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3,471,313  
PROCESS FOR CONDITIONING THE SURFACE OF  
POLYMER ARTICLES  
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303,670, Aug. 21, 1963. This application May 17, 1966,  
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U.S. Cl. 117—47 14 Claims

ABSTRACT OF THE DISCLOSURE

Process for imparting a hydrophilic property and receptivity for metal plating to a normally hydrophobic surface of a synthetic organic polymeric material involving contacting the surface with an acid solution comprising orthophosphoric acid and chromic acid in a weight ratio in the weight ratio range of about 8.5:1 to about 9:1 respectively until the hydrophobic surface is converted to a hydrophilic surface receptive to chemical reduction metal plating process aqueous solutions, and readily bondable to chemical reduction metal plating.

This is a continuation-in-part of our copending U.S. patent application Ser. No. 303,670, filed Aug. 21, 1963, now abandoned.

This invention relates to the conditioning of polymer surfaces, and more especially a new and improved process for conditioning a normally hydrophobic surface or surfaces of preformed articles of synthetic, hydrophobic organic normally solid polymeric material to render the surface hydrophilic and hence receptive to chemical reduction metal plating process aqueous solutions, and readily bondable to the metal plating. Additionally, this invention relates to the polymer article product of such conditioning.

In recent years molded high impact strength plastics or polymers such as, for example, acrylonitrile-butadiene-styrene copolymers have competed with metal plated zinc die castings in the production of automobile hardware, for instance decorative or garnish moldings, and of appliance hardware, for instance food mixer housings and knobs for appliances. However, such polymers have encountered a problem in penetrating the zinc die casting field as the appearance and feel of electroplated zinc die castings have been deemed of appreciable importance by the customer decoratively or functionally and the polymers do not possess the desired appearance or feel exhibited by the plated zinc die castings. By providing a metal plating or film over its exposed surface or surfaces, however, the polymer articles have the desired metallic appearance and feel.

Heretofore, procedures for plating metal on polymer or plastic surfaces have been either of the chemical or non-chemical type. Non-chemical plating processes involve metal deposition wherein the metal deposited does not undergo a chemical change during the plating operation. Examples of non-chemical plating processes are vacuum metalizing, and application of metallic paints and powders. Although these non-chemical processes produce decorative finishes or polymer surfaces and are useful for such applications as decorative escutcheons, such processes are of very limited utility for applications such as producing metal plated polymer or plastic hardware for automotive and appliance purposes for the reason no substantial bond is provided between the metal and polymer, and the metal is simply deposited as a layer on the polymer surface or substrate. Such metal deposits of rela-

tively weak or low bond strength are easily removed from the polymer surface by normal wear, abrasion, corrosiveness, thermal shock or thermal cycling, and other conditions normally encountered in the ordinary use of the plated polymer article.

In order to overcome the limitations of the non-chemical or physical application of metal coatings to polymer surfaces, chemical methods for plating the metal have been employed to increase the bond between the applied metal coating and the polymer surface, with the result that better adhesion and abrasive resistance of the metal plating or coating has been achieved. The chemical plating methods are valuably applicable to small articles or parts such as, for instance, buttons, curtain rings and letterings but have been non-competitive with zinc die casting procedures employed in the production of automotive hardware, for instance automotive dashboards and exterior door handles, and transistor radio housings, due to these prior chemical plating methods being too expensive with the total cost of the product metal plated polymer article being usually appreciably greater than the metal plated zinc die cast article.

Heretofore, mechanical roughening procedures have been employed as a first step in chemical metal plating of polymer surfaces to condition the polymer surface for subsequent plating. These mechanical procedures were required to enable the subsequent chemical metal plating to adhere to the polymer surface both through fairly weak chemical bonds and through a mechanical "keying" action arising from "hills and valleys" on the polymer surface due to the roughening. These mechanical roughening procedures are conventional for practically all non-conductive substrates including polymer surfaces or substrates prior to chemical plating, and are especially important for plating on thermosetting as well as thermoplastic surfaces. After the mechanical roughening, the polymer article surface or surfaces have been etched heretofore to further roughen and produce "hills and valleys" thereon employing a chemical etchant. The most commonly employed etchant for polymer surfaces was a chromate-sulfuric acid aqueous solution, typical examples of which follow:

Etchant A

CrO <sub>3</sub> , oz./gallon	10
H <sub>2</sub> SO <sub>4</sub> , fl. oz./gallon	32

Etchant B

K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , g.	15
H <sub>2</sub> SO <sub>4</sub> , ml.	100
H <sub>2</sub> O, ml.	50

The etching treatment was carried out at room temperature for a period of from one to five minutes as required to produce the desired roughening and hydrophilic surface, and such etching treatment was employed heretofore on surfaces of polymers or resins such as the epoxy, phenolic, acrylic, casein, cellulosic, polyamide, styrene and vinyl polymers or resins. After etching, the polymer surface or substrate was rinsed with water and neutralized with dilute aqueous alkali solution.

The next step in the prior procedure was sensitization of the hydrophilic surface by the deposition thereon of a readily oxidizable material, to enable later deposition thereon of a catalytic metal. This step usually involves the use of stannous chloride-containing solution, with a typical sensitizer containing stannous chloride, hydrochloric acid and water. The sensitized polymer surface was then activated by treatment with a solution containing a noble metal salt, whereby the metal is reduced on the polymer surface to act thereon as a catalytic surface for localizing further electroless metal plating. Virtually



all of the noble metals which are readily reduced by stannous chloride are catalytic for the common chemical reduction plating solutions, including gold, silver, nickel, copper and the platinum group metals.

Following the activating of the polymer surface, the surface was converted to an electrically conductive one by deposition of a thin, metallic coating, for instance of copper or silver, from a chemical reduction plating solution. After the electroless plating was carried out, the polymer or plastic article was usually placed in an electroplating bath and about 2 to 5 mils of metal, usually copper, applied to its surface or surfaces having the electroless metal deposited thereon. The electroplated surface was then polished or buffed, which was a fairly expensive mechanical operation, and then plated with bright nickel followed by being subjected to a chromium plating solution or, alternatively, a gold electrodeposit was applied in place of the chromium.

Although these prior chemical procedures for plating on polymer surfaces gave satisfactory results from the standpoint of the quality and attractiveness of the deposited metal plating, they suffered from the total cost of the plated polymer article being usually appreciably greater than the electroplated zinc die cast article or element. The reasons for this higher cost were the need to mechanically roughen the polymer surface to produce the surface irregularities and "hills and valleys," and the further requirement for mechanically polishing or buffing the electrolytic copper coating. Further these two mechanical steps prevent the use of a completely automated plating line, such as is commonly used in the bright plating of zinc die castings. Accordingly, these prior procedures have been of only limited commercial usefulness in the metal-plated plastic or polymer automotive and appliance areas.

One object of this invention is to provide a new and improved process for conditioning polymer surfaces or substrates in preparation for chemical reduction metal plating of the surfaces.

Another object is to provide a new and improved process for conditioning polymer surfaces or substrates in preparation for chemical reduction metal plating of the surfaces, which enables eliminating the mechanical roughening required by prior conditioning methods.

Another object is to provide a new and improved process for conditioning polymer surfaces or substrates which attains an appreciably stronger bond of the subsequent chemical reduction metal plating or deposit to the polymer surface.

Another object is to provide a new and improved process for conditioning polymer surfaces or substrates which enables the elimination of the mechanical polishing or buffing of the subsequent metal electrodeposits.

A further object is to provide a new and improved process for conditioning polymer surfaces or substrates in preparation for chemical reduction metal plating of the surfaces, which enables the use of conventional automatic equipment for the conditioning and subsequent metal plating of the surface or substrate.

In accordance with the present invention, we have found that the normally hydrophilic surface or surfaces destined to be electrolessly metal plated of a preformed solid article or articles of a synthetic hydrophobic organic polymeric material, for instance, molded articles of the polymeric material for automotive and appliance applications, are rendered hydrophilic and hence receptive to chemical reduction metal plating process aqueous solutions and readily bondable to the metal plating with good results and without the requirement of a prior mechanical roughening of such surface or surfaces, by a process comprising contacting the clean normally hydrophobic surface or surfaces with an acid conditioning solution comprising chromic acid ( $\text{CrO}_3$ ) and orthophosphoric acid until the hydrophobic surface is converted to a hydrophilic surface receptive to such metal plating process

