

tional plating processes in producing a plated product having good adhesion of the metal plate thereto.

Such conventional plating processes involve a pre-plating 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 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 procedures are representative of the conventional plating processes and conditions which can be used in the electroplating of plastics 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, so long as an HF treatment, as herein defined, precedes or follows the acid chromate etch.

(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 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.

(7a) 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 $\text{NaC}_2\text{H}_3\text{O}_2$, or

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

(8a) 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— $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

15.5 milliliters—Concentrated H_2SO_4

1 milliliter—UBAC Brightener No. 1¹

Sufficient water to make 1 liter of solution

¹ Supplied by Udylyte 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

Agitated bath

or

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

Composition of nickel strike bath

300–410 grams— $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$

30–45 grams— $\text{NiCl}_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$

45 grams— H_3BO_3

10 ml. nickel brightener N3E¹

10 Sufficient water to make 1 liter of solution

¹ Supplied by Udylyte Corporation, Detroit, Mich.

Plating conditions

Voltage—6–18 volts D.C.

15 Current density—30–80 amperes/ft.²

Current efficiency—100%

Anode—Nickel (99.5%)

Temperature—75–155° F.

Time—4–10 minutes

20 Agitated bath

(9) After electroless plating, the resulting electrically conductive product is then electroplated with any combination of conventional plating solutions.

25 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 were as follows:

Composition of the bright copper bath

212 grams— $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

35 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

45 Temperature—75 to 80° F.

Time—1 to 3 minutes¹

Agitated bath

¹ 45 minutes used in preparing the test specimens.

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

Composition of the nickel plating bath

55 1136 grams— $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$

312 grams— NiCl_2

185 grams— H_3BO_3

Sufficient water to make 1 gallon of solution

Plating conditions

60 Voltage—4 volts D.C.

Current density—40 to 50 amperes/ft.²

Current efficiency—95 to 100%

Anode—Nickel

65 Temperature—75 to 160° F.

Time—30 to 120 seconds

Agitated Bath

(12) Electroplate with chromium. The composition of the chrome plating bath and conditions for plating were as follows:

Composition of the chrome plating bath

350 grams— CrO_3

2 milliliters—Concentrated H_2SO_4

75 Sufficient water to make 1 liter of solution

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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—30 to 90 seconds
 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.

Step (4) of the above-described plating process is not required if the HF treatment of the conditioning step of this invention is carried out after the acid chromate etch, and was not used in the tests made to illustrate the process of the invention. When the HF treatment is carried out prior to the acid chromate etch in the conditioning step of the process of the invention, then step (4) of the conventional electroplating process can be utilized.

When the surface conditioned molded plastic 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 utilizing the combination of HF treatment and acid chromate etch, the resulting plastic 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 to further illustrate the invention but should not be interpreted to restrict or limit the invention.

The plastic-filler blends used in these examples were prepared by blending the indicated amounts of plastic and filler in either a Brabender Plastograph for 5 to 10 minutes at 50 to 75 r.p.m. 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. A precipitated hydrated silica having an average particle size of 0.022 micron or a pumice having a particle size less than 50 microns was used in the tests.

Adhesion values were determined in an adhesion test made by pulling the metal layer from the plastic or filled plastic 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 plastic 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 ½ to ¾ inch. A clamp attached to a wire about 2 feet long is attached to this loosened metal tab. The plastic or filled plastic 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 plastic surface. The average value of the force, in pounds, required to separate the metal and plastic 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 plating tests was carried out utilizing an ethylene/propylene copolymer containing about 3.5 weight percent ethylene and 96.5 weight percent propylene which had a melt flow of about 1.75 dg./min. (ASTM D 1238-62T, Condition L) and a density of 0.899 g./cc.

