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Wells

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[54] **ELECTROPLATING POLYPROPYLENE**

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[58] **Field of Search** ..... 204/20, 30, 38 E, 38 B; 117/47 A; 156/2; 29/195 P

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[57] **ABSTRACT**

Electroplating of propylene polymers containing a nonporous natural silica filler is achieved by conditioning a preformed article of said propylene polymer with a high acid content chromate conditioning agent, thereafter preplating the conditioned article with an electrolessly platable metal, and then electroplating the preplated article with a final finish to obtain a metal-plated propylene polymer product.

5 Claims, No Drawings

ELECTROPLATING POLYPROPYLENE

This invention relates to the electroplating of propylene polymers. In one aspect, this invention relates to an improved process for electroplating a conditioned molded article of a polymer of propylene. In another aspect, this invention relates to a method for conditioning articles formed of propylene polymers for use in an electroplating process. In a still further aspect, this invention relates to a method for providing electroplated articles of propylene polymers.

It is known in the plating art and disclosed in U.S. Pat. No. 3,567,594 that successful electroplating of a variety of molded plastic articles containing a siliceous filler is accomplished when the molded filled plastic article is conditioned by a combination treatment consisting of an acid chromate etch and an HF treatment. While such a process provides a significant improvement in the plating art, there are required, in carrying out the conditioning step of the process, the use of two separate treatment baths. Such a system thus requires in an already complex procedure the necessity of regulating the content of two further solutions. Accordingly, if one or more steps of the processes as now practiced could be eliminated while still achieving satisfactory plating, such a process would result in a still further improvement in the art of electroplating plastics.

It is an object of the present invention to provide an improved process for the metal plating of plastics.

Another object of the invention is to provide a process for electroplating plastics which permits the utilization of conventional electroplating systems while reducing the overall combination of steps required therein.

Other aspects, objects, and the several advantages of the invention will become apparent to one skilled in the art from a reading of the following disclosure and the appended claims.

According to this invention, I have now discovered that by use of certain polymers in combination with a certain type silica filler when conditioned by treatment with a high acid content chromate etch, there can be eliminated the use of the HF treatment as heretofore practiced in the electroplating of silica-filled plastics.

More particularly, I have discovered that if normally solid polymers of propylene containing a particular type natural silica filler, as hereinafter defined, are subjected to etching in a high acid content chromate etch bath, there will result a satisfactorily conditioned article for use in conventional electroplating processes such that the HF treatment heretofore required can be eliminated.

The overall improved method for electroplating solid polymers of propylene according to this invention comprises the steps of (1) incorporating the natural silica filler (as hereinafter described) into the propylene polymer; (2) molding the resulting filled polymer composition into the desired configuration; (3) conditioning the resulting molded article by treating in a high acid content chromate etch bath (as hereinafter described); (4) preplating the conditioned article with an electrolessly platable metal; and (5) electroplating the preplated article with a final finish to obtain a metal-plated polypropylene product.

Although the overall process for electroplating polymers of propylene in accordance with this invention utilizes the aforementioned steps, it is not essential that

all the steps be performed at one time. Accordingly, once conditioned by the acid chromate etch step, the surface-conditioned molded plastic article can be immediately preplated or can be shipped to some other location for further processing. Thus the acid treating step results in the formation of a novel product suitable for further processing in a conventional electroplating system. This is advantageous in some instances since it permits conventional plating processors to form plated plastic articles without having to alter their established operations or having to acquire suitable equipment for forming the treated article.

Similarly, the electrolessly plated article prepared by the above steps (1) through (4) represents a novel preplated product which, if desired, can be supplied in this form to a processor for electroplating. This is particularly advantageous when the final finish metal on the plastic article is to be of a type not normally utilized and the preparation of which by the preplator would be uneconomical.

The process of this invention is particularly suitable for electroplating polymers of propylene.

