

May 18, 1971

TOSHIHIKO KURODA ET AL

3,579,428

METHOD OF MANUFACTURING PLATED POLYPROPYLENE SHAPED ARTICLES

Filed Sept. 23, 1968

FIG. 1

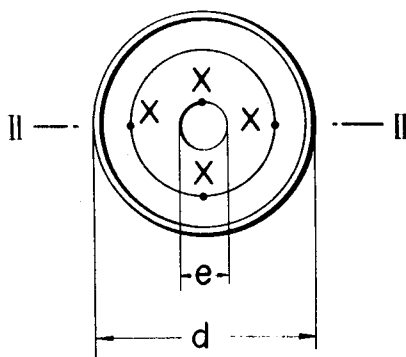


FIG. 2

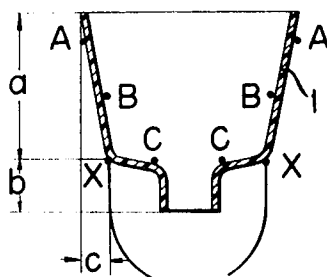
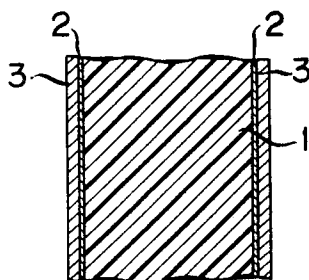


FIG. 3



1

3,579,428

**METHOD OF MANUFACTURING PLATED POLY-
PROPYLENE SHAPED ARTICLES**

Toshihiko Kuroda, Sotao Sutani, Haruo Nitta, Rikio Takahashi, and Sadao Saito, Yokkaichi-shi, Japan, assignors to Mitsubishi Petrochemical Co., Ltd., Tokyo, Japan

Filed Sept. 23, 1968, Ser. No. 761,767

Claims priority, application Japan, Sept. 30, 1967, 42/62,648; June 17, 1968, 43/41,335

Int. Cl. C23b 5/60, 3/02

U.S. Cl. 204—30

1 Claim

ABSTRACT OF THE DISCLOSURE

Method of manufacturing a plated polypropylene which comprises subjecting a polypropylene composition containing 20–50% by weight of an inorganic powder having an average particle size of less than 20 microns based on the total weight of said composition to a treatment with an acid solution containing an oxidizing agent and further subjecting thus treated polypropylene composition to a plating process.

BACKGROUND OF THE INVENTION**(1) Field of the invention**

This invention relates to a method of manufacturing shaped articles of polypropylene having a plated metal layer strongly adhered thereto.

(2) Description of the prior art

The technique of manufacturing shaped articles of synthetic resins having a metallic appearance by the electroplating thereof has been known heretofore with regard to ABS resins, viz. acrylonitrile/butadiene/styrene copolymers, and polyacetal resins.

The procedures for electroplating these synthetic resins generally comprises combinations of the following steps, i.e. (1) degreasing of the surface to be plated, (2) etching of thus degreased surface, (3) sensitizing process, (4) activating process, (5) chemical plating process for rendering the surface an electroconductivity and (6) electroplating process.

The typical prior art process for electroplating synthetic resins known heretofore comprises:

(1) washing a synthetic resin substrate to be electroplated sufficiently with an organic or inorganic solvent such as alkali, trichloroethylene or alcohols to remove greases and dirt from the surface thereof,

(2) immersing thus washed substrate into an etching solution prepared by dissolving a strong oxidizing agent such as chromic anhydride or potassium permanganate into a strong acid such as sulfuric acid, nitric acid or phosphoric acid, at a temperature ranging 50–60° C., for 10–30 minutes for oxidizing the surface of the synthetic resin so that a plating solution may be affiliated sufficiently therewith,

(3) activating the synthetic resin substrate by immersing the same into a hydrochloric acid solution of stannous chloride followed by washing with water, and further into a hydrochloric solution of palladium chloride followed by washing with water,

(4) rendering the synthetic resin substrate an electroconductivity by precipitating copper or nickel from a reducing reaction mixture consisting of copper sulfate and formalin, or, nickel salt and sodium phosphite, respectively,

(5) and electroplating the resulting electroconductive synthetic resin substrate with the desired metals such as

2

nickel, copper, chromium or the like according to conventional electroplating methods.

