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DYE TEST FOR DETECTING STRAINED AREAS IN MOLDED PLASTICS

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ABSTRACT OF THE DISCLOSURE

A method for qualitatively determining the surface strains in a molded plastic article, the strains being related to the plateability of said article, by contacting said article with a disperse dye solution having small dye particles, so as to stain said article, the depth and uniformity of shade of the stained article being an indication of the surface strains in the plastic article.

BACKGROUND OF THE INVENTION

Problems of applying a surface coating to a plastic substrate are well known. Much effort has been expended in improving methods of applying metallic coatings to non-polar surfaces. In this regard, significant advances have been made in techniques for the electrodeposition of metals on a plastic surface by modifying the surface to more readily accept the coating. For example, it has been found that fairly strong metal-to-plastic bonds may be obtained by chemically etching the plastic surface with a strong mineral acid, sensitizing the etched surface with an oxidizable tin salt, activating the sensitized surface with an aqueous solution of a noble metal salt, electroless plating the surface with copper, nickel or cobalt, and then electroplating with the final metal coating.

However, special problems are frequently encountered when attempting to electroplate molded plastic articles. Even the use of surface preparation and conditioning techniques frequently does not give satisfactory bonds between the plastic surface and the metal coating. It is believed that much of the difficulty is caused by a local surface straining of the plastic during the molding operation. Because of geometric effects and mold design, the plastic is not uniformly cooled and therefore strains may set in as the plastic proceeds from the melt to the solid form. Variations in surface crystallinity occur and it is believed that this causes problems in bonding the metal to the plastic substrate. In many cases it has been found that although certain portions of the plastic substrate may satisfactorily accept the metal coating, other portions of the same article may not be plateable. When the surface is severely strained, it is found that the metal coating may actually blister during the electroplating operation so that no metal deposits properly on the substrate.

It is desirable, both from an economic as well as from an efficiency standpoint, to be able to determine whether or not a molded plastic article will uniformly accept a metal coating by electrodeposition means prior to the application of the coating. Accordingly, it is desirable to determine whether the plastic surface is strained, and, if so, the relative degree of strain and the surface strain pattern. Clearly, the knowledge that a particular article cannot be satisfactorily plated is valuable in that it eliminates useless plating of the article and, in addition, provides information for the redesign of the mold and modification of the molding procedure.

SUMMARY OF THE INVENTION

Our invention relates broadly to coating of plastic surfaces. More particularly, our invention relates to the electroplating of molded plastic articles. Specifically, we have discovered a simple, inexpensive test for determining how successfully a metallic coating may be applied by electrodeposition means to the surface of a molded plastic article. The method provides a visual indication of the uniformity of bond strength which can be expected between the metal and the plastic substrate. In this regard, the method shows the presence of local surface strain caused by molding the plastic and provides a picture of the strain pattern.

Our method involves contacting the molded plastic article with a disperse dye having particles suspended therein which have an average diameter which is not substantially larger than that of irregularities in the plastic. The plastic should be in contact with the dye for a period of time sufficient to permit at least some staining of all plastic surfaces so contacted. It has been found that the strained areas will accept less dye stain than the strain-free areas. Therefore, an unstrained plastic article will, after contact with the dye, have a uniform shade of color. On the other hand, if the article is locally strained, the strained portions will be of a significantly lighter shade. Since the degree of strain is related to the bond strength, the results of this dye test may be used to predict the success with which a molded plastic article may be electroplated.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENT

Articles molded from various types of plastic, including polypropylene, ABS, impact polystyrene, polycarbonate, polyphenyl oxide, polysulfone, or any other plateable resins, are generally not completely free of strain. This is particularly true in gate areas or other thick portions of the molded plastic article. This condition is due to varying degrees of crystallization of the polymer from the melt to the solid form. Strained areas are not readily chemically etchable and, upon electroplating, either give poor metal-to-polymer bond strengths or simply blister during the depositing of the electrolytic metal plate. In the present invention, disperse dye solutions, containing suspended dye particles which have an average diameter that is not substantially greater than that of irregularities in the plastic surface, can be used in a test to determine whether the molded plastic articles have any strains which might cause difficulties in a subsequent electroplating step. The strained areas of the plastic pick up very small amounts of the dye whereas the strain-free areas stain uniformly in deeper shades. Since the greater the strain, the lighter the shade, the dyed surface clearly shows the surface strain pattern.