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(ASTM D 1505-63T) blended with 20 weight percent silica. Conventional electroplating techniques, as described above, were used except that the filled polymer was treated in a 50 weight percent aqueous solution of ammonium bifluoride following the acid chromate etch in the process of the invention. The following results were obtained:

Sample	Acid chromate etch		NH ₄ HF ₂ treatment		Total treating time, min.	Adhesion, lb./in.
	Time, min.	Temp. ° F.	Time, min.	Temp. ° F.		
1-----	2	160	2	80	4	16
2-----	2	160	3	80	5	26
3 (control)-----	5	160	None		5	2.5

EXAMPLE II

Plating tests were made with portions of the same filled polymer used in Example I. Conventional electroplating techniques, as described above, were used except that the filled polymer was treated in a 50 weight percent aqueous HF bath following the acid chromate etch in the process of the invention. The following results were obtained:

Sample	Acid chromate etch		HF treatment		Total treating time, min.	Adhesion, lb./in.
	Time, min.	Temp. ° F.	Time, min.	Temp. ° F.		
1-----	2	160	2	80	4	30+
2 (control)-----	5	160	None		5	2.5

EXAMPLE III

A series of plating tests was carried out utilizing a polypropylene which had a density of 0.905 g./cc. and a melt flow of about 4 dg./min. blended with 20 weight percent pumice. Conventional electroplating techniques, as described above, were used except that the filled polymer was treated in a 50 weight percent aqueous HF bath following the acid chromate etch in the process of the invention. The following results were obtained:

Sample	Acid chromate etch		HF treatment		Total treating time, min.	Adhesion, lb./in.
	Time, min.	Temp. ° F.	Time, min.	Temp. ° F.		
1-----	2	155	2	80	4	2.0
2-----	4	155	4	80	8	2.6
3 (control)-----	5	160	None		5	<1

EXAMPLE IV

A series of plating tests was carried out utilizing portions of the ethylene/propylene copolymer described in Example I blended with 20 weight percent pumice. Conventional electroplating techniques, as described above, were used except that the filled polymer was treated in a 50 weight percent aqueous HF bath following the acid chromate etch in the process of this invention. The following results were obtained:

Sample	Acid chromate etch		HF treatment		Total treating time, min.	Adhesion, lb./in.
	Time, min.	Temp. ° F.	Time, min.	Temp. ° F.		
1-----	2	155	2	80	4	4.0
2-----	4	155	4	80	8	4.0
3-----	6	155	3	80	9	3.0
4-----	8	155	4	80	12	4.0
5 (control)-----	5	160	None		5	<1

EXAMPLE V

A series of plating tests was carried out utilizing a polypropylene having a melt flow of about 10 dg./min. and an amorphous content⁴ of about 18 weight percent blended with either 10 or 20 weight percent silica. Conventional electroplating techniques, as described above, were used except that the filled polymer was treated in a 50 weight percent aqueous HF bath following the acid

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ELECTROPLATING PLASTICS

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36 Claims

ABSTRACT OF THE DISCLOSURE

Electroplating of a moldable plastic containing a siliceous filler is achieved by conditioning a preformed article of said plastic by a combination treatment consisting of an acid chromate etch and an HF treatment and thereafter preplating the conditioned article with an electrolessly platable metal and electroplating the preplated article with a final finish to obtain a metalplated plastic product.

This application is a continuation-in-part of Ser. No. 714,098, filed Mar. 18, 1968 now abandoned.

This invention relates to the electroplating of plastics. In one aspect, this invention relates to an improved process for electroplating plastics containing a siliceous filler. In another aspect, this invention relates to a method for providing electroplated plastic articles having an improved adhesion of the metal plate thereto. In a further aspect, there is provided a method for conditioning plastic articles for use in an electroplating process.

BACKGROUND OF THE INVENTION

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 both fabricators and 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.

