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3,682,786

METHOD OF TREATING PLASTIC SUBSTRATES AND PROCESS FOR PLATING THEREON

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ABSTRACT OF THE DISCLOSURE

Plastic substrates, such as polypropylene, ABS, etc. are plated with an adherent metal coating in a process which avoids completely the art-employed steps of etching in a chromic-sulfuric acid solution as well as the deposition of a thin coating of metal on the substrate from an electroless plating bath prior to the electrolytic plating operation. Plastic substrates are (1) treated with a solution or dispersion of sulfur in a suitable solvent, such as a trichloroethylene, (2) contacted with an aqueous solution of a cuprous salt; such as cuprous chloride, (3) optionally treated with an aqueous solution of palladium chloride and finally (4) electroplated to form a coating of the desired metal of the desired thickness.

This invention relates to a method for plating on plastic substrates, such as polypropylene, ABS, etc. In particular, this invention relates to a method in which plastic substrates prior to electroplating are pretreated by contacting the substrates with a solution of sulfur in a suitable solvent, and to a highly convenient plating process for non-conductive plastic objects in which the art-utilized step of electrolessly plating a thin coating of metal on the substrate prior to the electrolytic plating step is completely avoided.

Prior to this invention, in plating on plastics those in the art have utilized complicated, expensive processes embodying a multiplicity of steps in which the plastic substrates were, after precleaning if necessary, etched, sensitized, activated and then electrolessly plated before the plastic articles were finally ready for the electrolytic plating step in which a metal deposit of suitable thickness was developed over the electrolessly-formed coating. The sole function of the electroless plating step was to establish a thin, adherent conductive metal coating on the plastic substrate on which the desired metal could be electroplated to the desired thickness. Although the required metal thickness can be formed entirely by the electroless plating process, the cost of doing so is prohibitive and, in addition, the physical properties of such coatings are generally not satisfactory. As a practical measure, as much of the required metal thickness as possible is formed by electroplating.

In the electroless plating of a plastic substrate, the surface must be properly sensitized and/or activated prior to the chemical deposition if plated metal deposits of suitable thickness and adequate bonding strength are to be achieved. Further, the surface of the plastic substrate must first be cleaned to remove oil, grease or other foreign materials from the surface following which the normally hydrophobic surface of plastics, such as butadiene-acrylonitrile-styrene (ABS), polyethylene, polypropylene, etc. must be treated to render them hydrophilic prior to the sensitization step. Thus, the first step in preparing a plastic substrate for subsequent electroless plating after the usual precleaning processes employed in the art, generally is to etch the surface with a suitable chemical etchant to prepare the surface for the reception of

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the sensitizing agent which may be, for example, stannous chloride or another stannous salt. Various proprietary etchant solutions are available for this purpose but one that is preferred consists of approximately 14% by weight chromic acid, 40% by weight sulfuric acid (66° Bé.), the balance being water. This solution is used at approximately 145° F. and the substrate is immersed in or otherwise contacted with it for a period of about 1 to about 10 minutes or more.

The etched substrate is then thoroughly rinsed in water, several times if necessary, and is then immersed in a reducing agent solution to lower excessive hexavalent chromium concentration on the surface after which it is again rinsed in cold water. In the next step, the substrate is immersed in a sensitizing solution which, preferably, is an aqueous solution of stannous chloride. The substrate surface to be plated is then contacted with a solution of the catalytic or activating metal in ionic condition and the metal is reduced in situ on the treated substrate surface following which the substrate is ready for the electroless plating step. This procedure is employed successfully in many plating-on-plastic applications. It is subject to a disadvantage that, in general, it often requires re-racking the articles being plated to avoid contamination through drag-in from preceding steps and rapid deterioration of the plating baths. An alternative activating method is also known which largely avoids this difficulty. In this method, the substrate surface is contacted directly with the solution in which the catalyst metal is already in reduced, metallic state in the form of fine colloidal or at least semi-colloidal particles as described in copending application of D'Ottavio, Ser. No. 654,307, filed June 28, 1967, now Pat. No. 3,532,518.

