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ELECTROPLATED PREFORMED POLYMERIC ARTICLES OF MANUFACTURE

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ABSTRACT OF THE DISCLOSURE

Aliphatic 1-olefins are polymerized with sufficient quantities of a diolefin so that at least 2 trans-internal double bonds per 1,000 carbon atoms exist in the resulting polymer. The resulting polymer can be preplated with conventional electroless plating techniques presently being used for acrylonitrile-butadiene-styrene resins and then electroplated by conventional electrolytic techniques to produce new metallic-plated plastic products.

This invention relates to electroplated plastics. In one aspect, this invention relates to electroplating polymers of polymerizable olefins.

The market for electroplated-plastic articles has expanded tremendously in the last few years. By electroplating plastics the inherent advantages of plastics, i.e., economy, light weight, corrosion resistance, moldability, etc., become available to users of electroplated parts. Present applications for electroplated plastics include automotive accessories (e.g., knobs, handles, trim, bezels), appliance parts (e.g., housings, grills, handles), plumbing fixtures (e.g., valve bodies, sink strainers, P-traps, showerheads), houseware and furniture parts (e.g., knife handles, soap dishes, lamp bases, picture and mirror frames) and industrial uses where the characteristics of its abrasion resistance and shielding qualities are desirable. As more plastics capable of being electroplated become available, the market will be expanded even further.

The most attractive advantage of plated plastics from a commercial viewpoint is cost. A plated-plastic part, with plastics presently being used, can represent an average of 25 percent saving in cost, over a plated metal part.

The most widely used plastic for electroplating is acrylonitrile-butadiene-styrene, hereinafter referred to as ABS. Several processes have been developed for plating of ABS. It has been estimated that 85 to 90 percent of all plated-plastic products are ABS, primarily because ABS is strong and plating bonds weld to it. Although ABS is a high-performance plastic, other plastics are desirable either because they possess specific physical and chemical property advantages, or because of lower cost. It has been generally found that plate applied by conventional processes to many other plastics does not adhere readily thereto; therefore, they have seen limited use. Currently the most widely used technique for plating plastics other than ABS is an encapsulation process. The plating deposited during encapsulation does not involve chemical adhesion; consequently, the plate maintains adhesion to the plastic only as long as the mechanical bond to the plastic and the metal stays intact. This disadvantage has substantially limited the use of articles made from plated-plastics, other than ABS, to small parts such as knobs. For these reasons there has been a continuing effort to develop plastics which can be plated by conventional plating techniques.

The capability to electroplate olefin polymers with conventional plating processes is desirable because of their lower cost and density than ABS. Heretofore, any attempt to plate these plastics with conventional plating processes has resulted in a product with very poor adhesion between the plating and the plastic.

Accordingly, it is an object of this invention to provide a method for electroplating polymers of olefins with conventional plating techniques.

Another object of this invention is to provide an electroplated polymer of olefins which has a bright, metallic surface with good adherent and shock-resistant characteristics.

Other aspects, objects and several advantages of this invention will be apparent to those skilled in the art from the following detailed description and appended claims.

According to this invention an electroplatable olefin polymer is produced by polymerizing at least one aliphatic 1-olefin having 2 to 8 carbon atoms per molecule and no chain branching nearer the double bond than the 4-position with a diolefin having at least one terminal double bond, said diolefin being in sufficient quantities so that the polymerization product has at least two trans-internal double bonds per 1,000 carbon atoms. The polymerization product is subjected to a conventional electroless preplating process to make it electrically conductive and then electroplated with a final finish to obtain a plated-plastic product having a bright, adherent, shock-resistant metallic surface.

The polymers which can be electroplated in accordance with this invention can be prepared by processes disclosed by British Pat. 853,414. Reference is made to this patent for details of the process. In brief, this process comprises contacting a 1-olefin, such as ethylene, propylene and 1-butene, or a mixture of such aliphatic 1-olefins, and a diolefin, such as 1,3-butadiene or isoprene, at a temperature in the range of 150 to 450° F. with a catalyst comprising as its essential ingredient, from 0.1 to 10 or more weight percent chromium in the form of chromium oxide, including a substantial proportion of hexavalent chromium associated with at least one additional oxide selected from the group consisting of silica, zirconia and thoria. This catalyst is often a highly oxidized catalyst which has been activated by high temperature treatment with an oxidizing gas. The polymerization normally is carried out with the olefin and diolefin in solution with a hydrocarbon solvent, especially a paraffin or a naphthene which is liquid under the polymerization conditions. A pressure of at least 100 to 300 p.s.i. is generally required with a pressure of about 500 p.s.i. being preferred. Other methods of producing polymers having the desired characteristics, including well-known or organometal catalyst systems, can also be employed.