Although the demand for electroplated plastics has expanded, not all plastics are capable of being plated by conventional processes due to the failure to obtain a satisfactory adhesion of the metal plate to the plastic. Thus, for example, olefin polymers have found little utility in the formation of plated plastic articles because it has not been possible to obtain a strong bonding of the metal plate to the polymer surface and further because of the undesirably long time required for etching the polymer surface. Such difficulties are apparently due to the physical and chemical properties of the olefin polymers such as polyethylene, polypropylene, halogenated olefin polymers and the like which render them inert and, accordingly, unaffected by conventional etching techniques normally employed in electroplating.

Heretofore the most widely used plastic for electroplating was acrylonitrile-butadiene-styrene, hereinafter referred to as ABS, since conventional plating techniques can be employed with this plastic and the plating bonds well. For other plastics than ABS the poor bonding of the plate, if formed by conventional techniques, resulted in a limited use of the resulting product. The necessity of having to use other than conventional plating techniques for electroplating plastics not only materially in-

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creases the cost of the electroplated product but till now has been unable to overcome the problem of poor bonding or adhesion of the metal plate so that use of such plated products has been limited to small parts such as knobs.

For these reasons as well as the outstanding properties possessed by other plastics and particularly the olefin polymers there has been a continuing effort to develop a method for electroplating other plastics by conventional techniques.

THE PRESENT INVENTION

Accordingly, it is an object of this invention to provide an improved process for metal plating plastics.

Another object of this invention is to provide a method for producing a plated plastic article having improved adhesion of the plate to the plastic surface.

A further object of this invention is to provide a process for electroplating plastics which permits the utilization of conventional electroplating systems.

Another object of this invention is to provide a method for conditioning plastics so as to provide a product suitable for use in conventional electroplating systems.

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

According to this invention there is provided a method for electroplating a plastic which comprises the steps of:

- (1) incorporating a siliceous filler in the plastic;
- (2) molding the resulting plastic composition into the desired configuration;
- (3) conditioning the resulting molded plastic product by treating, in series, with (a) an acid chromate etch and (b) an HF treatment;
- (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 plastic product.

Although the overall process for electroplating plastics 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 HF-treating step of this invention, either alone or followed by an 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 HF-treating step results in the formation of a novel product suitable for further processing in a conventional electroplating system.

Likewise, while each step of the conditioning treatment of this invention is conventionally carried out immediately in sequence in one embodiment of this invention wherein the HF treatment is utilized following the acid chromate etch treatment, the HF treated plastic article resulting therefrom represents a novel surface conditioned article which can be supplied without further treatment to operators of conventional plating processes. 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 by having to acquire suitable equipment for forming the HF-treated article.

Likewise, the electrolessly plated plastic 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 replator would be uneconomical.

Although the process of this invention can be utilized for the plating of any moldable plastic as defined above, in one specific embodiment of this invention it has been found to be particularly suitable for electroplating olefin polymers.

The term "olefin polymer" as used herein and in the claims is intended to include both homopolymers and copolymers of aliphatic 1-olefins having 2 to 8 carbon atoms or mixtures thereof.

The process of this invention can be utilized with any moldable plastic material. As used herein and in the claims, the term "plastic" is intended to include any natural or synthetic polymeric material which can be molded into a desired final shape using heat and/or pressure. Examples of such materials, which are listed and described in *Modern Plastics Encyclopedia* for 1967, are: ABS resins, acetal resins, acrylics and modified acrylics, alkyd resins, allyl resins, amino resins, halogenated polyethers, epoxy resins, fluoroplastics, furane resins, ionomers, isocyanates, nylons, parylene polymers, phenolics, phenoxy resins, polyalkenes, polycarbonates, polyesters, polyimides, polyarylene oxides, polyarylene sulfides, polysulfones, silicones, styrene polymers and copolymers such as styrene/butadiene, vinyl polymers and copolymers, such as poly(vinyl chloride), poly(vinyl fluoride), vinylidene chloride/vinyl chloride copolymer, and the like, including blends.