The terms "polymers of propylene" or "propylene polymers" as used herein are intended to include homopolymers of propylene and copolymers of propylene and ethylene.

In one embodiment of the invention, the propylene-ethylene block copolymers are those in which the proportion of the polypropylene and predominantly polyethylene portions of the copolymer can be varied widely. Generally, the polyethylene portion constitutes 10–50, most preferably 12–15, percent by weight of the final product. The most preferred block copolymers are further characterized as having a melt flow in the range of about 2 to about 10, preferably about 4 to about 6; a flexural modulus in the range of about 100,000 to about 200,000, preferably about 150,000 to about 190,000, psi; a tensile strength in the range of about 2400 to about 4700, preferably about 2500 to about 4000, psi; a minimum notched Izod impact strength of about 1.2, preferably about 1.5, ft. lbs./inch as measured at 73.4° F.; and a minimum unnotched Izod impact strength, measured at 0° F., of about 5, of about 5, preferably about 10, ft.lbs./inch.

The terms "mold," "molded," "moldable," "molding" and the like as used herein and in the claims are intended to include any plastic forming process such as film formation by extrusion, casting or calendering, blow molding, injection molding, vacuum forming, pressure forming, compression molding, transfer molding, thermoforming and the like.

The surface-conditioning step of the present invention utilizes a high acid content chromate etch. Accordingly, the filled plastic article is treated with the acid chromate etch of the following formation:

	Oz./Gal.	Fl. Oz./Gal.	Wt. %
H_2SO_4 (Conc.)	52–65	27.2–34.0	28.1–33.0
H_2O	89.1–80.1	89.1–80.1	40.6–48.1
CrO_3	44–52	11.7–13.9	23.8–26.4

The "high acid content chromate etch" treatment is normally carried out at temperatures in the range of 75° to 200° F. The acid chromate etch treatment is generally carried out for a period of time in the range of 0.1 to 20 minutes. However, when used in the treatment of polymers in accordance with this invention, a

treating time of 6 to 8 minutes is preferred.

The acid chromate etch solution is formed by the addition of a chromate salt or Cro_3 to sulfuric acid.

Silicas used to fill the polymers are nonporous materials derived from natural sources. The particle sizes suitable for use in this invention are in the range of 1 to 50 microns, preferably less than about 10 microns. Good results are obtained with particle sizes ranging from about 1 to 4 microns, with the best results obtained with 1-micron material. Surface areas of the silicas are relatively low, i.e., they range from about 1 to about 40 cm^2/g. Oil absorption values of the silicas range from about 15 to 40 grams per 100 grams of silica (ASTM D1483-60).

The amount of silica to use as filler can range from about 10 to about 50 weight percent, based on total weight of polymer plus filler. Good results have been obtained at 30 weight percent filler level based on adhesion values which can range from about 10 to about 25 or more lbs./inch.

The silicas useful for this invention are those having an iron content less than about 0.05 weight percent. Use of higher iron content silicas will result in degrading of the propylene polymers containing them.

As indicated, it would be highly desirable in the electroplating of a plastic article to be able to utilize conventional plating processes to produce a plated product having good adhesion of the metal plate thereto. Such conventional plating processes involve a preplating process which includes cleaning; conditioning or etching the surface of the plastic with an acid chromate 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 platinng 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 procedures are representative of the conventional plating processes and conditions which can be used in the electroplating of propylene polymers in accordance with this invention.

It is to be understood that the recitation of specific plating solutions and steps in no way limits the invention to these specific solutions and steps. There are numerous plating systems available, and the process of the invention can be used with any of them.

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 0.1 to 20 minutes at 75° to 200° F.

4. Rinse with 10 percent HCl containing from about 5 to about 150 ppm of a surfactant such as a nonionic surfactant exemplified by an alkylphenoxypoly(ethyleneoxy)ethanol.

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.