In electroplating synthetic resins, it is most important that a metal precipitated in the chemical plating process is intimately adhered to the surface of the synthetic resin substrate.

Unsatisfactory adhesion therebetween leads to inconveniences such as scabbing of the plated metal layer, viz. swollen layer over a certain area of the plated surface which tends to be easily peeled off, during the electroplating operation or peeling off of the plated metal layer when applying heat in the electroplating process or thereafter. Thus, whether an electroplating of a synthetic resin is feasible or not depends upon whether or not a metal precipitated in the chemical plating process is securely adhered to the surface of the substrate.

In ABS resins which are often electroplated, it is considered that the butadiene portion thereof reacts with an oxidizing agent to form a surface polarity by the etching treatment as well as the butadiene portion is dissolved to give a finely coarsed surface thereby increasing the contacting surface area with a result in the enhancement of adhesive strength of the plated metal layer to the substrate surface.

Thus, it has been considered impossible to apply a chemical plating, consequently, an electroplating on a material in which the surface polarity as well as a coarse surface are difficultly produced and formed. For example, a polypropylene which is an excellent material for producing shaped articles has been considered almost impossible to apply a chemical plating due to its complete lack of reactive functionalities from the molecular structure.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide a method of manufacturing polypropylene shaped articles having plated metal layers strongly adhered to the surfaces thereof, which has been considered impossible heretofore.

The present inventors have found that the object mentioned above can be accomplished by subjecting a polypropylene into which an inorganic powder is intimately incorporated to the plating treatment for plating a synthetic resin substrate described above.

More specifically, the method of this invention comprises subjecting a shaped article obtained from a polypropylene composition containing 20–50% by weight of an inorganic powder having an average particle size less than 20 microns as a filler based on the weight of said polypropylene composition to degreasing and at least a treatment selected from etching, sensitizing and activating treatments, and further subjecting thus treated polypropylene shaped article to a chemical plating followed by an electroplating, if required, to produce a polypropylene shaped article having a plated metal layer securely adhered to the surface thereof.

The fillers which may be used in this invention have an average particle size less than 20 microns, preferably less than 5 microns, and most preferably less than 1 micron. Preferable are those having a coarse particle surface, uniform particle size free from exceptionally large ones, and good dispersibility. Also, those containing less water and other volatile components are preferable.

The inorganic powders referred to in this invention specifically include kieselguhr, calcium carbonate, barium carbonate, aluminum oxide, titanium oxide, sulfates of metals of Group II–A of the Periodic Table of the Elements such as barium sulfate, magnesium sulfate, strontium sulfate and calcium sulfate, and mixtures thereof.

It is an essential requisite of this invention that these fillers used have an average particle size less than 20 microns. The average particle size exceeding 20 microns leads to uneven precipitation of metals due to unsatisfactory dis-

3

persion of fillers into the polypropylene composition, or, results in coarse surface of the shaped article which gives rise to an irregular reflection of light when electroplating is applied, and the commercial value of the product shaped article is drastically degraded.

Among those inorganic powders exemplified above, most preferable is barium sulfate having an average particle size of less than 1 micron.

The amount of fillers to be incorporated in this invention ranges 20–50% by weight based on the total weight of the resulting composition. If the amount is less than 20% by weight on the basis set forth above, the adhesive strength afforded thereby is unsatisfactory so that the effect of this invention is unexpected, while the amount exceeding 50% by weight leads to a coarse surface which causes an irregular reflection of light when electroplating is applied, thus, the appearance of the product shaped articles is greatly degraded, though the adhesive strength may be enhanced.

Polypropylene resins into which those fillers exemplified above are incorporated and kneaded therewith in this invention include crystalline homopolymers or copolymers of propylene or polymer compositions substantially comprising a polypropylene resin such as polymer mixtures consisting of a major portion of crystalline homopolymers or copolymers of propylene and a minor portion of other synthetic resins.

No particular restriction is imposed on the method and apparatus adopted in mixing the polypropylene and fillers together in this invention so long as there is obtained a polypropylene composition in which the filler is uniformly dispersed. The polypropylene thus compounded with the fillers according to this invention is shaped into any desired configuration.

While the shaped articles of any desired configuration may be electroplated in accordance with this invention, the effect and advantage of the method of this invention may be fully enjoyed when electroplating polypropylene shaped articles having complicated configurations.