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

Examples of the aliphatic 1-olefins are ethylene, propylene, 1-butene, 1-pentene, 2-methylpentene, 1-hexene, 1-heptene, 1-octene, 1,3-butadiene, 1,4-hexadiene, 1,3-heptadiene, 1,5-octadiene, and the like. Examples of the olefin polymers and polymer blends that can be used are polyethylene, polypropylene, poly(butene-1), poly(2-methylpentene), ethylene/propylene copolymer, ethylene/butene-1 copolymer, ethylene/hexene-1 copolymer, ethylene/propylene/1,4-hexadiene terpolymer, ethylene/propylene/butene-1 terpolymer, polyethylene/polypropylene blends, polyethylene/polypropylene/polydiene blends, and the like.

Such polymers are known to be inert to most chemicals and when heretofore plated formed products having poor metal to plastic adhesion values. This, in turn, limited the end uses of such metal plated items to those applications where the strength of the bond or adhesion value was not critical.

When carrying out the process of the present invention with an olefin polymer there is achieved a substantial increase in the metal to plastic adhesion values of the plated article. In addition, the combination conditioning treatment can be carried out for reduced periods, thus providing the further advantage of reducing the overall etch time required to satisfactorily condition the polymer surface for plating as compared to plating techniques heretofore known in the art.

The surface conditioning step of the present invention utilizes a combination, in series of (a) an acid chromate etch and (b) an HF treatment. The specific sequence of these two operations is not critical. Accordingly, the filled plastic article can be treated with the acid chromate etch followed by the HF treatment or conversely by the HF treatment followed by the acid chromate etch. To avoid contamination of the various treating agents the plastic article should be rinsed after each separate treatment.

The term "HF treatment" as used herein and in the claims is intended to cover any treatment whereby the surface of the plastic article is contacted with hydrogen fluoride. For convenience, aqueous solutions of hydrofluoric acid or acid fluoride salts are employed in effect-

ing the treating of the surface of the plastic article with hydrogen fluoride. Examples of suitable acid salts are those of the formula $MF_x \cdot (HF)_x$ wherein M is the ammonium ion or a metal such as the alkali metals, alkaline earth metals, and the like and x is the valence of M. Such salts include NH_4HF_2 , $NaHF_2$, KHF_2 , CaH_2F_4 , and the like, including mixtures thereof. In addition, if desired, the HF treatment can be carried out in the vapor phase. The time required for successful treatment of the plastic article is dependent on the concentration of the HF in the treating zone. When utilizing an aqueous hydrofluoric acid solution, the concentration of the HF can be in the range of about 0.1 to saturation. When utilizing an aqueous solution containing a water-soluble acid fluoride salt, the concentration of the salt in the aqueous solution can likewise be in the range of about 0.1 weight percent to saturation, preferably 1.0 to saturation.

When carrying out a vapor phase HF treatment the minimum temperature will be determined by that required to vaporize the HF. Thus, a temperature of at least 67° F. is used when the process is operated at atmospheric pressure, with higher temperatures being used at higher treating pressures. The maximum temperature that can be used is at least 50° F. below the softening point of the plastic being treated. The HF treatment is ordinarily carried out utilizing an aqueous solution of the treating agent for a period of 0.1 to 10 minutes, and preferably 2 to 4 minutes.

The HF treatment is normally carried out at room temperature when utilizing an aqueous treating agent but can be carried out at temperatures up to essentially the boiling point of the solution. Temperatures above the normal boiling point can also be used provided the pressure is sufficient to maintain a liquid phase. Temperatures in the range of 30 to 200° F. are suitable for the aqueous systems.

The "acid chromate etch" treatment is that conventionally employed in metal plating and is normally carried out at temperatures in the range of 75° F. 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 treating of olefin polymers in accordance with this invention a treating time of 2 to 4 minutes is preferred.