7a. Immerse in an electroless copper plating solution for 5 to 30 minutes at 75° F. the typical plating solution comprises modified Fehling solutions: Solution A is $CuSO_4$ and solution B is NaOH, NaK tartrate, Na_2CO_3 and $NaC_2H_3O_2$, or

7b. Immerse in an electroless nickel plating solution for 5 to 30 minutes at 75° F. The plating solution usually contains nickel satls and a reducing agent such as sodium hypophosphite or a boron amine.

8a. Strike with copper. The composition of a typical copper strike bath and conditions for plating are as follows:

Composition of the copper strike bath	
98 grams	$CuSO_4.5H_2O$
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, Michigan

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
Agitated bath	

or

8b. Strike with nickel. The composition of a typical strike bath and conditions for plating are as follows:

Composition of nickel strike bath	
300–410 grams	$NiSO_4.6H_2O$
30–45 grams	$NiCl_2.3½H_2O$
45 grams	H_3BO_3
10 milliliters	Nickel brightener N3F[1]
Sufficient water to make 1 liter of solution	

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

Plating conditions	
Voltage	6–18 volts D.C.
Current density	30 to 80 amperes/ft.^{2}
Current efficiency	100%
Anode	Nickel (99.5%)
Temperature	75° to 155° F.
Time	4 to 10 minutes
Agitated bath	

9. After electroless plating, the resulting electrically conductive product is then electroplated with any combination of conventional plating solutions. The following are examples of typical solutions and conditions for plating with the indicated metal. Numerous other solutions are known and can be utilized if desired.

10. Electroplate with bright copper. The composition of the bright copper bath and conditions for plating are as follows:

Composition of the bright copper bath	
212 grams	$CuSO_4.5H_2O$
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.

-continued

Time	10 to 30 minutes[1]
Agitated bath	

[1]45 minutes used in preparing the test specimens.

11. Electroplate with nickel. The composition of the nickel plating bath and conditions for plating are as follows:

Composition of the nickel plating bath	
1136 grams	$NiSO_4.6H_2O$
312 grams	$NiCl_2$
185 grams	H_3BO_3
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 160° F.
Time	5 to 20 minutes
Agitated bath	

12. Electroplate with chromium. The composition of the chrome plating bath and conditions for plating are 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 140° F.
Time	1 to 4 minutes
Agitation of the bath effected by the evolution of gases	

Steps (1) and (2) of the conventional plating process form a cleaning operation to remove any dirt or other foreign matter from the surface of the preformed or molded object to be plated.

When the surface-conditioned molded article is to be immediately plated in the conventional plating process, steps (1) and (2) of the conventional plating process as described above are not required. Thus, following the conditioning treatment, the resulting article is sensitized with an oxidizable salt (5) followed by the remaining steps as described for electroless and electroplating.

Ordinarily, each conditioning and plating step is followed by one or more water rinses.

The following specific examples are presented further to illustrate the invention, but should not be interpreted as restricting or limiting the invention.

The polymer-filler blends used in these examples were prepared by blending the indicated amounts of polymer and filler in either a Brabender Plastograph for 5 to 10 minutes at 50 to 75 rpm and about 370° F. in a nitrogen atmosphere or in a Banbury mixer for about 5 minutes at about 350+ F. in an air atmosphere. Compression-molded or injection-molded slabs having a thickness of 50 to 75 mils were prepared from the blends, and 3½-inch by 1½-inch pieces were cut from the molded slabs for the plating tests.

Adhesion values were determined in an adhesion test made by pulling the metal layer from the polymer or filled polymer in an Instron tester at a 90° angle and at a rate of 2 inches per minute. In this test a steel bar ½-inch wide is laid down the center of the 3½-inch by 1½-inch piece of plated polymer and a sharp knife is used to cut through the electroplate along each side of the bar. One end of the resulting ½-inch-wide strip is pulled loose for 178 to inch. A clamp attached to a wire about 2 feet long is attached to this loosened metal tab. The polymer or filled polymer is attached to the traverse in the Instron tester and the wire to the upper jaw. The long wire is used so that the angle does not change appreciably as the metal is pulled at right angle from the polymer surface. The average value of the force, in pounds, required to separate the metal and polymer is multiplied by two to get the force required per lineal inch of contact. In the specimens prepared for this test the bright copper electroplate was 2 to 2.5 mils thick so that the metal itself would not yield during the test, and the nickel and chromium electroplating steps were not used.