The term "polymer" is used herein and in the claims to designate both homopolymers and copolymers. The aliphatic 1-olefins employed to produce the polymers which can be electroplated in accordance with this invention are selected from the class consisting of aliphatic 1-olefins having 2 to 8 carbon atoms and no branching nearer the double bond than the 4-position. Examples of aliphatic 1-olefins within this class are ethylene, propylene, 1-butene, 1-pentene, 1-heptene, and 1-octene. Either conjugated or nonconjugated diolefins having up to 8 carbon atoms per molecule can be copolymerized with the above 1-olefins to obtain the desired electroplatable characteristics. The diolefin must have at least one terminal double bond. The preferred diolefins are selected from a class consisting of conjugated diolefins with at least one terminal double bond. Examples of conjugated diolefins within this class are 1,3-butadiene, isoprene, 1,3-hexadiene, 1,3-pentadiene, and 1,3-octadiene. Examples of nonconjugated diolefins within this class are 1,4-pentadiene, 1,6-heptadiene, and 1,5-octadiene.

The quantity of the aliphatic 1-olefin or mixture of same and the diolefin used can vary over a wide range depending upon the specific chemical and physical char-

acteristics desired of the polymerization product; however, the product must have at least two trans-internal double bonds per 1,000 carbon atoms. To obtain a good electroplated-plastic product the trans-internal double bonds per 1,000 carbon atoms in the polymerization product should be 2 to 15, preferably 2.5 to 10. A product with fewer than two trans-internal carbon bonds per 1,000 carbon atoms will not provide a good bond when plated by conventional plating processes; one with more than 15 has reduced flexural modulus, tensile strength and other strength characteristics.

Conventional plating processes for ABS involve a preplating process which includes cleaning; conditioning or etching the surface of the plastic with a strong acid solution, such as chromic-sulfuric acid, at elevated temperatures; sensitizing the surface of the plastic with an oxidizable salt, such as stannous chloride, that is absorbed and later reduces the activator (not all conventional processes include this step); activating the surface with a precious metal salt, such as palladium chloride; and electroless plating with either copper (about 0.005 mil to 0.010 mil) or nickel (about 0.010 to 0.030 mil). Each conditioning step is followed by one or more water rinses. The continuous film of electrically conductive material applied by the preplating process provides the capability for applying the final finish by conventional electrolytic processes. Following the preplate process, normal plating of copper-nickel-chrome, or nickel-chrome or any of a whole variety of final finishes, including gold and silver, can be applied by conventional electroplating techniques. For most applications the final plate will be about 0.5 to 2.0 mils thick, but even thicker plate can be applied if desired.

The following specific example presents data which illustrate and clarify the invention but should not be interpreted to restrict or limit the invention unnecessarily.

EXAMPLE

Polymers of ethylene and 1,3-butadiene were made by the so-called "particle-form" process as described in British Pat. 853,414 with varying weight percentages of 1,3-butadiene in the feed to the polymerization zone. The various polymers were molded into discs 1⅛ inch in diameter and 300 to 500 microns thick. The number of trans-internal double bonds in each of the polymers was determined by a spectrum analysis performed by infrared scanning in a Perkin-Elmer Model 137 Infracord having a sodium chloride prism. The spectrum of each of the polymers was compared with those of normal olefins such as 1-hexadecene, trans-3-heptene, and the like. The exact number of trans-internal double bonds per 1,000 carbon atoms was determined by measuring the relative intensity band at 10.35 microns.

Following preparation of the disc and determination of the number of trans-internal double bonds contained therein, each disc was subjected to a somewhat conventional plating process under identical operating conditions. The following procedure was used:

(1) Immerse in a sodium pyrophosphate cleaning solution for 2 to 5 minutes at 140° F.

(2) Immerse in a sodium bisulfate neutralizing solution for 15 to 30 seconds at 75° F.

(3) Immerse in an acid chromate etching solution for 15 minutes at 130° F.

(4) Rinse with 5 weight percent hydrochloric acid.

(5) Immerse in a stannous chloride sensitizing solution for 15 to 60 seconds at 75° F.

(6) Immerse in a palladium ammonium chloride activating solution for 15 to 60 seconds at 75° F.

(7) Immerse in an electroless copper plating solution for 5 to 30 minutes at 75° F. The plating solution comprised modified Fehling solutions: solution A was $CuSO_4$ and solution B was NaOH, NaK tartrate, Na_2CO_3 and $NaC_2H_3O_2$.

(8) Strike with copper. The composition of the copper strike bath and conditions for plating were as follows:

Composition of the copper strike bath

98 grams—$CuSO_4 \cdot 5H_2O$
15.5 milliliters—concentrated H_2SO_4
1 milliliter—UBAC Brightener No. 1 [1]
Sufficient water to make 1 liter of solution.

[1] Supplied by Udylite Corporation, Detroit, Mich.

Plating conditions

Voltage—2 volts D.C.
Current density—10 to 15 amperes/ft.^{2}
Current efficiency—100%.
Anode—electrolytic copper
Temperature—75 to 80° F.
Time—4 to 10 minutes
Mechanical stirring of bath.

(9) Electroplate with bright copper. The composition of the bright copper bath and conditions for plating were as follows:

Composition of the bright copper bath

212 grams—$CuSO_4 \cdot 5H_2O$
28.8 milliliters—concentrated H_2SO_4
4 milliliters—UBAC Brightener No. 1
75 milligrams—NaCl
Sufficient water to make 1 liter of solution.