A number of other processes have been described in the art for converting the normally hydrophobic surfaces of plastic substrates to hydrophilic surfaces which are receptive to the sensitizing and/or the activating solutions. For example, in U.S. Pat. 2,970,078 polyethylene plastic surfaces are treated with a saturated aqueous solution of chromium trioxide to convert the hydrophobic surfaces to hydrophilic surfaces, and in U.S. 2,668,134 a similar process is described in which a saturated solution of sodium dichromate in concentrated sulfuric acid is utilized for the same purpose. In U.S. Pat. 3,317,330 substrates, such as polyethylene or polypropylene, are immersed for a few seconds in a bath consisting of concentrated sulfuric acid, water, potassium permanganate, chromic acid and a fluorochemical surfactant wetting agent. It has been found that plastic substrates, thus treated, are receptive to the sensitizing solution and after activation with a solution of a metallic ion, such as palladium chloride, they can be plated by the electroless method.

A complete commercial plating-on-plastic operation, as practiced in the art, is a complex process involving as previously pointed out, many separate operational steps including etching in a chromic-sulfuric acid solution and electroless plating. A typical operation of this type in which the electroless plating step is followed by an electrolytic plating step includes, after any precleaning of the plastic substrates which may be required, the following steps:

- (1) Etching the substrate surface with a suitable chromic-sulfuric acid etchant at 150° F. for five minutes.
- (2) Rinsing with cold water.
- (3) Immersing the plastic substrate in a reducing agent solution to lower excessive hexavalent chromium concentration on the surface of the plastic.
- (4) Rinsing with cold water.
- (5) Immersing the substrate in an acid stannous chloride-metal hydrosol such as the acid tin-palladium hydrosol disclosed in D'Ottavio application, Ser. No. 654,307,

filed June 28, 1967, now Pat. No. 3,532,518, in which the metal, such as palladium, catalyzes the deposition of the desired metal coating.

(6) Rinsing in cold water.

(7) Contacting the plastic substrate with an accelerator solution, such as a dilute solution of palladium chloride and hydrochloric acid.

(8) Rinsing in cold water.

(9) Electroless plating by immersing the plastic substrate in a solution containing copper, nickel or cobalt ions and a reducing agent.

(10) Rinsing in cold water.

(11) Electroplating the electroless plated metal surface to form a deposit of the desired composition and thickness.

Numerous attempts have been made in the art to provide processes which combine two or more of the above-mentioned precleaning, etching, reduction of hexavalent chromium concentration, sensitizing, and activating steps commonly employed in preparing a plastic substrate for electroless metal plating. However, prior to this invention no practical process for plating on plastic substrates existed in which electroless plating and chromic acid etching were not essential steps. For example, in U.S. Pat. 3,425,926 a process is described in which the precleaning, etching and sensitizing steps are combined. In this process a solution of a stannous compound, such as stannous chloride in a glycol ether is employed to treat plastic substrates at room temperature. The substrate, which may be ABS, is generally contacted with the stannous chloride-glycol ether solution in hydrochloric acid for about five minutes at room temperature following which it is rinsed with water to remove the excess of the solution from the surface. During the rinsing step, the pH rises and the stannous chloride breaks down to stannous hydroxide or oxide. Activation of the surface is accomplished in a separate step by applying to the substrate a one percent solution of palladium chloride. After the excess palladium chloride solution is thoroughly rinsed off, there is applied to the clean, wet surface a solution of a copper salt, such as copper sulfate, containing sodium hydroxide, Rochelle salts and formaldehyde, thus forming a copper deposit.

The chromic acid-sulfuric acid etching step, which is utilized today in practically every commercial process for plating on plastic substrates, is especially troublesome and expensive. Among the many disadvantages of the use of a chromic-sulfuric etchant to prepare plastic substrates for reception of the sensitizer and/or activator prior to electroless deposition of copper, nickel, or cobalt, the following may be mentioned:

(1) The efficiency of the chromic acid-sulfuric acid etching solution drops off rapidly, necessitating frequent replacement of the expensive etching solution.

(2) The present practice of discarding the spent chromic-sulfuric acid bath and concurrent waste disposal problems are particularly expensive and time consuming.

(3) The frequent handling of large quantities of the hot, highly-corrosive and poisonous etching solutions and the filling and discharging of etchant tanks in a manufacturing process is hazardous to personnel since contact with the skin may result in severe burns.