The shaped article of polypropylene thus compounded with the filler, after having degreased the surface thereof, is then subjected to an etching treatment by immersing the same into an acid solution containing a strong oxidizing agent. The treating conditions include, in general, a treating temperature of 50–90° C. and a treating time of 10–60 minutes.

The polypropylene thus pre-treated, after having been subjected to sensitizing and activating treatments, if required, is then subjected to a chemical plating process followed by an electroplating process. The electroplating process may be omitted depending upon need.

The plated metal layer formed on the surface of the polypropylene by the chemical plating and electroplating according to the method of this invention has an adhesive strength ranging 2.7–5.4 kg./cm. (15–30 lbs./in.) or higher, and, apparently, the adhesive strength of the plated layer afforded by this invention is higher than that obtained with regard to ABS resins heretofore which normally ranges 0.9–1.8 kg./cm. (5–10 lbs./in.).

The adhesive strengths referred to above are measured in the following manner:

On the surface of a plated test piece are carved two lines in a width of 1 cm. with a knife and the edge of thus hatched surface layer is lifted up with a tip of knife. Then, the surface layer is forcibly lifted upward in a right angle with respect to the plane of the surface at a rate of 500 mm./min., and the strength required to peel off the surface layer is measured as an adhesive strength.

While it should not be construed that the present invention is bound by any particular theory, the reason for the increment in the adhesive strength of the plated layer afforded by this invention may be explained as follows:

Observation of the shaped article of polypropylene compounded with the filler according to this invention and subjected to the etching treatment using an electron micro-

4

scope reveals that the filler on the surface layer as well as polypropylene therearound are oxidized and dissolved into the etching solution forming an unevenness of about 1–10 microns on the surface layer.

Furthermore, an infrared absorption spectrographic examination shows the presence of —OH and —COOH groups having affinities with the plating solution on the etched surface of the polypropylene resin.

Hence, it is presumed that the presence of the unevenness and the polar groups on the surface of the polypropylene according to this invention brings about the increment in the adhesive strength of the plated layer formed thereon.

Among those inorganic powders exemplified hereinbefore, the use of kieselguhr considerably enhances the adhesive strength of the plated layer to the shaped article because the kieselguhr is capable of highly roughening the surface thereof, and the use of the sulfates of metals of Group II-A of the Periodic Table of the Elements referred to hereinbefore is most preferable since there is afforded an excellent surface appearance of the resulting plated shaped article.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples will serve to illustrate this invention more fully and practically.

It should not be construed, however, that these examples will restrict this invention as they are given merely by way of illustration.

EXAMPLE 1

Polypropylene and kieselguhr having a particle size ranging 1–10 microns were compounded in such a manner that the resulting composition contains 10, 20, 30, 40 and 50% by weight of kieselguhr based on the total weight of the resulting composition, respectively, then, kneaded in a Banbury mixer for 10–30 minutes and injection-moulded into a sheet of 10 cm. square having a thicknesses of 2 mm.

The surface of the sheet thus obtained was washed with a 50% aqueous NaOH solution followed by sufficient washing with water.

The sheet thus washed was immersed into an acid solution consisting of 500 ml. of a 95% sulfuric acid containing 30 g./l. of chromic anhydride and 500 ml. of water at 65° C. for 20 minutes followed by washing.

The sheet was further immersed into an aqueous solution containing 40 g./l. of stannous chloride and 10 ml./l. of hydrochloric acid for 10 minutes followed by sufficient washing with water.

The sheet was still further immersed into an aqueous solution containing 1 g./l. of palladium chloride and 5 ml./l. of hydrochloric acid followed by sufficient washing with water.

Next, the non-electrode plating (chemical plating) process was carried out. The plating solution employed herein consisted of a solution A and a solution B having the following composition, respectively:

Solution A

	G./l.
Rochelle salt -----	200
Caustic soda -----	100
Copper sulfate -----	60
Sodium bicarbonate -----	60

Solution B

Formalin—37%.

There were mixed 5 volumes of the solution A and a volume of the solution B and into the resulting mixed solution thus prepared was immersed the polypropylene sheet mentioned above at normal temperature for 20 minutes of precipitate a chemical copper on the surface thereof in a thickness of 0.5–1.0 micron.