Plating conditions

Voltage—4 volts D.C.
Current density—30 to 40 amperes/ft.^{2}
Current efficiency—98 to 100%
Anode—electrolytic copper
Temperature—75 to 80° F.
Time—1 to 3 minutes
Air agitation of the bath.

(10) Electroplate with nickel. The composition of the nickel plating bath and conditions for plating were as follows:

Composition of the nickel plating bath

1136 grams—$NiSO_4 \cdot 6H_2O$
312 grams—$NiCl_2$
185 grams—Boric acid
Sufficient water to make 1 gallon of solution.

Plating conditions

Voltage—4 volts D.C.
Current density—40 to 50 amperes/ft.^{2}
Current efficiency—95 to 100%
Anode—nickel
Temperature—75 to 80° F.
Time—30 to 120 seconds
Mechanical stirring of the bath.

(11) Plate with chrome. The composition of the chrome plating bath and the conditions for plating were as follows:

Composition of the chrome plating bath

350 grams—CrO_3
2 milliliters—concentrated H_2SO_4
Sufficient water to make 1 liter of solution.

Plating conditions

Voltage—6 to 8 volts D.C.
Current density—90 to 110 amperes/ft.^{2}
Current efficiency—20%
Anode—lead
Temperature—80 to 100° F.
Time—30 to 90 seconds
Agitation of the bath effected by the evolution of gases.

Each conditioning and plating step was followed by one or more water rinses.

Adhesion tests similar to those conventionally used for paints and varnishes were used. First, a razor blade was used to cut a horizontal line through the electroplate on

each disc. A piece of pressure-sensitive, adhesive cellophane tape (Mystik #6450, manufactured by Mystik Tape, Inc., a Division of Borden Chemical Co.) was then pressed onto the surface and pulled off. If the electroplate came loose from the plastic, the adhesion was considered poor. If the plated disc passed this preliminary test, an additional test for adhesion was performed. This additional adhesion test consisted of cutting through the plate with eleven No. 16 Exacto knife blades bolted together in a parallel fashion so that the distance from the first to the eleventh blade was about $\frac{3}{16}$". Right angle cuts were made with the eleven knife blades so that the plating was cut into 100 squares in a surface area approximately $\frac{3}{16}$" by $\frac{3}{16}$", or in other words, each square had a side approximately 1.875×10^{-2} inch. This cutting action imposed considerable stresses into the small squares. A pressure sensitive cellophane adhesive tape, like that used above, was then pressed firmly over the 100 squares and jerked off. If none of the squares of plating were removed from the disc when the tape was so removed, the adhesion was rated good. If more than ten squares were removed, the adhesion was rated poor.

The discs, which were rated good by the last adhesion test above, were then subjected to a shock test consisting of first immersing the plated disc in boiling water for 30 minutes followed by plunging it into ice water. Discs of each polymer with and without the scoring for the last adhesion test above were subjected to this shock test. Each disc was visually inspected for blistering, other evidence of a loss of bond and general plating appearance and was rated on this basis. The following results from the above tests were obtained on ethylene-1,3-butadiene polymer samples with varying numbers of trans-internal double bonds:

Trans-internal double bonds per 1,000 carbon atoms	Adhesion rating	Shock rating
0.1 [1]	Poor	
1.0	do	
2.0	Good	Poor.
2.5	do	Good.
2.6	do	Do.
3.3	do	Do.
4.5	do	Do.
5.4	do	Do.
6.3	do	Do.
8.9	do	Do.

[1] This sample was a polyethylene containing no butadiene. All other polymers were made with ethylene-butadiene feeds containing 1.2 to 6.9 weight percent butadiene.

From the foregoing test results, it can be seen that there must be a minimum of two trans-internal double bonds in the polymerization product plated by conventional plating techniques to obtain a good chemical bond. It can also be seen from these results that when this number of trans-internal double bonds exists there is a good adhesion between the plating and the plastic when a conventional plating process is employed.

As will be evident to those skilled in the art, many

variations and modifications can be practiced within the scope and spirit of this invention and it should be understood that the latter is not necessarily limited to the aforementioned discussion.

I claim:

1. An electroplated plastic article of manufacture which comprises

(a) a nonconductive substrate consisting essentially of a preformed ploymeric composition formed by copolymerization of at least one aliphatic 1-olefin having from 2 to 8 carbon atoms per molecule and no branching nearer the double bond than the 4-position and a diolefin having at least one terminal double bond and present in an amount sufficient so that the resulting polymerization product has from about 2.5 to 15 trans-internal double bonds per 1,000 carbon atoms,

(b) a continuous intermediate electroless plated layer of electrically conductive material bonded to said nonconductive substrate,

(c) an outer layer consisting of an electroplated metal bonded to said intermediate electroless plated layer.

2. An electroplated article according to claim **1** wherein said aliphatic 1-olefin is ethylene and said diolefin is 1,3-butadiene.

3. An electroplated article according to claim **1** wherein said polymeric composition contains 2.5 to 10 trans-internal double bonds per 1,000 carbon atoms.

4. An article according to claim **1** wherein said intermediate layer is electroless plated copper and said electroplated layer is electroplated copper or nickel.

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