The acid chromate etch solution is usually formed by the addition of a chromate salt or CrO_3 to a strong acid such as sulfuric acid or a sulfuric acid-phosphoric acid mixture. Typical of such a solution is that obtained by mixing the following:

- (1) Concentrated H_2SO_4 (238 ml.) saturated with K_2CrO_7 at 80° F.,
- (2) H_2O (262 ml.) saturated with CrO_3 at 80° F., and
- (3) H_2O to make a total of 1100 ml.

The siliceous fillers which are utilized in the polymer are generally those having a particle size of less than 50 microns and preferably less than 10 microns.

The filler is utilized in an amount in the range of 1-60, preferably 1-30 weight percent based upon the total weight of filled plastic and filler. All percentages recited hereinafter are on this basis. By "filled" plastic is meant that portion of a plastic molding into which the filler has been incorporated. The filler or mixtures thereof can be incorporated into the plastic by any known technique using the known milling and blending equipment, such as a Banbury mixer, a Brabender Plastograph, and the like.

Examples of suitable siliceous fillers are the synthetic silicas and hydrated silicas, and naturally-occurring minerals having a high—i.e., greater than about 70 weight percent—silica content, such as pumice, diatomaceous earth, and the like, including mixtures thereof.

As indicated, it would be highly desirable in the electroplating of a plastic article to be able to utilize conven-

chromate etch in the process of the invention. The following results were obtained:

Sample	SiO ₂ , wt. percent	Acid chromate etch		HF treatment		Total treating time min.	Adhesion lb./in.
		Time, min.	Temp., ° F.	Time, min.	Temp., ° F.		
1-----	10	2	155	2	80	4	6.0
2-----	10	2	155	5	80	7	13.0
3 (control)-----	10	5	155	None		5	<1
4-----	20	2	155	2	80	4	28.0
5-----	20	2	155	5	80	7	13.0
6 (control)-----	20	5	155	None		5	<1

* Amorphous polypropylene was determined by the following xylenes solubility test: 0.95 g. of polymer was mixed with 95 ml. mixed xylenes, heated for 15 minutes at 285° F., cooled, and centrifuged. The solvent was evaporated from a 25-ml. aliquot of the supernatant liquid, the residue was weighed, and the weight was multiplied by 400.

EXAMPLE VI

A series of plating tests was carried out as in Example V utilizing a similar polypropylene having a melt flow of 12.4 dg./min. and an amorphous content of about 19 weight percent. The following results were obtained:

Sample	SiO ₂ , wt. percent	Acid chromate etch		HF treatment		Total treating time min.	Adhesion lb./in.
		Time, min.	Temp., ° F.	Time, min.	Temp., ° F.		
1-----	10	2	155	2	80	4	17.0
2-----	10	5	155	2	80	7	15.0
3 (control)-----	10	5	155	None		5	<1
4-----	20	2	155	2	80	4	30.0
5-----	20	5	155	2	80	7	12.0
6 (control)-----	20	5	155	None		5	<1
7 (control)-----	0	2	155	2	80	4	0.9
8 (control)-----	0	5	155	2	80	7	0.9

EXAMPLE VII

A series of plating tests was carried out utilizing an ethylene/hexene-1 copolymer containing about 98 weight percent ethylene and 2 weight percent hexene-1 and having a density of 0.949 g./cc. and a melt index (ASTM D-1238-62T, Condition E) of about 0.3 dg./min. blended with 20 weight percent silica. Conventional electroplating techniques, as described above, were used except that the filled polymer was treated in a 50 weight percent aqueous HF bath following the acid chromate etch in the process of the invention. The following results were obtained:

Sample	Acid chromate etch		HF treatment		Total treating time, min.	Adhesion, lb./in.
	Time, min.	Temp., ° F.	Time, min.	Temp., ° F.		
1-----	0.5	155	0.5	80	1	6.0
2-----	1	155	1	80	2	10.0
3-----	2	155	2	80	4	10.0
4-----	4	155	4	80	8	7.0
5 (control)-----	4	155	None		4	<1

