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ACIDIC CONDITIONER FOR PLASTIC MATERIALS
James L. Jezl, Swarthmore, and Habet M. Khelghian,
Springfield, Pa., assignors to Avisun Corporation, Philadelphia, Pa.

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9 Claims

ABSTRACT OF THE DISCLOSURE

In an acidic conditioning bath containing (a) a strong, liquid mineral acid, (b) a hexavalent chromium compound and (c) water, from about 0.01% to about 5% by weight of an aryl sulfonic acid or an aryl phosphonic acid is added to the aforementioned conditioning bath components. The acidic conditioner is useful for chemically etching the surface of a plastic article prior to treating the article with a metallizing process. Adhesion of the deposited metal to the surface of the plastic article is improved when the plastic article is immersed in the acidic conditioning bath.

BACKGROUND OF THE INVENTION

This invention relates to an acidic conditioning bath for conditioning or chemically etching the surface of a plastic article in order to improve the adhesion of the resulting metal plate to the surface of the plastic article. More particularly, this invention also relates to a novel conditioning bath for treating the surface of polyolefin articles.

The electroplating of plastic articles comprises a series of steps which include a conditioning or chemical etching of the surface of a plastic article by oxidizing in a strong acid solution followed by sensitizing the surface with an oxidizable, metallic salt that is adsorbed and later reduces the activator. The surface is then activated with a precious metal salt and thereafter electroless plating is performed followed by final plating in an electrolytic bath.

It is well known that metal coatings deposited by such techniques as electroplating fail to adhere firmly to unmodified surfaces of plastic articles. Many processes have been described in the literature that deal with the problem of adherability of metallic coatings to non-conductive surfaces of plastic articles. One approach to solving this problem has been to modify the surface of the polyolefin by etching. For example, a polyolefin article may be chemically etched by a modified strong mineral acid solution containing hexavalent chromium such as the solution described in United States patent application Ser. No. 635,685, filed May 3, 1967, now Pat. No. 3,475,167. Still other processes that aid in improving the bond strength between the metal coating and the polymer substrate involve the application of various adhesive layers to the surface of the plastic articles. Improved adhesion of the deposited metal to the surface of the plastic article is accomplished in this invention by immersing the plastic article in an improved acidic conditioning (chemical etching) bath.

The successful deposition of metals on plastic surfaces to accomplish a firm adhesive bond to the plastic substrate constitutes a highly desirable goal in view of the many recently developed engineering plastics which can be used as substitutes for zinc or other metals. A metallized plastic having good adhesion between the metal and the substrate further improves the structural properties of the plastic and thereby enhances the use of plastics as substitutes for metals. The advantage of using metallized plastics include lower costs of materials, less ex-

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pensive tooling and tool maintenance, reduced finishing costs in buffing and polishing and lower shipping costs. Furthermore, plastics permit greater versatility of product design and result in a more corrosion-resistant end product. Metallized plastics having satisfactory bond strength between the metal and the plastic substrate improve such physical properties as flexural modulus, impact strength and temperature deflection.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an acidic conditioner for the surface treatment of plastic articles. It is another object of the present invention to provide an acidic conditioner that contributes to improved adhesion between the metallic coating and the plastic substrate and particularly to improved adhesion of electroplated metals to plastic articles, particularly polyolefin articles. Still another object of the present invention is to provide a process for the treating of plastic surfaces to increase adhesion of deposited metal coatings. These and other objects of the present invention will become apparent in the following description and claims.

The acidic conditioner of the present invention comprises (a) from about 50% to 85% by weight of a strong, liquid mineral acid such as sulfuric acid or a mixture of sulfuric acid and phosphoric acid, (b) from about 1% to 10% by weight of a hexavalent chromium compound such as an alkali metal dichromate or chromium trioxide, (c) from about 10% to 40% by weight of water and (d) from about 0.01% to about 5% by weight, and preferably about 0.1% to about 2% by weight, based on the total weight of components (a), (b) and (c) of an aryl sulfonic acid or an aryl phosphonic acid. Since the maximum amount of water in the acidic conditioner bath is about 40%, it is necessary to employ sulfuric acid or phosphoric acid in concentrated form. The term "hexavalent chromium" defines chromium in the hexavalent valence state as contained in soluble salts or oxides of such hexavalent chromium.