EXAMPLE I

A series of blends were formed of nonporous, fine particle-size, natural silica with a normally solid propylene-ethylene block copolymer having 12–15 weight percent average ethylene content at several filler levels and several silica particle sizes. In addition, blends of a presently preferred natural silica (Minusil 5 , manufactured by Penn Glass Sand Corporation, 3 Penn Center, Pittsburgh, Pa. 15235 were made with a normally solid propylene homopolymer and a normally solid linear copolymer of ethylene and 1-butene. Each mixture of polymer and silica was tumble-blended together briefly in a plastic bag, and the resulting blend was then compounded for about 5 minutes in a Banbury mixer at 375° F. in an air atmosphere. Each cooled, chopped product blend was extruded at 450° F. in an electrically heated extruder and pelletized. Silica I had an average particle size of 1.1 microns and a surface area of 2.06 m^2 / g. Silica II had an average particle size of 3 microns and a surface area of about 2 m^2/g. Silica III had an average particle size of 4 microns and a surface area also of about 2 m^2/g. the physical properties of the unfilled polymers are given in Table I. The physical properties of the filled polymers are given in Table II.

TABLE 1

		Unfilled Polymer Properties				
		Physical Properties				
Polymer Description	Polymer No.	Melt Flow[a] (g/10 min.)	Density[b] g/cc)	Flexural Modulus[c] (psi × 10^{-3})	Izod Impact[d] (ft.lbs./ in. notch) 73.4° F.	Tensile Yield[e] (psi)
Propylene/ethylene block copolymer	1	4.2	0.900	171	2.0*	3150
Polypropylene	2	5	0.905	225	0.7	5000
Ethylene/1-butene						

TABLE 1-continued

Polymer Description	Polymer No.	Unfilled Polymer Properties Physical Properties: Melt Flow[a] (g/10 min.)	Density[b] g/cc)	Flexural Modulus[c] (psi × 10^{-3}	Izod Impact[d] (ft.lbs./ in. notch) 73.4° F.	Tensile Yield[e] (psi)
random copolymer	3	6.5[f]	0.950	165	0.5	3800

[a]ASTM D1238-62, condition L.
[b]ASTM D1505-68
[c]ASTM D790-70
[d]ASTM D256-56
[e]ASTM D638-61
[f]ASTM D1238-62, condition E
[g]14.5 ft.lbs., unnotched at 0° F.

TABLE II

Resin	Blend No.	Filled Polymer Properties Physical Properties: 1	2	3	4	5	6	7
Propylene/ethylene block copolymer, wt.%		70	65	60	60	60		
Polypropylene, wt. %							70	
Ethylene/1-butene random copolymer, wt.%								70
Silica I (Minusil 5), wt. %		30	35	40			30	30
Silica II (Novacite L-337), wt. %					40			
Silica III (Novacite L-338), wt. %						40		
Melt flow, g/10 min.		3.0	2.5	2.3	3.0	3.1	4.7	9.4 (4.9)[h]
Flexural modulus, psi × 10^{-3}[g]		280	307	348	302	303	336	235
Izod impact, ft.lbs./in. notch		0.65	0.64	0.60	0.70	0.70	0.26	0.28
Tensile yield, psi		2630	2560	2490	2250	2250	3820	2510[i]

