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SEQUENTIAL CHLORINATED HYDROCARBON-CHROMIC ACID PRECONDITIONING FOR PLATING POLYOLEFIN ARTICLES

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7 Claims

ABSTRACT OF THE DISCLOSURE

In a process for electroplating polyolefin articles wherein the article is treated with an etching solution comprising a strong mineral acid, followed by treatment with a tin salt, a noble metal salt solution, and an electroless nickel or copper plating solution, followed by electroplating, the adhesion of the metal to the article is enhanced by contacting the article with a chlorinated hydrocarbon prior to contacting with the etching solution.

This invention relates to a method of preconditioning the surfaces of thermoplastic articles prior to the deposition thereon of metallic coatings, and more particularly to a method for treating the surface of polyolefin articles to render them more easily oxidizable by the conditioning solutions commercially used in the plating of ABS plastics.

The problem of causing ink, paint, or other types of coating to adhere to the non-polar surface of polyolefins is well-known. In general, the approach to solving the problem has been to modify the surface of the polyolefin to introduce polar groups, such as by surface oxidation. In films, satisfactory printability may be obtained by subjecting the film to a corona discharge in the presence of air, but the corona discharge cannot be practically applied to articles of irregular shape. Another approach has been to incorporate polar materials into the polyolefin prior to moulding, but this adds greatly to the cost of the material. Another approach has been to treat the polyolefin article with a strong mineral acid solution containing chromium trioxide, in order to induce surface oxidation. Although this treatment enhances the adherence of paint to the surface of the polyolefin, it has found only limited success in causing a superior bond between the polyolefin and metal plated thereon, especially when the article to be plated is of a complicated shape.

The electroplating of a polyolefin article in which the metal plate, having thicknesses in the range of 1 mil, is tightly bonded to the polyolefin substrate constitutes, however, a highly desirable goal in view of the more recently developed polyolefins which can be considered engineering plastics and thus substitutes for zinc die casts and other materials in applications such as automobile grilles. An electroplated metal coating having good adhesion to the plastic substrate improves the structural properties of the plastic, such as resistance to deformation, thereby enhancing its use as a substitute for metals. The advantages of using polyolefins in such applications include lower cost of materials, cheaper tooling and tool maintenance, lower finishing cost in buffing and polishing, and lower shipping cost. The use of polyolefins, furthermore, allows greater versatility of product design and gives a more corrosion-resistant end product. Good adhesion between the metal plate and the polyolefin substrate causes improvement in physical properties such as flexural modulus, impact strength, and temperature deflection.

In the plating of plastics such as ABS (acrylonitrile-butadiene-styrene copolymer) it is conventional to plate the plastic by the following procedure:

(1) The surface to be plated is cleaned using a mild alkaline bath to remove oils, mould 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 concentrated sulfuric or phosphoric acid, or mixtures thereof, containing chromium trioxide or an alkali metal dichromate.

(4) The resultant etched surface is sensitized with a readily oxidized tin salt solution such as stannous chloride which causes tin to be adsorbed 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 activated surface is subjected to electroless plating using copper, nickel, or cobalt as the metal. This is accomplished by immersing a 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 metal is deposited on the surface to form a continuous film capable of conducting electricity.

(7) The article is then conventionally electroplated with copper, followed by nickel or chromium, or with nickel followed by chromium. The thickness of the electroplated coating is generally within the range of 0.1 to 1.5 mil.

It is desirable to rinse the surface with water following each of the foregoing steps. Since the various outlined steps employed in the electroplating of non-conductive surfaces are well-known in the electroplating art no further description is deemed necessary for a full understanding of the present invention.

The foregoing procedure is satisfactory for plating the surface of polymers containing polar units, and with ABS bond strengths of 8-10 pounds per inch may be obtained. Bond strength is measured by a pull test in which two parallel cuts are made in the metal coating 1/2 inch apart, a vertical cut is made between the parallel cuts to form a tab, one end of which 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.

When the foregoing plating procedure is applied to commercial grades of polyolefins such as crystalline polypropylene and high and low density polyethylenes, little or no bond strength is obtained. It is believed that this is due to the very hydrophobic nature of these polymers, which prevents adequate wetting of the surface during the etching step.

It has been found possible to obtain good adherence of a metal coat to polyolefin articles if the polyolefin contains a small amount of a surfactant or is filled with from 20% to 60% by weight of a sulfate of a Group II metal, and if the acid solution used to chemically etch the article contains a small amount of an oxidized hydrocarbon. Polymers modified by the addition of a surfactant are described and claimed in the copending application of Khelghatian et al., Ser. No. 637,316, filed concurrently herewith, and polymers filled with Group II metal sulfates are described and claimed in the copending application of Poppe et al., Ser. No. 635,661, filed concurrently herewith. The preparation and use of the acid solutions modified with the oxidized hydrocarbon is described and claimed in the copending application of

Khelghatian et al., Ser. No. 635,683, filed concurrently herewith. Alternatively, a conditioner containing a major proportion of phosphoric acid can be used. Such a conditioner is described and claimed in the copending application of Fitzpatrick et al., Ser. No. 635,711, filed concurrently herewith.

While such modified polyolefins can be successfully plated in accordance with the procedures described in these applications, there are drawbacks attendant on their use. The polyolefins modified with surfactants, if not plated immediately after moulding, tend to pick up static charge and accumulate dust which is difficult to remove prior to plating, whereas polymers filled with Group II metal sulfates are difficult to mould into intricate shapes. It is therefore desirable to provide a process by means of which commercially available polyolefins, unmodified except for the presence of heat and light stabilizers, may be successfully plated.

It is the object of this invention to precondition the surfaces of articles formed from commercially available unmodified polyolefins in order to render them platable by standard means applicable to the commercial plating of other plastics.