(4) Cleaning of the etched parts to prevent carryover and subsequent poisoning of additional plating steps can create problems on the production line.

(5) Because of the high temperature employed (150° F.) and strong oxidizing power of the chromic-sulfuric acid solutions, the surfaces of the plastic articles which have been treated with the chromic acid-sulfuric acid etch are sometimes degraded and roughened.

It is a primary object of this invention to provide the art with a convenient, inexpensive process for plating on plastic substrates in which the chromic-sulfuric acid etching operation is eliminated.

Another important object of this invention is to pro-

vide a process for plating on plastic substrates in which an electroless plating step prior to electrolytic plating is not required.

Another object of this invention is to reduce the number of operating steps in preparing plastic substrates for electrolytic deposition of metals.

Another object of this invention is to reduce the investment required in equipment and to also reduce the labor cost involved in preparing plastic substrate for subsequent electrolytic plating.

Another important object of this invention is to provide a highly efficient plating process in which the metal coating deposited on the plastic substrate exhibits a high peel strength.

The process of this invention, by which a plastic substrate is plated with a metal, comprises in general, the following steps:

(a) contacting the plastic substrate with a sulfur-containing solvent solution,

(b) rinsing the thus-treated substrate in a solvent to remove any excess of the said solution and/or sulfur from the surface of the plastic substrate,

(c) immersing or otherwise contacting the treated plastic substrate in an aqueous solution of a cuprous salt,

(d) optionally contacting the treated substrate with an aqueous solution of a metal salt selected from the group consisting of silver, palladium, gold, and other precious metals,

(e) electroplating a metal coating of suitable thickness on the plastic substrate.

The present invention provides a highly efficient, simplified process for plating on plastic surfaces directly by the electrolytic process. No chromic acid etching step or electroless plating operation is required or employed in the process of this invention. Many of the difficulties and disadvantages of the complex prior art plating methods are eliminated entirely in practicing the plating process set forth in this application. Metal coatings deposited on plastic substrates in accordance with the novel process herein described exhibit excellent peel strength values.

During the treatment of the plastic substrate with the sulfur-containing solvent solution, the surface of the plastic substrate swells, and the sulfur-containing solvent solution is carried into the surface. On rinsing with a suitable solvent after the initial treatment with the sulfur-containing solution the excess of the sulfur-containing solution and/or sulfur is washed away from the surface and, in addition, the remaining sulfur is firmly trapped or bonded in the plastic surface.

By the process of this invention a wide variety of plastic substrates can be prepared for the deposition of adherent metal coatings including acrylonitrile-butadiene-styrene (ABS), polysulfones, polypropylenes, polystyrenes, polycarbonates, polyphenylene oxides, polyvinylchloride, phenolics, acrylics and the like.

TREATMENT WITH SULFUR-CONTAINING SOLVENTS

The sulfur-containing solvent solutions of this invention comprises sulfur dissolved in an organic solvent. Any organic solvent having a boiling point greater than 70° F. at atmospheric pressure which is capable of dissolving at least 1 gram of sulfur per liter at 70° F. and which will swell the surface of the plastic substrate can be utilized in preparing the solutions utilized in practicing this invention.

An especially useful group of organic solvents include the halogenated aliphatic hydrocarbon solvents having at least one halogen substituent selected from the group consisting of chlorine, bromine and iodine and having boiling points of not less than 70° F. at atmospheric pressure. Typical halogenated hydrocarbons suitable for preparing the sulfur-containing solutions include compounds having not more than five carbon atoms, such as methylene chloride, chloroform, carbon tetrachloride, ethylene

dichloride 1,1 - dichloroethylene, 1,2 - dichloroethylene, 1,1,1-trichloroethylene, 1,2,2-trichloroethane, propylene dichloride, 1,2-dichloroethylene, 1,3-trichloropropylene, 2,2-dichloropropylene, 1,2,3-trichloropropylene, 1,1,1,3-tetrachloropropylene 1,2,3-trichloropropane, butylene dichloride, 1,3-dichlorobutylene, 1,1,1,2-tetrachlorobutylene, 1,2,2-trichlorobutane, etc. and the corresponding bromine and iodine derivatives.