aqueous solutions and readily bondable to metal plating. The contacting is usually effected by immersing the normally hydrophobic surface or surfaces of the article in the conditioning solution. It is important that the article surface or surfaces be clean when conditioned in accordance with this invention and, if not already clean, the surface or surfaces should be cleaned to remove dirt, debris, etc. that may be present thereon prior to the conditioning. After the conditioning, the article or articles are separated from the conditioning solution, usually by withdrawal of the articles from the solution, and their conditioned surface or surfaces water rinsed. The conditioning process herein creates by oxidation a superficial deglazing of the polymer and open bonds as reactive sites on the surface of the polymer, with the result the subsequent metal plating or deposits adhere to the polymer surface by firm bonds. By reason of eliminating the prior mechanical roughening, conventional automatic plating equipment can be utilized for the conditioning and subsequent electroless metal plating. Further subsequent electrodeposits when produced from bright plating formulations will be bright ab initio by virtue of the use of the novel conditioning solutions herein, thereby eliminating the need for polishing or burnishing, a manual or semi-manual operation. With the prior processes involving the mechanical roughening, due to the "hills and valleys" on the polymer surface and the resultant unevenness of the metal plate, the electroplated polymer substrate had to be polished or burnished to produce an attractive, bright or lustrous surface. Further, since polishing or burnishing of the metal plate is not required by reason of the present invention, the thickness of electroplated copper required for plating on polymer surfaces need be only that of the electroplate of electroplated zinc die castings, with a resultant further savings in the costs of the entire operation.

The conditioning of the polymer surface or surfaces herein is effected without any substantial degradation of the polymer surface. Such is very important to the bond strength of the ultimate metal plating or deposit to the polymer surface, as the strength of the bond of the metal plating or deposit to the polymer surface is dependent on having a sound, non-degraded or substantially non-degraded polymer forming the surface or surfaces to be metal plated. With any appreciable degradation of the polymer surface or surfaces, the bond strength of the metal plating or deposit to the polymer surface is substantially reduced. A slight amount of etching of the polymer or surfaces may be effected by the process herein, but this will not detrimentally affect the bond strengths of the metal plating to the polymer surface, as the polymer at the surface, except for a slight roughening, will be non-degraded and sound. For the most part, the conditioned polymer surface or surfaces produced by the process of this invention will on visual examination be entirely smooth and show but a surface deglazing. Open bonds as reactive sites are also provided on the polymer surface as disclosed previously herein.

Preferably the conditioning solutions of the process herein are free of sulphuric acid as it was found that appreciably stronger bonding of the subsequent chemical reduction metal plating or deposit to the polymer surface was obtained in the absence of sulfuric acid than when sulfuric acid was present. This use of sulfuric acid-free conditioning solutions herein resulted in a Jacquet Test or "pull" test result of  $4\frac{1}{2}$  lbs. per inch with a chemical reduction copper plate bonded to certain poorly-platable acrylonitrile-butadiene-styrene copolymer panels, while use of conditioning solutions containing sulfuric acid in addition to chromic acid and orthophosphoric acid resulted in a Jacquet Test result of  $3\frac{1}{2}$  lbs. per inch on substantially identical acrylonitrile-butadiene-styrene copolymer panels.

Less preferably sulfuric acid can be an ingredient of



the conditioning aqueous solutions herein in addition to the orthophosphoric acid and chromic acid.

It was entirely unexpected and surprising that the presence of the orthophosphoric acid and the conditioning solutions of the process herein would result in the elimination of the mechanical roughening of the polymer surface previously required prior to the conditioning. It was also entirely unexpected and surprising that the elimination of the sulfuric acid from the conditioning solutions herein resulted in appreciably greater bond strengths of the chemical reduction metal plating or deposit to the polymer surface than when sulfuric acid was present.

The conditioning process herein is carried out with the conditioning solution at a temperature in the range of about 60° F.-170° F.

The time of conditioning will in general be in the range from 15 seconds to 30 minutes inclusive, usually 90 seconds to 20 minutes.