We have now found that the foregoing object may be attained by contacting the article to be plated with a chlorinated hydrocarbon having a boiling point between 50° C. and 120° C. for a short period of time, followed by drying to remove residual chlorinated hydrocarbon from the surface of the article. Chlorinated hydrocarbons useful in so treating shaped polyolefin articles include carbon tetrachloride, chloroform, 1,1- and 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,2-dichloroethylene, trichloroethylene, tetrachloroethylene and the like. While strictly speaking, carbon tetrachloride and tetrachloroethylene are not chlorinated hydrocarbons for the purposes of this disclosure they are considered to be such. The contacting is preferably made at the boiling point of the chlorinated hydrocarbon except that with materials boiling above 90° C. it is preferred to contact with liquid below 90° C. The treatment may be either in liquid or vapor phase. The preferred contacting temperature range is 50° C.-90° C. The halogenated hydrocarbon must be sufficiently volatile to be essentially completely removed before conditioning. The time and temperature must be carefully selected so that gross swelling of the surface does not occur, while at the same time surface annealing has taken place.

In order that those skilled in the art may more fully appreciate the nature of our invention, and the results obtained thereby, the following control and examples are given. All parts are by weight.

CONTROL

A number of plaques were moulded from a commercial grade of crystalline polypropylene marketed under the trade name "Avisun 1016."

A conditioner was made up by adding to a 500 ml. inorganic acid composition consisting of 40% by weight of sulfuric acid 96% concentration), 39.5% phosphoric acid (85% concentration), 3% chromium trioxide, and 17.5% water, 18 g. of an additive consisting of 64% by weight of chromium trioxide and 36% of sodium hydrogen sulfate. The acid solution was heated to 80° C., and 3% by volume of a commercially available mineral spirit having a boiling point of 159° C.-193° C. and consisting predominantly of C11-C15 cycloparaffins was added slowly to the acid solution. An exotherm occurred which raised the temperature to 85° C. After about two hours no excess mineral spirit was observed, and the evolution of gas ceased, indicating complete conversion of the mineral spirits to oxidation products. During the reaction about 9% by weight of water was volatilized.

One of the plaques was immersed in this conditioner for a period of 10 minutes at 85° C. The plaque was then washed and inspected. No change in appearance of the

surface was noted. It was then consecutively immersed in a stannous chloride solution containing, per liter, 10 g. of SnCl₂ and 40 ml. of HCl at ambient temperature for two minutes; in an activator solution containing per gallon of solution 1 g. of palladium chloride and 10 ml. of HCl for a period of two minutes at ambient temperature; and in an electroless copper plating solution containing per liter of solution 29 g. of copper sulfate, 140 g. of Rochelle salt, 40 g. of sodium hydroxide, and 166 g. of formaldehyde at a temperature of 70° C. for 15 minutes. Between each of the immersions described, the plaque was thoroughly rinsed with distilled water. The resultant plaque was 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. While the entire plaque was encapsulated with copper, the bond strength was less than 1 lb./in.

Example 1

Another plaque was immersed in the vapors of boiling carbon tetrachloride for one minute, while being rotated slowly to expose all surfaces to the vapor. The plaque was then air dried for several hours to remove residual CCl₄. No change in the appearance of the surface of the plaque was noted. The plaque was then treated with a chromic acid conditioner as in the control for a time of 8 minutes at 85°-90° C. Upon removal and washing it was observed that the surface of the plaque had changed from a shiny finish to a satin finish. The plaque was then successively treated with stannous chloride solution, palladium solution and electroless copper solution, as in the control, and was electroplated under the same conditions used in the control. A bond strength of 18 lbs./in. was obtained.

Example 2

Example 1 was repeated, substituting 1,2-dichloroethane for the carbon tetrachloride used in Example 1. Essentially, the same bond was obtained.

Example 3

Example 1 was repeated, except that an azeotropic mixture of 1,2-dichloroethane and trichloroethylene boiling at 81° C. to 82° C. was used instead of carbon tetrachloride. A bond strength of 20 lbs./in. was obtained.

Example 4

Example 1 was repeated, substituting 1,1,1-trichloroethane for the carbon tetrachloride. Essentially the same bond was obtained.

Example 5

Example 4 was repeated, except that the plaque was immersed in the boiling 1,1,1-trichloroethane rather than exposed to the vapors thereof. A bond of 21 lbs./in. was obtained.

What is claimed is:

1. In a process wherein a shaped crystalline polypropylene article is successively treated with a strong mineral acid solution containing chromium trioxide or an alkali metal chromate; a solution of a tin salt; a solution of a noble metal salt; and a solution of a reducible salt of nickel or copper containing a reducing agent, followed by electroplating to deposit a film of metal on the surface of the article, the improvement which consists in contacting the article, at a temperature between about 50° C. and 90° C., with a chlorinated hydrocarbon boiling between about 50° C. and 120° C. or mixtures thereof and thereafter removing adherent chlorinated hydrocarbon from the article by drying, prior to treating the article with the strong mineral acid solution.

2. The process of claim 1 in which the chlorinated hydrocarbon is carbon tetrachloride.

3. The process of claim 1 in which the chlorinated hydrocarbon is 1,1,1-trichloroethane.

4. The process of claim 1 in which the chlorinated hydrocarbon is 1,2-dichloroethane.

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5. The process of claim 1 in which the chlorinated hydrocarbon is a mixture of 1,2-dichloroethane and 1,1,1-trichloroethylene.

6. The process of claim 1 in which the contacting is with vapors of the chlorinated hydrocarbon.

7. The process of claim 1 in which the contacting is with the chlorinated hydrocarbon in liquid form.

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