal stripping and pickling operations was prepared by combining equal volumes of concentrated hydrochloric acid and water. The 300-ml solution was divided into two 150-ml portions. The first 150-ml portion received no further treatment whatsoever and was designated as the control. To the second portion was added 0.76 grams of hydrophobic silica (Aerosil R–972 brand hydrophobic silica). The hydrophobic silica was blended into the 150-ml acid sample and then each of the two samples was transferred to a separate 400-ml beaker to provide identical surface areas at the air-liquid interfaces. The concentration of the hydrophobic silica in terms of grams per square decimeter of air-liquid interface was 2.0 g/dm². To each sample was added 20 chromium-plated screws of identical size and shape. As the chromium dissolved in each of the samples, gas was observed to evolve. The gas bubbles from the untreated (control) solution were large and were easily observed to break at the surface and to form droplets and mist. The gas bubbles

which formed in the solution containing the hydrophobic silica were observed to be small, were entrained, and were released gently through the blanket of foam-like material which was observed to coat the air-liquid interface of the second sample which contained the hydrophobic silica. No fumes were detected. After standing for a time period of 66 hours, the control sample had lost a total of 20 ml in volume due to fuming and evaporation, whereas the treated solution containing the hydrophobic silica in accordance with the invention had lost only 10 ml of its volume. The chromium-plated screws used in the test were observed to be equally stripped and pickled from each sample.

EXAMPLE 6

A 400-ml sample of a chromium plating bath containing approximately 240 g/l of chromic acid, 1.0 g/l of sulfate ion, and 2.0 g/l of fluosilicate ion in the presence of strontium and potassium ions was prepared as a standard mixed-catalyst, self-regulating chromium plating bath. To this chromium plating bath composition was added 1 gram of powdered solid polypropylene wherein the average diameter of the polypropylene particles was approximately 35 microns. The 400-ml sample was placed in a 1-liter beaker to give a concentration of mist-suppressing agent per area of air-liquid interface of 1 gram of polypropylene powder per square decimeter of air-liquid interface. On electrolysis of the treated composition in the 1-liter beaker, spray formation was completely eliminated and a mist-suppressing layer was observed to form at the air-liquid interface.

Although this invention has been illustrated by reference to specific embodiments, modifications thereof which are clearly within the scope of the invention will be apparent to those skilled in the art.

I claim:

1. A process for suppressing mist formation in a chromium electroplating bath solution which comprises incorporating an effective amount of hydrophobic particles having a particle size of 0.002–100 microns into said aqueous composition and wherein the concentration of said particles is at least 0.04 grams per square decimeter of gas-liquid interface.

2. A process as claimed in claim 1 wherein the hydrophobic particles have an average diameter of 0.005–10 microns.

3. A process for suppressing the production of fumes and mists from a chromium electroplating bath composition which comprises passing current from an anode to a metal cathode through an aqueous electroplating bath solution containing a chromium metal compound providing chromium metal ions for electroplating metal and including an effective amount of a blended dispersion of hydrophobic particles having a particle size of 0.002–100 microns to produce a plated article from said electroplating bath solution, and wherein the concentration of said particles is at least 0.04 grams per square decimeter of gas-liquid interface.

4. A process as claimed in claim 3 wherein the electroplating bath is maintained at a temperature of 5°–100° C.

5. A process as claimed in claim 3 wherein the concentration of the hydrophobic particles in the electroplating bath solution is about 0.04–75 grams of hydrophobic particles per square decimeter of aqueous electroplating bath composition at the gas-liquid interface.

6. A process as claimed in claim 3 wherein the hydrophobic particles contain hydrophobic silica having an average particle diameter of 0.005–10 microns.

7. A novel composition containing an aqueous chromium electroplating bath composition and an effective amount of a blended dispersion of hydrophobic silica particles having a particle size of 0.002–100 microns wherein the concentration of the hydrophobic particles is about 0.04–75 grams of hydrophobic particles per square decimeter of aqueous acid surface at the gas-liquid interface of the aqueous acid and the atmosphere.

8. A novel composition as claimed in claim 7 wherein the hydrophobic particles have an average diameter of 0.005–10 microns.

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