EXAMPLE VIII

A series of plating tests was carried out utilizing a polymer blend containing 80 weight percent of a polypropylene having a density of 0.905 g./cc. and a melt flow of about 4 dg./min., 10 weight percent of a polyethylene having a density of 0.960 g./cc. and a melt index of 0.1 dg./min., and 10 weight percent of an ethylene/propylene

copolymer containing about 43 weight percent ethylene and 57 weight percent propylene and having a Mooney

viscosity (ML-4 at 212° F., ASTM D-1646-63) of 45, blended with 20 weight percent silica. Conventional electroplating techniques, as described above, were used except that the filled polymer was treated in a 50 weight percent aqueous HF bath, following the acid chromate

etch in the process of the invention. The following results were obtained:

Sample	Acid chromate etch		HF treatment		Total treating time, min.	Adhesion, lb./in.
	Time, min.	Temp., ° F.	Time, min.	Temp., ° F.		
1-----	0.5	155	0.5	80	1	4.0
2-----	1	155	1	80	2	4.0
3-----	2	155	2	80	4	7.0
4-----	4	155	4	80	8	7.0
5 (control)-----	4	155	None		4	<1

EXAMPLE IX

A series of plating tests was carried out utilizing a polyethylene having a melt index of 5 dg./min. and a density of 0.960 g./cc. blended with 20 weight percent silica. Conventional electroplating techniques, as described above, were used except that the filled polymer was treated in a 50 weight percent aqueous HF bath following the acid chromate etch in the process of the invention. The following results were obtained:

Sample	Acid chromate etch		HF treatment		Total treating time, min.	Adhesion, lb./in.
	Time, min.	Temp., ° F.	Time, min.	Temp., ° F.		
1-----	2	155	2	80	4	8.6
2-----	2	155	5	80	7	8.0
3 (control)-----	4	155	None		4	<1

EXAMPLE X

A series of plating tests was carried out utilizing portions of the same filled polymer used in Example I. Con-

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ventional electroplating techniques, as described above, were used except that the filled polymer was treated in a 50 weight percent aqueous HF bath before the acid chromate etch in the process of the invention. The following results were obtained:

Sample	Acid chromate etch		HF treatment		Total treating time, min.	Adhesion, lb./in.
	Time, min.	Temp., ° F.	Time, min.	Temp., ° F.		
1-----	1	80	1	155	2	4.5
2-----	2	80	2	155	4	2.7
3-----	4	80	4	155	8	5.6
4 (control)...	None		4	155	4	<1

EXAMPLE XI

A series of plating tests was carried out utilizing portions of the same filled polymer used in Example I. Conventional electroplating techniques, as described above, were used except that the filled polymer was treated with HF vapor following the acid chromate etch in the process of the invention. The following results were obtained:

Sample	Acid chromate etch		HF treatment		Total treating time, min.	Adhesion, lb./in.
	Time, min.	Temp., ° F.	Time, min.	Temp., ° F.		
1-----	0.5	155	0.5	80	1	9.0
2-----	1	155	1	80	2	9.0
3-----	2	155	2	80	4	8.0
4-----	4	155	4	80	8	12.0
5 (control)...	4	155	None		4	<1

In Examples I-X electroplating steps (7b) and (8b) were used—i.e., a nickel electroless step was followed by a nickel strike. In Example XI, electroplating steps (7a) and (8a) were used—i.e., a copper electroless step was followed by a copper strike.

EXAMPLE XII

A further series of plating tests was carried out utilizing portions of an ethylene/propylene copolymer (Marlex 9600) containing 3 weight percent ethylene and having a melt flow of 4.2 dg./min. and a density of 0.898 g./cc. blended with 20% silica (HiSil404). Conventional electroplating techniques, as described above, were used, except the filled polymer was (1) treated for 2 minutes at 155° F. with an acid chromate etch solution consisting of 283 ml. water, 45 g. chromium trioxide, 918 ml. sulfuric acid (96%), 300 ml. phosphoric (85%) and 0.2 gram wetting agent and thereafter (2) treated with an aqueous HF or ammonium bifluoride (NH_4HF_2) bath at an HF or ammonium bifluoride concentration as indicated below. Adhesion was determined following the electroplating of a nickel strike and bright copper (Step 10 supra). The following results were obtained.