The weight ratio of the orthophosphoric acid to the chromic acid in the preferred conditioning solution herein is preferably in the ratio range of about 8.5:1 to about 95:1, respectively. Preferred conditioning solutions herein can be free or substantially free of water—obtainable by utilizing anhydrous acids as ingredients—or can contain material quantities of water. Thus the water including that contained in the acids is preferably present in amount of about 0.30 weight percent of the total conditioning solution. In the less preferred sulfuric acid-containing conditioning solutions, the weight ratio of the sulfuric acid to the orthophosphoric acid is preferably in the ratio range of about 1.0:1 to about 5:1, respectively, and the weight ratio of the orthophosphoric acid to chromic acid is preferably within the ratio range of about 10:1 to about 95:1, respectively. The water is preferably contained in such sulfuric acid-containing solutions in amount of about 5-30 weight percent of the product conditioning solution, and includes the water present in the acids.

Synthetic organic polymers suitable for forming the preformed articles the surfaces of which are conditioned by this invention are normally solid synthetic organic hydrophobic polymeric materials or polymers of the thermoplastic and thermosetting type, and that may be linear or branched and oriented or unoriented. Exemplary of such polymers are acrylonitrile-butadiene-styrene copolymers, phenol-formaldehyde resins, vinyl polymers, e.g. polyvinyl chloride and polyvinylidene chloride, polystyrenes, butadiene-styrene copolymers, styrene-acrylonitrile copolymers, and acrylic polymers, e.g. polymethyl methacrylate and methyl methacrylate-styrene copolymers. The phenol-formaldehyde polymers can be glass fiber-filled or reinforced.

Prior to conditioning the polymer surface or substrate, the surface or substrate unless already clean is preferably cleaned, for instance by being chemically cleaned by immersion in an alkaline cleaner, preferably a non-silicated alkaline cleaner. Exemplary of the alkaline cleaners are the aqueous cleaner compositions set forth hereafter:

#### Cleaner A

	Grams per liter
Borax	30
Sodium pyrophosphate	30
Anionic wetting agent	2

#### Cleaner B

	Grams per liter
Trisodium phosphate	30
Sodium pyrophosphate	30
Anionic wetting agent	2

After cleaning, the polymer surface or substrate is rinsed with water. The anionic wetting agent of Cleaners A and B supra is one of the conventional anionic surfactant wetting agents readily obtainable in commerce.

The cleaned polymer surface or substrate is then con-

ditioned by contacting the surface with the conditioning aqueous solution of this invention to render the normally hydrophobic polymer surface hydrophilic and thereby receptive to chemical reduction metal plating process aqueous solutions, and readily bondable to metal plating. After conditioning, the polymer surface or substrate is rinsed with water.

The conditioned polymer surface is then sensitized by being contacted with, by immersion in or otherwise, a sensitizer solution. While not meant to be restrictive, the following solution has been found to be a suitable sensitizer:

#### Sensitizer solution

SnCl <sub>2</sub> , g.	10
HCl, ml.	40
H <sub>2</sub> O, ml.	1000

After sensitizing, the polymer surface or substrate is rinsed thoroughly with water.

The sensitized polymer surface is then activated by being contacted with, by immersion in or otherwise, an activator solution in known manner. While not being restrictive, the following solution has been found to be a suitable activator.

#### Activator solution

PdCl <sub>2</sub> , g.	1
HCl, ml.	10
H <sub>2</sub> O, gallon	1

The polymer surface is rinsed thoroughly with water after activation.

Alternatively, the polymer surface can first be activated followed by sensitizing, or a single step sensitizing-activating may be employed following the method of U.S. Patent 3,011,920. Rinsing must follow this single step sensitizing-activating, optionally followed by a solubilizing step to dissolve any remaining insoluble tin salts. Perchloric acid or a mixture of oxalic acid and fluoroborates can be used for such solubilizing step.

The activated polymer surface is then electrolessly metal plated in conventional manner with, for instance, copper, nickel or silver, by contacting the activated surface, by immersion in or otherwise, with a suitable chemical reduction plating solution or bath. Suitable chemical reduction plating baths utilizable herein are those given in the article by E. B. Saubestre entitled "Electroless Plating Today" in Metal Finishing, vol. 60, No. 6, pp. 67-73; No. 7, pp. 49-53; No. 8, pp. 45-49; and No. 9, pp. 59-63, 1962, but are not intended to be restrictive. The electroless plating is continued until the surface being plated is fully or substantially fully electrically conductive.

The conductive plated polymer surface is then electroplated in a conventional copper plating solution of the acid sulfate, fluoborate or sulfamate type. If the substrate is to have a final bright decorative finish, the plating solution should contain a brightener or brighteners, which are readily obtainable in commerce. The copper electroplate is preferably of about 0.1-1.5 mils thickness.