Other hydrocarbon solvents useful in preparing the sulfur-containing solvent solutions of this invention include benzene, toluene, xylene, terpenes, such as pinene, turpentine, etc., carbon disulfide, dioxane, olive oil and halogenated aromatic solvents such as chlorobenzene, 1,3-dichlorobenzene, 2,4-dichlorotoluene, 1,3,5-trichlorobenzene, chloroxylene, etc. and the corresponding bromine and iodine derivatives. Mixtures of the solvents mentioned above can be utilized.

In preparing the sulfur-containing solvent system employed in this invention, sulfur of any commercial grade is satisfactory. Usually, sulfur in finely-divided form is added with mixing to the solvent or mixture of solvents at a temperature of about 70° F. to about 180° F. and the mixing is continued until the sulfur has completely dissolved in the solvent. The concentration of the sulfur in the solvent is not critical although generally solutions containing from about 1 gram per liter to saturation are utilized. Preferably, the sulfur-containing solvent solution will contain from about 10 grams per liter to about 90 grams per liter of sulfur.

The plastic substrate is generally immersed in or otherwise contacted with the sulfur-containing solvent solution for a period of from about 15 seconds to about 20 minutes or more. The temperature employed in the treating process may be varied widely and usually will be from about 65° to about 200° F. and, preferably, will be from about 130° to about 175° F. depending upon the other processing conditions such as the sulfur concentration, particular solvent employed, the time of contacting, type of plastic substrate, etc.

SOLVENT RINSING

Generally, the step in which the excess sulfur is removed from the plastic substrate surface by rinsing in a suitable solvent is conducted at a temperature ranging from about 65° to about 110° F. and for a period of time ranging from about 5 seconds to about 60 seconds or more. The rinsing operation may be applied by spraying, dipping or by contacting the treated substrate in any suitable manner.

Preferably, the solvent employed in the rinsing step is the same as that used to prepare the sulfur-containing solvent solution. However, any of the solvents or mixtures thereof, mentioned as suitable compositions for use in the sulfur-containing solvent solutions may be employed.

By carefully controlling the time, temperature, strength of solution, and other processing variables, it is possible to treat the plastic substrate with the sulfur-containing solvent solution so that the solvent rinsing step may be omitted entirely if desired.

TREATMENT WITH THE CUPROUS SALT SOLUTION

Preferably, after being air-dried under ambient conditions for about 30 seconds to about 5 hours or more, the plastic substrate is immersed in an aqueous solution of a cuprous salt at a temperature of about 65° to about 200° F. for a period of from about 30 seconds to about 30 minutes or more. Usually, the pH of the solution is maintained between about 1.5 and about 3.5 through the addition of hydrochloric, sulfuric, acetic or phosphoric acid. The concentration of the cuprous ion in the aqueous solution can be varied from about 0.2 g./l. up to saturation. Generally, the temperature of the cuprous salt

solution is maintained at about 90° to 180° F., the concentration of the cuprous ion at about 0.5 to about 3 g./l. and the time of immersion at about 5 to 10 minutes.

Useful cuprous salts include cuprous chloride, cuprous bromide, cuprous iodide, cuprous fluoride, cuprous acetate, cuprous nitrate, etc. Preferred cuprous salts include cuprous chloride and cuprous acetate.

The exact mechanism by which the cuprous salt unites with the sulfur on and in the surface of the plastic substrate is not known although it is believed that the cuprous salt reacts with the sulfur to form what is believed to be a metal sulfide. The surface of the plastic substrate with the so-called copper sulfide developed thereon is not water-wettable, but is relatively conductive.

TREATMENT WITH A METAL SALT SOLUTION

Generally, the next step in the novel process of this invention is, after a cold water rinse, to immerse the plastic substrate in an aqueous solution of a palladium salt, or another noble metal salt, at a temperature of about 65° to 200° F. for about 15 seconds to 10 minutes or more. The concentration of the noble metal ion in the solution may be varied widely and usually will be about 0.1 g./l. to about saturation. Preferably, the aqueous metal salt solution is maintained at a temperature of about 125° to about 180° F. while the concentration of the noble metal ion is about 1 to about 5 g./l. and the time of treatment of the substrate by immersion, spraying, or by any other convenient method is about 30 seconds to about 5 minutes.