The present invention is based on the discovery that an aryl sulphonic acid or an aryl phosphonic acid in certain defined amounts and in combination with an acidic conditioning (chemical etching) bath comprising a strong, liquid mineral acid, a hexavalent chromium compound and water, when used for the conditioning of surfaces of plastic articles, produces a surface that aids in achieving enhanced adherability of metallic coatings in such processes as electroplating compared to adherability that could heretofore be obtained with conditioners based on a strong, liquid mineral acid and a hexavalent chromium compound alone.

The aryl sulfonic acid may be selected from benzenemonosulfonic acid, benzenedisulfonic acids, naphthalenesulfonic acids and naphthalenedisulfonic acids. The corresponding aryl trisulfonic acids may also be employed. Similarly, aryl phosphonic acids that may be used in the acidic conditioner include benzenemonophosphonic acid, benzenediphosphonic acid, naphthalenephosphonic acid and naphthalenediphosphonic acid as well as the corresponding aryl triphosphonic acids.

The novel conditioner of the present invention is particularly useful in preparing synthetic plastic surfaces for electroplating. Although a variety of processes have been developed for electroplating non-conductive surfaces and particularly plastics, the same general steps are usually employed and comprise conditioning (chemical etching), sensitizing, activating, electroless plating and final electrolytic plating.

The conditioning bath of the present invention may be applied in the etching of all plastic articles having a multiplicity of carbon to carbon bonds of which at least one carbon atom is bonded to at least one hydrogen atom.

Preferred plastics are synthetic polymeric materials such as the polyolefins.

DETAILED DESCRIPTION OF THE INVENTION

The acidic conditioning bath of the present invention comprises (a) from about 50% to 85% by weight of a strong, liquid mineral acid such as sulfuric acid or a mixture of sulfuric acid and phosphoric acid, (b) from about 1% to 10% by weight of a hexavalent chromium compound such as an alkali metal dichromate or chromium trioxide, (c) from about 10% to 40% by weight of water, and (d) from about 0.01% to about 5%, preferably from about 0.1% to 2%, of an aryl sulfonic acid or an aryl phosphonic acid, (d) being based on the total weight of (a) to (c).

Aryl sulfonic acids that may be incorporated into the conditioning bath of this invention include aryl mononuclear sulfonic acids, aryl mononuclear phosphonic acids, naphthalene sulfonic acids, naphthalene phosphonic acids and the like. Representative sulfonic acids and phosphonic acids are benzenemonosulfonic acid; (o, m, and p)-benzenedisulfonic acid; 1,3,5-benzenetrisulfonic acid; 1-naphthalenesulfonic acid; 2-naphthalenesulfonic acid; 1,3-naphthalenedisulfonic acid; 1,5-naphthalenedisulfonic acid; 2,6-naphthalenedisulfonic acid; 2,7-naphthalenedisulfonic acid; and 1,3,6-naphthalenetrisulfonic acid, phenylphosphonic acid, phenylenediphosphonic acids such as p-phenylenediphosphonic acid, and naphthalenephosphonic acids such as 2-naphthylphosphonic acid.

The components of the acidic conditioning bath may be mixed by conventional techniques. The bath may be prepared by mixing and heating at elevated temperatures such as from 60° to 100° C., preferably 80° to 90° C., the mineral acid, hexavalent chromium compound and water components and thereafter adding the aryl sulfonic acid and the aryl phosphonic acid and continuing the heating and stirring until all components are thoroughly mixed. If, as a result of heating to admix the conditioner components, the water concentration is decreased below the desirable levels indicated, such can be readily replenished. It is to be emphasized that the components of the conditioner described by the present invention are not limited to the specific additives described hereinabove, but may contain various additional salts such as sodium sulfate or sodium acid sulfate which have heretofore been employed in conditioners for plastic surfaces.