The use of a disperse dye having very small dye particles is necessary for purposes of this invention. The reason for this may be that the dye particle attaches to the porous surface. If the dye particle is too large, it may not attach to the surface because it cannot work into the surface irregularities. Since strain is related to the variation in crystallinity and, therefore, to the variation in size of irregularities, it seems to follow that a plastic surface having uniformly large irregularities will stain easier and more evenly than a surface having smaller irregularities of less uniform size. Also, if the dye particle size is much greater than the surface irregularities, the plastic will not stain well even where it is unstrained. On the other hand, using a disperse dye having particles much smaller than the surface irregularities is not undesirable since other variables, e.g. contacting time and dye solution temperature, may be controlled to provide adequate staining.

Disperse dyes are water-soluble, colored organic substances which can be dispersed in water in a very fine particle size. Chemically, these dyes fall mainly into the following defined chemical classes: (a) nitroarylamine, (b) azo and (c) anthraquinone. Generally, the dyes will have a nitrogen-containing group but no solubilizing sulfonic acid groups.

By way of illustration, the following disperse dyes may be used in the practice of this invention: Navy Blue Rit Dye No. 30, Dark Green Rit Dye No. 410–36, Setacyl Violet P–2B, Setacyl Blue P–RFL, Setacyl Brilliant Red P–BLM, Setacyl Orange P–RFL, Latyl Blue 4R, Latyl Orange 3R, Celliton Fast Blue FFRN, Calcosyn Blue RP and Duranol Brilliant Violet TG 300. Additional disperse dyes are listed in the Colour Index, published jointly by the (British) Society of Dyers and Colourists and the American Association of Textile Chemists and Colourists.

If surface strains are detected on the molded polyolefin article, they may be readily relieved by various annealing procedures including thermal treatment and chemical treatment. Thermal treatment includes the application of heat from any source to relieve the surface strain. Appropriate chemical treatments are described in U.S. patent application Ser. No. 635,696, filed May 3, 1967, and the U.S. patent application, filed concurrently herewith.

After relieving the surface strains, the molded plastic article is now prepared for metallizing by any conventional electroplating technique.

EXAMPLE 1

A molded polypropylene plastic article was immersed in a dye bath containing a disperse dye and a wetting agent for a period of 5 minutes. The dye bath was made using 0.5 gram per liter of water of Navy Blue Rit Dye No. 30, a disperse dye obtained from Best Foods Co. In addition, 0.01% Triton–X–100 wetting agent was added to the dye bath. Triton–X–100 is manufactured by Rohm and Haas Company and is a nonionic 100% active wetting agent, comprising t-octylphenoxypolyethoxyethanol. After the polypropylene was removed from the dye bath, the strain pattern was clearly evident from the variations in surface shading.

The above test was repeated using articles made of various plastics such as those mentioned above. The tests were performed using dye bath temperatures of from 120° F. to 212° F. In all cases, the contact time was selected so as to provide adequate staining of the plastic.

EXAMPLE 2

Molded polypropylene plastic articles were immersed in a dye bath in accordance with the procedure outlined in Example 1. In this case, however, Dark Green Rit Dye No. 410–36 was used in the bath instead of the Navy Blue Rit Dye No. 30 of Example 1. Dark Green Rit Dye No. 410–36 is a disperse dye also having very fine dye particles. The results obtained in this example were similar to those of Example 1 and it was concluded that this dye would be suitable for use in detecting strained areas in molded plastic articles.

EXAMPLE 3

A molded polypropylene article was immersed in accordance with the procedure of Example 1 in a dye solution containing Sophenylfast Blue-Green dye. This particular disperse dye has a relatively large pigment particle size. It was found that the polypropylene article did not accept a stain that would be suitable for determining locally strained areas.