[g]ASTM D790-70
[h]ASTM D1238-62, condition E
[i]Tensile break

Comparing filled polymers at the same level in blends 1, 6 and 7, it is seen that melt flow values are decreased somewhat but that adequate flow still remains for molding articles by conventional methods, i.e., injection molding, extrusion, compression molding, thermoforming, etc. The filled polymers exhibit increased flexural modulus values, decreased tensile strengths and decreased impact strengths as expected. However, the filled propyleneethylene copolymer of blend 1 shows the best balance of desirable physical properties since its impact strength is more than double that of the other comparable filled polymers, and its tensile strength and flexural modulus are high although intermediate those of the filled polymers of blends 6 and 7. A tensile break value obtained for the ethylene/1-butene filled polymer of blend 7 suggests that low elongation is present at this filler level and that higher filler levels might result in brittle compositions.

EXAMPLE II

Specimens for determining adhesion values of subsequently applied metal were made by injection molding the various blends 1–7 of Example I using a machine with an in-line reciprocating screw and a polystyrene rated shot size of about 3 ounces. The barrel temperature used was 450° F., the mold temperature was 150° F. and the pressure was about 5,000 psig using the fastest injection speed possible with the machine. Two plaques were molded per shot, each plaque measuring 3 inches wide, 4 inches long and ⅛-inch thick. Ordinary care was exercised in removing the specimens and in handling them prior to conditioning them in the various baths in order not to unduly contaminate the specimens with oil and grease.

The plaques were conditioned for electroless plating by immersing them in an etch bath at 145° F. Two plaques of each composition were treated. One was conditioned for 6 minutes and one was conditioned for 8 minutes. The etch bath contained 63 ounces (32.6 wt. %) concentrated H_2SO_4 per gallon of solution, 47.9 ounces (24.7 wt. %) CrO_3 per gallon of solution and the remainder was water amounting to 82.4 ounces (42.6 wt. %).

Following the conditioning treatment, each specimen was rinsed in water and dipped in 10 weight percent hydrochloric acid containing 10–15 ppm of a nonionic surfactant identified as a nonylphenoxypoly(ethyleneoxy)ethanol containing about 9 to 10 mols ethylene oxide per mol nonylphenol, available commercially as Igepal CO-630 from General Aniline and Film Corporation.

Each specimen was then immersed for 2 minutes, without an intervening water rinse, in a commercially available stannous chloride-palladium chloride colloidal suspension at room temperature (80° F.). The concentrated solution is available from the Shipley Company, Inc., Newton, Mass. Such a solution has a formulation believed to consist of $SnCl_2$, about 2 g/l; $PdCl_2$, about 0.2 g/l; and HCl (37%), about 10 ml/l.

The treated plaques were then water-rinsed and immersed in a proprietary accelerating solution for 1 minute at 150–155° F. to remove the tin salts. The solution is an acid salt accelerator, fluoride-containing, supplied commercially as Marbon D-25 by Marbon Division, Borg-Warner Corp., Washington, W. Virginia.

The conditioned plaques were then rinsed in water and treated for 5 minutes at 80° F. in a commercially available electroless nickel bath (Macuplex 9340, MacDermid, Inc., Waterbury, Conn.) to apply the conductive coating needed for the electroplating operation, then rinsed again. Such commercial electroless nickel plating solutions contain nickel salts and a reducing agent such as sodium hypophosphite or a boron amine.

EXAMPLE III

The plaques of Example II were given a nickel strike and then a coating of bright copper approximately 1.5 to 2 mils thick to provide sufficient metal to determine adhesion of metal to the conditioned substrate. The composition of the nickel strike bath and the plating conditions used were as follows:

Nickel strike bath[1]		
Nickel sulfamate	43.6	oz./gal.
Nickel metal	10.2	"
Boric acid	4.0	"
Barrett Additive "A"	0.4	"
Barrett SNAP (antipit additive)	0.005	"

[1]Barrett Sulfamate Nickel Plating Process, Type SN, available from Allied Research Products, Inc., Baltimore, Mayland