Run No.	Time, etch, step 2, min.	Concentration (wt., percent)	Adhesion, lbs./in.
1-----	0	0-----	(1)
2-----	2	25 NH_4HF_2 -----	9.0-9.4
3-----	2	10 NH_4HF_2 -----	20
4-----	8	10 NH_4HF_2 -----	25
5-----	2	5 NH_4HF_2 -----	(2)
6-----	8	5 NH_4HF_2 -----	(2)
7-----	2	2 NH_4HF_2 -----	12.0-14.4
8-----	10	2 NH_4HF_2 -----	21.0-21.0
9-----	10	1 NH_4HF_2 -----	6.6-6.8
10-----	2	0.1 NH_4HF_2 -----	2.6
11-----	8	0.1 NH_4HF_2 -----	2.8-3.8
12-----	2	5 HF-----	22.8-20.0

¹ Would not plate.

² Metal broke.

EXAMPLE XIII

A further series of plating tests was carried out utilizing portions of the same polymer and same silica filler used in Example XII. Fifty parts by weight of polymer were blended with 50 parts by weight of filler in a Brabender Plastograph at 195° C. for six minutes in a nitrogen atmosphere. Compression-molded samples were

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plated in the same manner as in Example XII using a portion of the same acid chromate etch solution at the same temperature (155° F.) in etch step (1), and using an aqueous solution containing 25 weight percent ammonium bifluoride at the same temperature used in Example XII (room temperature) for two minutes in etch step (2). Adhesion was determined in the same manner as in Example XII. The following results were obtained:

Run No.:	Time, etch, step 1, min.	Adhesion, lb./in.
1-----	1	6.0
2-----	2	7.0
3-----	3	6.8
4-----	4	6.4

The above clearly demonstrates that substantially improved adhesion is achieved for the metal platings when the combination etch system is employed.

From the foregoing examples it can be seen that utilization of the combination treatment consisting of an acid chromate etch and an HF treatment for the conditioning of a moldable plastic article containing a siliceous filler therein results in the obtaining of a metal plated product having improved adhesion.

In addition, the examples clearly demonstrate that utilization of the conditioning treatment of the present invention permits the satisfactory plating of a plastic 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 claim:

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

- (1) incorporating a siliceous filler into said plastic;
- (2) molding the resulting composition of plastic and filler;
- (3) conditioning the molded plastic product of step (2) by contacting with a combination, in series, of (a) an acid chromate etch and (b) an HF treatment;
- (4) preplating the resulting conditioned product of step (3) with an electrolessly platable metal; and
- (5) electroplating the preplated product of step (4) with a final finish to obtain a metal-plated plastic product.

2. A process according to claim 1 wherein the molded product of step (2) is washed prior to conditioning with the combination treatment of step (3).

3. A process according to claim 1 wherein the molded product of step (2) is conditioned by contacting first with an acid chromate etch (a) and then with the HF treatment (b).

4. A process according to claim 1 wherein the molded product of step (2) is conditioned by first carrying out the HF treatment (b) followed by the acid chromate etch (a).

5. A process according to claim 1 wherein said plastic is an olefin polymer.

6. A process according to claim 1 wherein said siliceous filler is present in an amount in the range of 1 to 60 weight percent.

7. The product of the process of claim 1.

8. A process according to claim 1 wherein said acid chromate etch is carried out utilizing a mixture of phosphoric acid and sulfuric acid.

9. A process for conditioning a molded plastic product having a siliceous filler incorporated therein so as to render same susceptible to electroplating which comprises treating said molded plastic product with a combination in series of (a) an acid chromate etch and (b) an HF treatment.