The conditioner of the present invention is useful in etching all plastic materials that have heretofore been employed as substrates for the deposition of metallic films. Suitable plastic materials, the surface of which can be etched by the novel conditioner of the present invention, include vinyl aromatic polymers such as polystyrene, acrylonitrile-butadiene-styrene copolymers (ABS), styrene-acrylonitrile polymers, and rubber-containing polystyrenes; acrylic polymers such as poly(methyl methacrylate); cellulosic plastics such as cellulose butyrate; epoxy resins such as reaction products of bisphenol-A with epichlorohydrin; phenolic resins such as resins of phenol and formaldehyde; polyester resins such as alkyd resins or unsaturated polyester resins, as well as cross-linked polyester resins; polyurethanes; polyacetals; polyimides; polyamides; polycarbonates; polyolefins such as polypropylene and particularly solid, substantially crystalline polypropylene, poly(4-methylpentene-1), poly(3-methylbutene-1), ethylene propylene copolymers (including random amorphous ethylene-propylene copolymers as well as solid, substantially crystalline block copolymers of propylene and ethylene), ethylene acrylic copolymers, and ionomers; polyphenylene oxides; polysulfones; and vinyl resins such as polyvinyl chloride; polyvinylidene chloride, and polyvinyl fluoride. The treated polymer surface can be that of a thermoplastic as well as a thermosetting resin. The plastic can, furthermore, contain inert inorganic fillers such as glass fibers,

asbestos, talc, carbon, silica, and heavy metal salts. Particularly preferred for purposes of metallizing are vinyl aromatic resins, polyacetal resins, polyamide resins, polycarbonate resins, and polyolefin resins. The novel conditioner of the present invention is particularly suitable for polyolefin resins, such as polypropylene, which show a surprising improvement in adherability of the metal coating to the polyolefin substrate.

The treatment or conditioning of plastic articles with the conditioner is generally accomplished by immersing the article to be treated in a bath of the conditioner for periods of time ranging from 1 minute or less to 60 minutes or more at an elevated bath temperature, preferably in a range of 80° to 90° C. As a practical matter, higher bath temperatures and longer immersion times generally result in increased adherability until a maximum is reached beyond which no additional adherability can be obtained. Optimum conditions for the treatment of particular plastic surfaces are established experimentally.

As indicated above, the novel conditioner of the present invention is particularly useful in preparing plastic surfaces for electroplating. Although a variety of processes have been developed for the electroplating of non-conductive surfaces and particularly plastics, the same general steps are usually employed. Thus, the plating of plastic surfaces is generally conducted using the following steps:

(1) The surface to be plated is cleaned using a mild alkaline bath to remove oils, mold-release agents, and fingerprints.

(2) The alkaline material retained by the surface is neutralized using a mild acid.

(3) The clean surface is then chemically etched with a conditioner such as the novel conditioner of the present invention.

(4) The conditioned surface is sensitized with a readily oxidizable tin salt solution, such as a stannous chloride solution, which causes tin to be absorbed on the surface.

(5) The surface is then activated or nucleated by treatment with an aqueous solution of a noble metal salt, such as palladium chloride, which forms a metallic film at discrete activated sites.

(6) The surface is then subjected to electroless plating using copper, nickel, or cobalt as the metal. This is accomplished by immersing the treated surface in a solution of such metal salt containing in addition to the metal salt such as copper sulfate or nickel chloride, a reducing agent such as formaldehyde, trioxymethylene, or the like. Sufficient copper, nickel or cobalt is deposited on the surface of the plastic to achieve a continuous coating capable of conducting electricity.

(7) The electroless deposition of metal is then followed by conventionally plating the surface with copper, nickel, and/or chromium, or just nickel and chromium. The thickness of the electroplated coating is generally within the range of 0.1 to 1.5 mil.

It is furthermore highly desirable, if not essential, to rinse and clean the surface being treated with water between each of the steps outlined and in some instances it may also be desirable to dry the surface between the various treating steps. Since the various outlined steps employed in the electroplating of nonconducting surfaces and particularly plastic surfaces are well known in the electroplating art, no further description beyond that given above is deemed necessary for a full understanding of the present invention. The conditioner of the present invention can be employed for the purpose of etching the plastic surface in all of the processes heretofore developed for metallizing of plastic surfaces.

Although the acidic conditioner described herein is effective in improving adhesion, as measured by a pull test, of the metal coating to the plastic article, the mechanism by which this is accomplished is not clearly understood. Nevertheless, it has been established that the con-

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ditioner substantially improves the bond strength of the deposited metal to the surface of the plastic article. In measuring the bond strength by the pull test, two parallel cuts are made into the plated metal coating, $\frac{1}{2}$ " apart, an additional vertical cut is made to form a tab; one end of the resulting tab is raised sufficiently to allow gripping by a tensile testing machine; the specimen is then placed into a tensile rig and the tab is pulled vertically from the surface. The force required to pull the tab is measured as the bond strength.

The invention is further illustrated by the following examples wherein all parts and percentages are by weight unless otherwise indicated. Examples 1-4 are directed to the preparation of the acidic conditioning bath and Examples 5-11 are directed to electroplating processes.