Plating conditions	
Voltage	6 to 18 volts D.C.
Current density	30 to 80 amperes/ft.[2]
Current efficiency	100%
Anode	99.5% nickel
Temperature	125° to 130° F.
Time	5 minutes
Agitated bath	

The composition of the bright copper bath and the plating conditions used were as follows:

Bright copper bath[1]	
$CuSO_4.5H_2O$	27 oz./gal.
H_2SO_4, concentrated	7 oz./gal.
Chlorine ion	36 mg/l
EK-M[2]	0.5% by volume

[1]Harshaw Plating Process, Harshaw Chemical Company, Cleveland, Ohio

[2]Acid copper plating addition agent sold under the trademark Electra

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	55 minutes
Agitated bath	

After removal of the plaques, they were rinsed and conditioned at ambient temperature and humidity for 7 days before adhesion was determined. Adhesion results were obtained in the manner described in the paragraph preceding Example I, above, and the results obtained are presented in Table III.

TABLE III

Blend No.	Resin Source	Adhesion Values for Filled Polymer Wt. %	Silica Size(microns)	Etch time, minutes	Adhesion (Lbs/In.)
1	Propylene-ethylene copolymer	30	1.1	6	14.0
1	"	30	1.1	8	16.5
2	"	35	1.1	6	19.0
2	"	35	1.1	8	22.0
3	"	40	1.1	6	16.0
3	"	40	1.1	8	13.5
4	"	40	3	6	11.0
4	"	40	3	8	12.5
5	"	40	4	6	9.0
5	"	40	4	8	12.5
6	Propylene homopolymer	30	1.1	6	5.0
6	"	30	1.1	8	8.0
7	Ethylene/1-butene copolymer	30	1.1	6	10.0
7	"	30	1.1	8	10.0

Inspection of the data shows that superior adhesion results are obtained with the compositions made from the propylene-ethylene block copolymer used in this invention and a natural, nonporous silica filler of about 1 micron particle size. The best adhesion was obtained with this silica at a filler level of 35 weight percent. Very good results were obtained at the 30 weight percent and the 40 weight percent levels as well. The optimum composition to use depends upon the end use requirements which will involve the degree of adhesion desired, whether or not encapsulation of the part is desired, and the economics involved.

Silicas with particle sizes of 3 and 4 microns can be employed in making up the compositions with some sacrifice in adhesion. Even so, it is seen that the propylene copolymer composition of the present invention, filled with natural silica of the particle sizes noted above, permits the obtaining of superior metal adhesion compared to a propylene homopolymer and an ethylene/1-butene copolymer. When the metal adhesion results of the same polymers are compared with the 1-micron silica at 30 weight percent silica (blends 1, 6 and 7), it is clearly evident that the novel propylene-ethylene copolymer-nonporous silica combination is the superior combination.

EXAMPLE IV

A series of silica-filled compositions was prepared by compounding a propylene-ethylene block compolymer containing about 12–15 weight percent polymerized ethylene, further characterized by a melt flow of 5.1 (ASTM D1238-70, condition L), a flexural modulus of 162,000 psi (ASTM D790-70), a desnity of 0.900 g/cc (ASTM D1505-68) and a brittleness temperature of −27° F. (ASTM D746-70), at two filler levels with natural silicas of various particle sizes. The samples were blended in a Banbury mixer at 375° F. for 5 minutes in an air atmosphere. Each cooled, chopped product was extruded in an electrically heated extruder at 450° F. and pelletized. Silica I (Minusil 5, manufactured by Penn Glass Sand Corporation, 3 Penn Center, Pittsburgh, Pa. 15235) had an average particle size of 1.1 microns and a surface area of 2.06 m^2/g. Silica II (Novacite L-337, manufactured by Malvern Minerals Co., P.O. Box 1246, Hot Springs, Ark. 71901 had an average particle size of 3 microns and a surface area of about 2 m^2/g. Silica III (Novacite L-338, manufactured by Malvern Minerals Co., P.O. Box 1246, Hot Springs, Ark. 71901) had an average particle size of 4 microns and a surface of about $2m^2/g$.