10. A process according to claim 9 wherein said molded plastic product is washed prior to conditioning.

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11. A process according to claim 9 wherein said molded product is conditioned by first treating with (a) an acid chromate etch and (b) an HF treatment.

12. A process according to claim 9 wherein said molded product is conditioned by treating with (b) an HF treatment and then (a) an acid chromate etch.

13. A process according to claim 9 wherein said plastic is an olefin polymer.

14. The conditioned molded plastic product of the process of claim 9.

15. A process for electrolessly preplating a moldable plastic which comprises the steps of:

- (1) forming a composition of said plastic having a siliceous filler therein;
- (2) molding the resulting siliceous filler containing plastic composition;
- (3) conditioning the molded product by treating, in series, with (a) an acid chromate etch, and (b) an HF treatment; and
- (4) thereafter preplating the resulting conditioned molded plastic product with an electrolessly platable metal.

16. A process according to claim 15 wherein the molded product of step (2) is washed prior to conditioning.

17. A process according to claim 15 wherein said molded plastic product is conditioned by first treating with (a) an acid chromate etch and then (b) an HF treatment.

18. A process according to claim 15 wherein said molded plastic product is conditioned by first treating with (b) an HF treatment and then (a) an acid chromate etch.

19. The electrolessly preplated plastic product of the process of claim 15.

20. The process of claim 15 wherein said plastic is an olefin polymer.

21. A process for preplating a filled plastic which comprises the steps of:

- (1) conditioning a molded product of said filled plastic having a siliceous filler therein by treating with a combination in series of (a) an acid chromate etch and (b) an HF treatment and
- (2) thereafter preplating the resulting conditioned product with an electrolessly platable metal.

22. A process according to claim 21 wherein said molded product is washed prior to conditioning.

23. A process according to claim 21 wherein said molded product is conditioned by contacting first with (a) an acid chromate etch and then (b) an HF treatment.

24. A process according to claim 21 wherein said molded product is conditioned by contacting first with (b) an HF treatment and then (a) an acid chromate etch.

25. The process of claim 21 wherein said plastic is an olefin polymer.

26. A process for electroplating a moldable plastic which comprises the steps of:

- (1) conditioning a preformed product of said plastic having 1 to 30 weight percent of a siliceous filler therein by treating said product with a combination, in series, of (a) an acid chromate etch, and (b) an HF treatment;

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(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 plastic product.

27. A process according to claim 26 wherein said molded product is washed prior to conditioning.

28. A process according to claim 26 wherein said molded product is conditioned by treating first with (a) an acid chromate etch and then (b) an HF treatment.

29. A process according to claim 26 wherein said molded product is conditioned by treating first with (b) an HF treatment and then (a) an acid chromate etch.

30. A process according to claim 26 wherein said plastic is an olefin polymer.

31. A process for conditioning a molded article formed of a moldable plastic having a siliceous filler therein which comprises contacting the surface of said article with an HF treating agent.

32. A process according to claim 31 wherein said HF treating agent is selected from the group consisting of aqueous hydrofluoric acid having a concentration of at least 0.1 weight percent HF and an aqueous solution of a water soluble acid fluoride salt having a concentration of at least 0.1 weight percent salt therein.

33. A process according to claim 31 wherein said plastic is an olefin polymer.

34. The HF-treated product of the process of claim 31.

35. A process for electroplating a plastic containing a siliceous filler which comprises conditioning said plastic by contacting with a combination, in series, of (a) an acid chromate etch and (b) an HF treatment and thereafter plating the resulting conditioned plastic by first preplating with an electrolessly platable metal and thereafter electroplating the resulting preplated plastic.

36. A process for conditioning a plastic having a siliceous filler incorporated therein so as to render said plastic susceptible to electroplating which comprises treating said plastic product with an HF treatment.

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