A wide variety of noble metal salts may be employed in preparing the aqueous salt baths including silver nitrate, palladium chloride, gold chloride, platinum chloride, etc.

Although, as set forth above, the surface of the plastic after the cuprous ion treatment is conductive, in some areas of a plastic part, i.e. the low current density areas, the surface is not conductive enough to permit satisfactory electrolytic plating. For this reason the above-described step in which the plastic part is immersed in a noble metal salt bath is, if needed, employed in the novel plating process of this invention.

The step of treating the plastic substrate with an aqueous solution of a silver salt or a noble metal halide is an optional one and, where desired, the plastic substrate, after being contacted with the aqueous cuprous ion solution, may be directly electroplated to form on its surface a highly adherent conductive metal coating.

ELECTROPLATING THE SUBSTRATE

After a cold water rinse and acid activation the plastic substrate is electroplated, in a conventional manner with copper, nickel or any other desired metal, to build up a highly adherent deposit of plated metal of suitable thickness.

The following examples illustrate various embodiments of this invention and are to be considered not limitative:

Example I

A solution of sulfur in perchloroethylene was prepared by dissolving sulfur in finely divided form with mixing in perchloroethylene at a temperature of 150° F. until a concentration of 45 grams per liter had been obtained. A polypropylene article was immersed in the perchloroethylene sulfur solution for 5 minutes at a temperature of 160° F. after which it was removed and then rinsed by immersing it in a bath consisting solely of perchloroethylene at room temperature for about 25 seconds.

The polypropylene article was removed from the perchloroethylene rinsing bath, air dried at room temperature for about 3 minutes following which it was immersed

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for 10 minutes at 140° F. in an acidic cuprous chloride solution of the following composition:

	G./l.	
CuCl ₂ H ₂ O	2	
HCl conc. 37%	3	5
Water—Balance.		
(pH 1.8–2.0).		

After being rinsed in cold water, the polypropylene article was immersed for 1 minute at 125° F. in a solution of palladium chloride of the following composition:

Palladium chloride—1 g./l.	
Water—Balance	
pH 2.0 with hydrochloric acid.	

In the next step, the polypropylene substrate, after being rinsed again in cold water, was given a strike or flash coating by electroplating in a typical nickel bath for 10 minutes at about 2.5 volts. In a final step, the polypropylene substrate was electroplated in a conventional bright acid copper bath for about 10 minutes at 40 a.s.f. After the plated polypropylene article had been removed from the bright acid copper bath, rinsed and dried it exhibited a bright copper finish. The adhesion of the plated metal coating was measured and found to be about 20 pounds per inch.

Example II

In this example, a polypropylene article was treated in the same manner and with the same solutions as in Example I through the step of immersing the plastic substrate in the acidic cuprous chloride solution. Following a cold water rinse, the polypropylene article was electroplated in a Watt's nickel bath at 40 a.s.f. for 20 minutes. After the electroplating operation, the polypropylene article was rinsed in cold water and dried. The highly adherent metal coating exhibited a peel strength of 15 pounds per inch.

Example III

A polypropylene article was subjected to the same treatment steps utilizing the same solutions as described in Example I through the step in which the article was immersed in the acidic cuprous chloride solution. Next, the polypropylene article was treated with an aqueous solution of gold chloride of the following composition:

AuCl₃—2 g./l.
(Dissolve in water with stirring)

at a temperature of about 130° F. for 2 minutes. The plastic article, following a cold water rinse, was electroplated in an acid copper bath for 10 minutes at 40 a.s.f. The adhesion of the adherent metal coating was measured and found to be 3 pounds per inch.

Example IV

An ABS plastic substrate was immersed in a perchloroethylene solution containing 70 g./l. of sulfur at 160° F. for about 3 minutes. In the next step the substrate was rinsed by contacting it with perchloroethylene at room temperature for about 30 seconds following which it was air dried for 3 minutes. The plastic ABS substrate was immersed for 6 minutes at a temperature of 140° F. in a cuprous salt bath of the following composition:

	G./l.	
CuCl ₂ ·2H ₂ O	10	
HCl conc. 37%	4	
Water—Balance.		