5

After the sheet thus chemically copper-plated was washed with water, the electroplating of the sheet was carried out using a plating solution containing 200 g./l. of copper sulfate and 50 g./l. of sulfuric acid having a specific gravity of 1.7 and employing a copper plate as an anode and the chemically copper-plated polypropylene sheet as a cathode with an electric current of 0.5 A. for the initial 5 minutes and of 2 A. for the following 20 minutes. Thus, the thickness of the plated copper layer was increased to about 25–30 microns.

The adhesive strength of the resulting plated copper layer was evaluated, respectively, as follows:

TABLE 1

Kieselguhr content (percent)	Adhesive strength (kg./cm.-lb./in.)	Heat cycle test, ¹ 80° C. (15 min.) → 30° C. (15 min.)	Appearance
0	0.05–0.3	-----	Scabbed.
10	0.2–1	-----	Do.
20	0.9–5	Stable for more than 10 cycles.	Good.
30	3.6–20	Stable for more than 30 cycles.	Do.
40	4.5–25	do	Do.
50	4.5–25	do	Fair

¹ A test cycle including a heating at 80° C. for 15 minutes and a cooling to 30° C. for 15 minutes was repeated consecutively and the surface conditions were examined by naked eyes.

EXAMPLE 2

Polypropylene and anhydrous calcium carbonate were compounded in such a manner that the resulting composition contains 10, 20, 30, 40 and 50% by weight of anhydrous calcium carbonate based on the total weight of the resulting composition, respectively, then, kneaded in a Banbury mixer for 30 minutes and injection-moulded into a sheet of 10 cm. square having a thickness of 2 mm.

The sheet thus obtained was copper-plated according to the same procedures as described in Example 1 and the adhesive strength of the plated copper layer was evaluated, respectively, with the results as shown in the following Table 2:

TABLE 2

Calcium carbonate content (percent)	Adhesive strength (kg./cm.-lb./in.)	Heat cycle test, ¹ 80° C. (15 min.) → 30° C. (15 min.)	Appearance
0	0.05–0.3	-----	Scabbed.
10	0.1–0.6	-----	Do.
20	0.6–3.5	Stable for more than 10 cycles.	Good.
30	2.5–14	Stable for more than 30 cycles.	Do.
40	3.1–17.5	do	Do.
50	3.2–18.0	do	Fair.

¹ Same as shown in Table 1.

EXAMPLE 3

A polypropylene powder having a melt index of 20, an average particle size of 100 microns and a bulk density of 0.45, and barium sulfate BaSO₄ having an average particle size of 0.6 micron and containing less than 0.1% by weight of volatile component were compounded in such a manner that the resulting composition contains 10, 20, 25, 30, 40, 50, 60 and 70% by weight of barium sulfate based on the total weight of the resulting composition, respectively, in a super-mixer for 3 minutes, then, kneaded and extruded by a vent-type extruder and pelletized to give a pellet.

The pellet thus obtained was injection-moulded into a shaped article 1 as shown in the accompanying drawings, FIGS. 1 and 2, in which:

a—8 cm.

b—3 cm.

c—1 cm.

d—15 cm.

Thickness—2.2 mm.

Referring to the accompanying drawings, FIG. 1 shows a plan view of the polypropylene shaped article thus ob-

6

tained. In this drawing, the contacts X which are located on the lower surface and not to be seen are also shown.

FIG. 2 shows a sectional side view of FIG. 1 along the line II—II, and FIG. 3 is a partly enlarged view of FIG. 2.

In FIGS. 2 and 3, numeral 1 designates a shaped article of polypropylene compounded with a filler having a particle size of less than 1 micron, numeral 2 designates a chemically plated layer and numeral 3 designates an electroplated layer.

The surface of the shaped article thus obtained was washed sufficiently with a 50% aqueous NaOH and subsequently with water. The washed shaped article was then immersed into an acid solution consisting of 500 ml. of a 95% sulfuric acid containing 30 g./l. of chromic acid anhydride and 500 ml. of water at 65° C. for 20 minutes followed by washing with water.

The shaped article was further immersed into an aqueous solution containing 40 g./l. of stannous chloride and 10 ml./l. of hydrochloric acid for 10 minutes followed by sufficient washing with water.

The shaped article was still further immersed into an aqueous solution containing 1 g./l. of palladium chloride and 5 ml./l. of hydrochloric acid for 10 minutes followed by sufficient washing with water.