The plaques used in plating tests were prepared by injection molding. An in-line reciprocating screw machine having a polystyrene rated shot size of about 3

ounces was used to mold the ⅛-inch-thick × 3-inches-wide × 4-inches-long plaques, two at a time. Molding conditions consisted of a 450° F. barrel temperature, 150° F. mold temperature, 5000 psig injection pressure and the fastest injection speed possible with the machine. Ordinary care was exercised in removing specimens from the mold and in subsequent operation in order to minimize undue contamination with oil and grease.

The plaques were conditioned for electroless plating by immersing them in a high acid etch bath at the indicated times listed in Table IV. The etch bath consisted of 63 oz. of concentrated H_2So_4 (32.6 wt. %), 47.9 oz. of CrO_3 (24.7 wt. %), and 82.4 oz. (42.6 wt. %) water per gallon of solution. After rinsing, some of the treated plaques were additionally immersed in a second bath containing about 25 weight percent NH_4HF_2 for 1 minute at 80° F. and rinsed. All treated plaques were then dipped for 1 minute in 10 weight percent HCl containing 10–15 ppm of a nonionic surfactant identified as a nonylphenoxypoly(ethyleneoxy)ethanol containing about 9 to 10 mols ethylene oxide per mol nonylphenol, available commercially as Igepal CO-630 from General Aniline and Film Corporation. Each specimen, without an intervening rinse, was then immersed 3 minutes in a commercially available stannous chloride-palladium chloride collodial suspension diluted with an equal volume of water at room temperature (80° F.). The concentrated solution is available commercially from the Shipley Company, Inc., as Catalyst 9F. Such a solution is believed to consist of about 2 g/l $SnCl_2$, 0.2 g/l $PdCl_2$ and 10 cc/l of 37% HCl. After rinsing, the treated plaques were immersed in a proprietary acid salt accelerator solution, non-fluoride-containing, for 1 to 2 minutes at 130°–140° F. to remove the tin salts. Such a solution is sold as Marbon D-270 by Marbon Division, Borg-Warner Corp., Washington, W. Virginia. The conditioned plaques, after rinsing, were immersed for 5 minutes at 80° F. in an electroless nickel bath, available commercially as Macuplex 9340, MacDermid, Inc., Waterbury, Conn., to apply the conductive coating needed for the electroplating operation and rinsed again. The plaques with the electroless nickel coating were then in sequence given a nickel strike in a bath available from Allied Research Products, Inc., as the Barrett Sulfamate Nickel Plating Process, Type SN, and a layer of bright copper about 1.5 to 2 mils thick applied by using a bath available from the Harshaw Chemical Co., Cleveland, Ohio, to provide sufficient metal to determine adhesion of metal to the conditioned substrate. The plated samples after rinsing were conditioned at ambient temperature and humidity for 7 days before adhesion was determined. The results are presented in Table IV.

TABLE IV

Run No.	Adhesion Values for Filled Polymer Silica Size (microns)	Silica Wt. %	Etch Treatment, Minutes Acid	Etch Treatment, Minutes NH_4HF_2	Adhesion, Lbs./Inch.
			Chromate		
1	1.1	20	8	0	5.0
2	1.1	20	8	1	5.5
3	1.1	20	6	0	2.0
4	1.1	20	10	0	9.0
5	1.1	30	8	0	18.0
6	1.1	30	8	1	17.5
7	1.1	30	6	0	20.0
8	1.1	30	10	0	25.0
9	3	20	8	0	2.5
10	3	20	8	1	3.0
11	3	20	6	0	1.0
12	3	20	10	0	5.0
13	3	30	8	0	13.5
14	3	30	8	1	11.5
15	3	30	6	0	6.5
16	3	30	10	0	16.0
17	4	20	8	0	3.0
18	4	20	8	1	2.5
19	4	20	6	0	2.0
20	4	20	10	0	2.0
21	4	30	8	0	9.0
22	4	30	8	1	8.0
23	4	30	6	0	5.0
24	4	30	10	0	10.5