Example 1

500 ml. of an acidic conditioner is prepared by combining 60% by weight of sulfuric acid (96% concentration), 5% by weight of chromium trioxide and 35% by weight of water. The acid solution is heated by the exothermic reaction and then cooled to about 80° C.; thereafter 0.5 gram of m-benzenedisulfonic acid is added to the solution and the resulting mixture is thoroughly stirred and gradually heated during a 45-minute period to 88-90° C. No reaction is observed with the benzenedisulfonic acid and other components of the acidic conditioning bath. During the heating, about 10% by weight of the water in the bath is volatilized from the reaction mixture. The resulting acidic conditioning bath is now ready for the treatment of plastic articles or the bath may be stored and used at a later date.

Example 2

Another 500 ml. solution of a similar acidic conditioning bath containing sulfuric acid, chromium trioxide and water was prepared according to Example 1 and 0.25 gram of benzenedisulfonic acid was added to the conditioning bath and thoroughly mixed with the other acidic components by the procedure described in Example 1. Again, about 10% by weight of water was volatilized from the reaction mixture. The resulting conditioner may now be used for the treatment of synthetic, polymeric articles or the bath may be stored for use at a later date.

Example 3

500 ml. of a conditioning bath containing the same components described in Example 1 was prepared with the exception that the amount of benzenedisulfonic acid additive added to the bath was 0.13 gram. The bath was gradually heated over a thirty-minute period to 88-90° C. and during this heating about 9% by weight of water is volatilized from the reaction mixture. The resulting conditioner is now ready for use in the treatment of plastic surfaces.

Example 4

Following the procedure of Example 1, 500 ml. of an acidic conditioning composition is prepared from 60% by weight of sulfuric acid (96% concentration), 5% chromium trioxide and 35% of water. To this solution 20 grams of an additive consisting of 64% by weight of chromium trioxide and 36% of sodium hydrogen sulfate is added and thoroughly mixed with the other components. Thereafter, 0.5 gram of benzenesulfonic acid is added and the mixture heated to about 90° C. during a 60-minute period. About 10% by weight of the water was volatilized from the reaction mixture.

Example 5

A polypropylene plaque, 5" x 5" x 110 mil, molded from a commercially-available substantially crystalline polypropylene homopolymer having a flow rate of 3.4 and containing 0.5% by weight of a nonionic surfactant of t-octylphenoxy-polyethoxyethanol having about 10 ethoxy

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groups, 5.0% of titanium dioxide, 0.15% of calcium stearate, 0.2% of 2,6-ditertiarybutyl 4-methyl phenol and 0.5% of dilauryl thiodipropionate is immersed in the acidic conditioning bath described in Example 1 to 85° C. for 5 minutes and then consecutively immersed in a stannous chloride sensitizer solution containing 30 g. per l. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 10 ml. per l. of concentrated HCl at ambient temperature of 30-60 seconds; in an activator solution containing 0.05 g. per l. of $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ and 10 ml. per l. of concentrated HCl for a period of one to two minutes at ambient temperature; and into an electroless copper plating solution containing per liter of solution 29 g. of copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), 40 g. of sodium hydroxide, 140 g. of Rochelle salt, and 166 g. of formaldehyde (37% solution). Between each of the immersions the plaque is thoroughly rinsed with deionized water. The resulting plaque after washing with water is then electroplated with copper for about 20 minutes at a current density of approximately 30 amps/sq. ft., resulting in a 1 mil coating of copper on the plaque. The pull strength was evaluated according to the previously-described procedure and measured about 31 lbs./in.

The foregoing electroplating procedure described in the above example was repeated using the same conditioning, sensitizing, activating, electroless plating, and electrolytic plating procedures with the exception that the polypropylene plaque was immersed in the conditioning bath for 10 minutes at 85° C. and another plaque was immersed for a period of 15 minutes at the same temperature. The bond strength of each of these two additional plaques measured an average of 31 lbs./in.

Example 6

A polypropylene plaque containing the stabilizing and additive system described in Example 5 was electroplated according to the procedure described in Example 5 with the exception that the conditioning bath of Example 2 was used. The polypropylene plaque was immersed in the conditioning bath for 5 minutes and after electroplating the bond strength was measured as 21 lbs./in.

The procedure for this example was repeated except that the polypropylene plaque remained in the conditioning bath for a period of 15 minutes. A bond strength value of 22-24 lb./in. was obtained.