Next, the non-electrode plating (chemical plating) process was carried out. The plating solution employed herein consisted of a solution "A" and a solution "B," having the following composition, respectively:

Solution A

	G./l.
Rochelle salt	200
Caustic soda	100
Copper sulfate	60
Sodium bicarbonate	60

Solution B

	Percent
Formalin	37

There were mixed 5 volumes of the solution A and a volume of the solution B and into the resulting mixed solution was immersed the polypropylene shaped article at normal temperature for 20 minutes to precipitate a chemical copper on the surface thereof in a thickness of 0.5–1 micron, followed by washing with water.

The shaped article thus chemically copper-plated was subjected to copper pyrophosphate plating, copper sulfate plating, bright nickel plating and bright chrome plating, respectively, according to conventional electroplating method.

The electroplating conditions were as follows (referring to FIG. 2, the plating electrode was located in upward direction and the contact points were shown by X):

(1) Copper pyrophosphate plating

(a) Plating solution composition:

Ingredients:	G./l. of solution
Copper pyrophosphate·dihydrate	15
Anhydrous copper pyrophosphate	120
Potassium oxalate·monohydrate	10
Aqueous ammonia	10

(b) Current density: 4 A./dm.²

(c) Time: 2 minutes

(d) Temperature: 25° C.

(2) Copper sulfate plating

(a) Plating solution composition:

Ingredients:	G./l. of solution
Copper sulfate·pentahydrate	250
Concentrated sulfuric acid	50

(b) Current density: 4 A./dm.²

(c) Time: 30 minutes

(d) Temperature: 25° C.

7

(3) Bright nickel plating

(a) Plating solution composition:

Ingredients:	G./l. of solution	
Nickelous sulfate·heptahydrate	300	5
Nickelous chloride·hexahydrate	90	
Boric acid	50	

(b) Current density: 4 A./dm.²

(c) Time: 10 minutes

(d) Temperature: 55° C.

(4) Bright nickel plating

(a) Plating solution composition:

Ingredients:	G./l. of solution	
Chromic acid anhydride (CrO ₃)	250	15
Concentrated sulfuric acid	2.5	

(b) Current density: 20 A./dm.²

(c) Time: 1.5 minutes

(d) Temperature: 45° C.

RESULTS

(1) Adhesive strengths of the plated metal layers

The adhesive strengths measured at points A in vertical direction with respect to the surface plane were as follows: 25

BaSO ₄ (percent by weight):	Adhesive strength (kg./cm.)	Remarks
10.....	0.3	Adhesion unsatisfactory.
20.....	0.8	Practicable.
25.....	1.0	Do.
30.....	1.5	Do.
40.....	2.0	Do.
50.....	1.8	Do.
60.....	1.5	Do.
70.....	0.5	Appearance unsatisfactory.

(2) Thicknesses and appearances of plated metal layers

Among the practicable samples using 20-50% by weight of BaSO₄ mentioned above, the luster and thickness of 40

8

the plated layer were measured at points A, B and C with regard to a sample piece obtained by using 40% by weight of BaSO₄.

The results were as follows:

Measuring point.....	A	B	C
Thickness (microns).....	35	31	29
Appearance.....	(1)	(1)	(1)

¹ Smooth metallic luster.

As noted above, there were obtained substantially uniform thicknesses at these points A, B and C, and the appearances were excellent at respective points.

We claim:

1. A method of manufacturing a plated polypropylene which comprises subjecting a polypropylene composition containing 20 to 50% by weight of barium sulfate having an average particle size of less than one micron based on the total weight of said composition to a treatment with an acid solution containing an oxidizing agent and further subjecting the thus treated polypropylene composition to a plating process. 20

References Cited

UNITED STATES PATENTS

2,663,663	12/1953	Weltman et al.	204—30
3,305,460	2/1967	Lacy	204—30
3,429,788	2/1969	Parstorfer	204—30
3,466,232	9/1969	Francis et al.	204—20

OTHER REFERENCES

Handbook of Physics and Chemistry, pp. 540 and 541.

HOWARD S. WILLIAMS, Primary Examiner 35

T. TUFARIELLO, Assistant Examiner

U.S. Cl. X.R.

117—47A; 156—2; 204—20