Although the invention is applicable to any molded polymeric article, particularly preferred are articles derived from polymers which contain a major proportion (i.e., greater than 50%) of an aliphatic olefin, having from 2–8 carbon atoms. Such polyolefins, therefore, include polyethylene, polypropylene, ethylene-propylene copolymers, ethylene-butene-1 copolymers, polybutene-1, poly (4-methylpentene-1), poly (3-methylbutene-1), and the like. The term "polyolefin" is intended to include copolymers of hydrocarbon monomers with copolymerizable polar monomers in which such functional monomers constitute a minor proportion of the copolymer. Functional monomers frequently employed in combination with hydrocarbon monomers are in particular the acrylic monomers such as methyl methacrylate, ethyl acrylate, and acrylonitrile and the vinyl esters such as vinyl acetate. The molded polymeric articles treated according to the present invention, furthermore, can contain inert inorganic fillers such as asbestos fibers, glass fibers, carbon, silica, talc and alkaline earth salts which are frequently added to improve the rigidity of the polymer. In addition, the plastic articles can contain other additives normally added to the polymer in order to improve fabricability or solid state properties of such polyolefin.

The foregoing examples are to be considered merely as illustrative of the invention and are not intended in any way to limit its scope. Many variations and modifications of the procedures, materials and conditions employed in the examples would be obvious to those skilled in the art. The critical limitation of this invention is that the disperse dye must have particles suspended therein which have an average diameter not substantially greater than the diameter of the irregularities in the surface of the molded plastic material and that the dye be capable of staining the surface of said material.

Having thus described our invention, what is claimed is:

1. A method for detecting strained areas in molded plastic articles having surface pores, prior to electroplating said plastic articles, comprising:

(a) contacting said plastic article with an aqueous solution containing a disperse dye, said dye having particles suspended therein which have an average diameter which is not substantially greater than that of irregularities in the plastic surface, for a period of time sufficient to cause at least some straining of the contacted portions of the plastic article, and

(b) inspecting said stained plastic article as to the uniformity, depth, and shade of color caused by the action of the dye thereon, the strain-free portion being uniformly stained to a relatively deep shade and the strained portion being stained to a lighter shade.

2. The method of claim **1** wherein said dye solution is maintained at a temperature between about 120° F. and about 212° F.

3. The method of claim **2** wherein said plastic article is contacted with said dye solution by immersion of said article in a heated bath of said dye solution for about 5 minutes at a temperature of about 180° F. and wherein said dye solution includes about 0.01% of a wetting agent.

4. The method of claim **2** wherein the composition of the molded plastic article includes polypropylene.

5. The method of claim **2** wherein the composition of the molded plastic article includes acrylonitrile-butadiene-styrene.

6. The method of claim **2** wherein the composition of the molded plastic article includes impact polystyrene.

7. The method of claim **2** wherein the composition of the molded plastic article includes polycarbonate.

8. The method of claim **2** wherein the composition of the molded plastic article includes polyphenyl oxide.

9. The method of claim **2** wherein the composition of the molded plastic article includes polysulfone.

10. The method of claim **2** wherein the composition of the molded plastic article includes any other plateable resins.

11. In a process for electroplating a molded porous plastic article wherein said article is

(a) chemically etched with a surface conditioner containing a concentrated mineral acid,

(b) sensitized with a readily oxidizable tin salt solution,

(c) activated by treatment with an aqueous solution of a noble metal salt to form a metallic film at discrete surface sites,

(d) subjected to electroless plating by immersion in a solution of a metal salt and a reducing agent, and

(e) plated with metal by electrodeposition of the metal thereon,

the improvement comprising

(f) contacting the molded plastic article, prior to chemically etching the surface with a disperse dye having dye particles suspended therein, which particles have an average diameter which is not substantially larger than that of irregularities in the surface of the plastic article, for a time sufficient to cause at least some staining of the plastic article in contact with the disperse dye, said disperse dye being at a temperature between about 120° F. and about 220° F., and

(g) inspecting the stained surface with respect to the depth and uniformity of shade, the depth and uniformity of shade being an indication of the strained condition of the plastic article.

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CERTIFICATE OF CORRECTION

Patent No. 3,558,444 Dated January 26, 1971

Inventor(s) James E. Fitzpatrick and Habet M. Khelghatian

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 5, the name of inventor "khelghtian" should be --Khelghatian--. Column 4, line 38 (Claim 1), the word "straining" should be --staining--.

Signed and sealed this 11th day of May 1971.

(SEAL)
Attest:

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