The above data show that the best adhesion results are obtained at a filler level of 30 weight percent instead of 20 weight percent, and that a filler particle size of about 1 micron is preferable in the compositions to attain the best adhesion at the 30 weight percent filler level. Generally, as the etch time in the acid chromate bath was increased from 6 to 10 minutes, the adhesion of subsequently applied metal also increased. Run 7 appears to be an exception since the 6-minute etch gave better results than the 8-minute etch used in run 9. In comparing runs 1 and 2, 5 and 6, 9 and 10, 13 and 14, 17 and 18, and 21 and 22, where the effects on metal adhesion of an acid chromate etch alone and in combination with an ammonium bifluoride etch are shown, it can be seen that slightly better adhesion is obtained in run 2 and run 10 with the combination etch. However, slightly better adhesion is obtained with the acid chromate etch alone as is seen in the results of runs 5, 13, 17 and 19. The results show that good adhesion of metal to the conditioned filled propylene-ethylene block copolymer substrate is obtained with an etch treatment consisting only of etching in a high acid chromate bath of the composition described.

From the foregoing example, it can be seen that the utilization of a high acid chromate etch for the conditioning of a molded propylene polymer article containing a nonporous, natural silica filler results in the obtaining of a metal-plated product having satisfactory adhesion.

In addition, the examples clearly demonstrate that use of the conditioning treatment of the invention in combination with the specified siliceous filler permits the satisfactory plating of a polymer article in conventional metal-plating processes.

Reasonable variations and modifications of this invention can be made, or followed, in view of the foregoing disclosure, without departing from the spirit or scope thereof.

I calim:

1. A process for electroplating a moldable propylene polymer which comprises the steps of

1. incorporating a nonporous natural silica filler having a particle size in the range of 1 to 50 microns, a surface area in the range of 1 to 40 cm^2/g and an oil absorption value in the range of 15 to 40 grams of oil per 100 grams filler into said polymer;
2. molding the resulting composition of propylene polymer and filler;
3. conditioning the molded propylene polymer product of stpe (2) by contacting same with an acid chromate etch consisting of 28.1 to 33.0 weight percent H_2SO_4, 23.8 to 26.4 weight percent CrO_3 and 40.6 to 48.1 weight percent H_2O for a period of 0.1 to 20 minutes at a temperature in the range of 75° to 200° F.;
4. preplating the resulting conditioned polymer product of step (3) with an electrolessly platable metal; and
5. electroplating the preplated product of step (4) with a final metal finish to obtain a metal-plated propylene polymer product.

2. A process according to claim **1** wherein said silica filler is present in an amount in the range of about 10 to about 50 weight percent.

3. The product of the process of claim **1.**

4. A process for electroplating a moldable propylene polymer which comprises the steps of

1. conditioning a preformed product of said propylene polymer containing from about 10 to 50 weight percent of a nonporous, naturally occurring silica filler having a particle size in the range of 1 to 50 microns, a surface area in the range of 1 to 40 cm^2/g and an oil absorption value in the range of 15 to 40 grams of oil per 100 grams filler by treating said product with an acid chromate etch consisting of from 28.1 to 33.0 weight percent sulfuric acid, form 23.8 to 26.4 weight percent chromate and from 40.6 to 48.1 weight percent water for a period of 0.1 to 20 minutes at a temperature in the range of 75° to 200° F.;
2. preplating the resulting conditioned product with an electrolessly platable metal; and
3. electroplating the resulting preplated product with a final finish to obtain a metal-plated propylene polymer product.

5. The electroplated product of the process according to claim **4.**

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