After being rinsed in cold water, the ABS plastic substrate was immersed for 5 minutes at a temperature of about 160° F. in a palladium salt solution of the following composition:

	G./l.	
PdCl ₂	.56	
HCl	.38	
NaHSO ₄	1.5	
Water—Balance.		
(pH 1.6).		

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Following an additional cold water rinse, the ABS plastic substrate was electroplated in a conventional manner utilizing a nickel electroplating solution. The ABS plastic substrate was removed from the electroplating bath, and dried. The adhesion of the plated metal coating to the plastic surface was measured and found to be 4 pounds per inch.

Example V

In this example an ABS plastic article was treated in the same manner and with the same solutions as employed in Example I with the exception that the perchloroethylene sulfur solution was prepared by dissolving sulfur to a concentration of 40 grams per liter in a mixture of 80% by volume of perchloroethylene and 20% by volume of the monobutyl ether of ethylene glycol.

The ABS plastic article after being nickel plated electrolytically was removed from the bath and dried. The adhesion of the adherent metal coating was measured and determined to be 4½ pounds per inch.

Example VI

A polyvinyl chloride article was treated in the same manner and with the same solutions as those employed in Example I. After the plastic specimen had been electroplated, as in Example I, it was dried and the adhesion of the metal plating was measured. The highly-adherent, metal coating exhibited a peel strength value of 30 pounds per inch. Coverage of the article surface by the metal plating was excellent.

Example VII

A polyphenylene oxide plastic article was immersed for 10 minutes at a temperature of 160° F. in a bath prepared by dissolving sulfur to a concentration of 40 grams per liter in a mixture of 15% by volume of the monobutyl ether of diethylene glycol, and 85% by volume trichloroethylene. The polyphenylene oxide, after being rinsed in cold water was immersed in a cuprous salt solution of the same composition as that employed in Example IV at a temperature of about 150° F. for 7 minutes. After an additional cold water rinse, the plastic article was immersed in a silver salt bath of the following composition:

	Percent by wt.
AgNO ₃	8.53
Citric acid	8.53
Water	70.99
Conc. nitric acid	11.95

for about 2 minutes at a temperature of 100° F. Following a cold water rinse, the polyphenylene oxide article was electroplated in a Watts nickel bath for a period of about 20 minutes at 40 a.s.f. The adhesion of the highly adherent plated metal coating was measured and found to be 12 pounds per inch. Complete coverage of the plastic substrate was achieved.

Example VIII

In this example a polysulfone article was treated in the same manner utilizing the same solutions as those employed in Example I with the exception that the initial sulfur containing solution was a solution of perchloroethylene containing 80 grams of sulfur per liter. After the plated polysulfone article has been removed from the electroplating bath and dried, the peel strength of the metal coating deposited was determined and found to be 9 pounds per inch.

Example IX

Polycarbonate and polyurethane articles were treated in the same manner as described in Example I with the exception that the activating solution employed was a solution of perchloroethylene containing 85 grams per liter of sulfur. After electroplating, all of the plastic articles exhibited highly adherent metal coatings and, on measurement, the peel strengths were found to vary from about 5 to 10 pounds per inch.

Example X

An epoxy plastic substrate was immersed in a solution of trichloroethylene, containing 90 grams per liter of sulfur for 10 minutes at 170° F. Following the initial immersion treatment in the trichloroethylene-sulfur solution, the plastic article was treated in the same manner and with the same solutions as employed in Example I and finally electroplated as set forth in that example. The metal coating laid down on the plastic article surface during electroplating operation was adherent and the adhesion value, as measured, was found to be 5 pounds per inch.

What is claimed is:

1. A process for treating a plastic substrate which comprises:

- (a) contacting said substrate with a sulfur-containing organic solvent solution for a period of time sufficient to swell the said plastic substrate, said organic solvent having a boiling point greater than 70° F. at atmospheric pressure and capable of dissolving at least one gram of sulfur per liter at 70° F., and
- (b) treating the said plastic substrate with an aqueous solution of a cuprous salt.