Example 7

A polypropylene plaque having the same additive system described in Example 5 was electroplated according to the procedure of Example 5 with the exception that the acidic conditioner employed was the bath described in Example 3. The plaque was immersed in the conditioning bath for a period of 5 minutes but otherwise the electroplating procedure of Example 5 is followed. Evaluation of the bond strength gave a result of 22-24 lbs./in.

The procedure of the above example was repeated except that the plaque was immersed in the conditioner for a period of 15 minutes and the resulting bond strength averaged 34-36 lbs./in.

Example 8

A polypropylene plaque having the same additive system described in Example 5 was electroplated according to the procedure of Example 5 and immersed in the same acidic conditioner employed in Example 1, with the exception that 0.25 gram of phenylphosphonic acid was added in lieu of benzenedisulfonic acid, for a period of 15 minutes. Thereafter the plaque was electroplated by the steps described in Example 5. Evaluation of the bond strength gave a value of 8 lbs./in.

Example 9

A plaque, 5" x 5" x 110 mil, molded from a commercially-available, substantially crystalline propylene-ethylene terminal block copolymer having a flow rate of 4.0 (ASTM-1238-62T) and containing 5.0% of titanium di-

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oxide, 0.15% of calcium stearate, 0.2% of 2,6-ditertiary-butyl 4-methyl phenol and 0.5% of dilauryl thiodipropionate was immersed in the acidic conditioning bath described in Example 1 at 85° C. for 10 minutes and then electroplated according to the procedure of Example 5. The bond strength measured about 26 lbs./in.

Example 10

Example 9 was repeated except that the additive system of the propylene-ethylene terminal block copolymer contained 0.5% by weight of t-octylphenoxyethoxyethanol having about 10 ethoxy units, 5.0% of titanium dioxide, 0.15% of calcium stearate, 0.2% of 2,6-ditertiary-butyl 4-methyl phenol and 0.5% of dilauryl thiodipropionate. Following electroplating according to the procedure of Example 9, the bond strength measured about 32 lbs./in.

Example 11

For purposes of comparison and understanding the benefit obtained by employing the conditioning bath of this invention, a control was run using the same crystalline polypropylene described in Example 9 and the same conditioning, sensitizing, activating, electroless plating and electrolytic plating described in Example 5 with the exception that the acidic conditioning bath did not contain the benzenedisulfonic acid additive but consisted of 60% sulfuric acid, 35% water and 5% chromium trioxide. The polypropylene plaque was immersed in the conditioning bath for a period of 5 minutes and following electroplating severe blistering was observed.

We claim:

1. In an acidic conditioning composition for the surface treatment of plastic articles wherein said acidic composition contains as essential components (a) at least one strong, liquid mineral acid selected from the group consisting of sulfuric, phosphoric, and mixtures thereof in an amount of about 50% to 85% by weight, (b) a hexavalent chromium compound in an amount of about 1% to 10% by weight, and (c) water in an amount of about 10% to 40% by weight, the improvement wherein said acidic conditioning composition additionally contains

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from about 0.01% to about 5% by weight, based on the total weight of components (a), (b) and (c), of an aryl sulfonic acid or an aryl phosphonic acid.

2. An acidic conditioning composition according to claim 1 wherein said mineral acid is sulfuric acid.

3. An acidic conditioning composition according to claim 1 wherein said aryl sulfonic acid is used in an amount of about 0.1% to about 2%.

4. An acidic conditioning composition according to claim 1 wherein said aryl sulfonic acid is selected from the group consisting of benzenemonosulfonic acid, benzenedisulfonic acids, naphthalenemonosulfonic acids and naphthalenedisulfonic acids.

5. An acidic conditioning composition according to claim 1 wherein said hexavalent chromium component is selected from the group consisting of chromium trioxide and alkali metal dichromates.

6. An acidic conditioning composition according to claim 4 wherein said aryl sulfonic acid is a benzenedisulfonic acid.

7. In a process for preparing metallized plastic articles by electrodeposition of metal on the surface of a plastic article, the step comprising immersing said plastic article in an acidic conditioning composition defined by claim 1.

8. A process according to claim 7 wherein said plastic article is a polyolefin.

9. A process according to claim 8 wherein said polyolefin is a solid, substantially crystalline propylene polymer.

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JACOB H. STEINBERG, Primary Examiner

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