2. The process of claim 1 wherein the said plastic substrate is ABS.

3. The process of claim 1 wherein the said plastic substrate is polypropylene.

4. The process of claim 1 wherein the concentration of sulfur in the said solvent solution is about 1 gram per liter up to saturation.

5. The process of claim 1 wherein the contacting of the plastic substrate with the solvent solution is carried out at a temperature ranging from about 65° to about 200° F.

6. The process of claim 1 wherein the time of contacting the plastic substrate with the said solvent solution is from about 15 seconds to about 20 minutes.

7. The process of claim 1 wherein the said substrate is treated with the aqueous cuprous salt solution at a temperature of about 65° to about 200° F. and for about 30 seconds to about 30 minutes.

8. The product produced by the process of claim 1.

9. The process of claim 1 wherein the said solvent is a halogenated hydrocarbon solvent and wherein the concentration of sulfur in the said solvent solution is about 10 to about 90 grams per liter.

10. The process of claim 9 wherein the said halogenated hydrocarbon solvent is selected from a group consisting of carbon tetrachloride, trichloroethylene and perchloroethylene.

11. The process of claim 1 wherein the said cuprous salt solution is an acidic aqueous cuprous chloride solution.

12. The process of claim 11 wherein the concentration of the cuprous ion in the cuprous chloride solution is about 0.2 gram per liter up to saturation.

13. The process of claim 1 wherein after the step in which the plastic substrate is contacted with the sulfur-containing solvent solution, it is rinsed with a hydrocarbon solvent prior to being treated with the aqueous cuprous salt solution.

14. The process of claim 13 wherein the said plastic substrate is rinsed with a halogenated hydrocarbon solvent.

15. The process of claim 1 wherein after the said substrate has been treated with the aqueous cuprous salt solution, it is air dried for a period of about 30 seconds to about 5 hours.

16. The product produced by the process of claim 15.

17. A process for plating on a plastic substrate which comprises:

(a) contacting the substrate with a sulfur containing organic solvent solution for a sufficient time to swell the substrate, said organic solvent having a boiling point greater than 70° F. at atmospheric pressure and capable of dissolving at least one gram of sulfur per liter at 70° F.,

(b) contacting the said plastic substrate with an aqueous solution of a cuprous salt,

(c) electroplating the substrate to build up a deposit of plated metal of suitable thickness.

18. The process of claim 17 wherein after step (a) the thus-treated substrate is rinsed in an organic solvent and afterwards air dried.

19. The process of claim 17 wherein prior to electroplating step (c) the substrate is treated with an aqueous solution of a noble metal salt.

20. A process for plating on a plastic substrate which comprises:

(a) contacting the said substrate with a sulfur-containing hydrocarbon solvent solution for about 15 seconds to about 20 minutes at a temperature from about 65° to about 200° F., said hydrocarbon solvent having a boiling point greater than 70° F. at atmospheric pressure and capable of dissolving at least one gram of sulfur per liter at 70° F.,

(b) rinsing the thus-treated substrate in a hydrocarbon solvent,

(c) air drying the substrate,

(d) contacting the said substrate with an aqueous solution of cuprous chloride for about 30 seconds to about 30 minutes at a temperature of about 60° to about 200° F., and

(e) electroplating the substrate to build up a deposit of plated metal of suitable thickness.

21. The process of claim 20 wherein the said substrate is ABS.

22. The process of claim 20 wherein the said substrate is polypropylene.

23. The process of claim 20 wherein the said hydrocarbon solvent of steps (a) and (b) is a halogenated hydrocarbon solvent.

24. The process of claim 20 wherein the said hydrocarbon solvent is perchloroethylene.

25. The process of claim 20 wherein the said hydrocarbon solvent is trichloroethylene.

26. The process of claim 20 wherein the said hydrocarbon solvent is carbon tetrachloride.

27. The product formed by the process of claim 20.

28. The process of claim 20 wherein prior to the electroplating step (e) the plastic substrate is treated with an aqueous solution of a noble metal salt.

29. The process of claim 28 wherein prior to the electroplating step (e) the plastic substrate is treated with an aqueous solution of palladium chloride.

30. The product formed by the process of claim 28.

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