The copper electroplating can be followed by any desired final plating such as, for instance, nickel-chromium plating or nickel-gold plating.

Alternatively, a low-stress nickel plating can be applied directly after the electroless deposition.

The following Examples 1-5 disclose aqueous conditioning solutions of this invention that have been successfully used for conditioning ABS, i.e. acrylonitrile-butadiene-styrene copolymer surfaces. The examples are illustrative only and not restrictive.

#### Example I

	Percent by weight
H <sub>2</sub> SO <sub>4</sub>	40.0
H <sub>3</sub> PO <sub>4</sub>	39.5
CrO <sub>3</sub>	3.0
H <sub>2</sub> O	17.5

The solution is used to condition the polymer surfaces at a solution temperature in the range of 70° F.-170° F.



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## Example 2

	Percent by weight
H <sub>2</sub> SO <sub>4</sub> -----	53.0
H <sub>3</sub> PO <sub>4</sub> -----	22.0
CrO <sub>3</sub> -----	1.7
H <sub>2</sub> O -----	23.3

This solution is used for conditioning the polymer surfaces at a solution temperature in the range of 70° F.-170° F.

## Example 3

	Percent by weight
H <sub>2</sub> SO <sub>4</sub> -----	71.3
H <sub>3</sub> PO <sub>4</sub> -----	22.0
CrO <sub>3</sub> -----	1.7
H <sub>2</sub> O -----	5.0

This solution is utilized for conditioning the polymer surfaces at a solution temperature in the range of 80° F.-170° F.

## Example 4

	Percent by weight
H <sub>2</sub> SO <sub>4</sub> -----	53.0
H <sub>3</sub> PO <sub>4</sub> -----	40.0
CrO <sub>3</sub> -----	1.7
H <sub>2</sub> O -----	5.3

This solution is utilized to condition the synthetic hydrophobic organic polymer surfaces at a solution temperature in the range of 80° F.-170° F.

## Example 5

	Percent by weight
H <sub>2</sub> SO <sub>4</sub> -----	53.0
H <sub>3</sub> PO <sub>4</sub> -----	22.0
CrO <sub>3</sub> -----	1.0
H <sub>2</sub> O -----	24.0

This solution is utilized for conditioning the polymer surfaces at a solution temperature of 60° F.-170° F.

## Example 6

	Percent by weight
H <sub>2</sub> SO <sub>4</sub> -----	5
H <sub>3</sub> PO <sub>4</sub> -----	80
CrO <sub>3</sub> -----	5
H <sub>2</sub> O -----	10

This solution is utilized for conditioning the polymer surfaces at a solution temperature of 70 F.-170° F.

The conditioning solutions of Examples 1-6 were found to render hydrophilic the normally hydrophobic surfaces of acrylonitrile-butadiene-styrene copolymer articles, whereby such polymer surfaces were receptive to the aqueous sensitizer, activator and electroless plating bath solutions of the chemical reduction metal plating process for plating metals such as for instance copper and nickel. Further the conditioning solutions of Examples 1-6 were found to render the polymer surface readily bondable to Cu and Ni metal plating, which was due to the solution by oxidative action opening up chemical bonds on the polymer surface, which open bonds served as reactive sites for bonding of the metal. And no mechanical roughening or reglazing of the polymer surface was required prior to the conditioning with the solutions of Examples 1-6.

The following examples are illustrative of the preferred sulfuric acid-free conditioning solutions herein without being restrictive.

## Example 7

	Percent by weight
H <sub>3</sub> PO <sub>4</sub> -----	94.5
CrO <sub>3</sub> -----	5.5

This solution is used to condition the polymer surfaces at a solution temperature in the range of 70° F.-170° F.

## 8

## Example 8

	Percent by weight
H <sub>3</sub> PO <sub>4</sub> -----	90
CrO <sub>3</sub> -----	5
H <sub>2</sub> O -----	5

This solution is utilized to condition synthetic hydrophobic organic polymer surfaces at a solution temperature of 70° F.-170° F.

## Example 9

	Percent by weight
H <sub>3</sub> PO <sub>4</sub> -----	70
CrO <sub>3</sub> -----	10
H <sub>2</sub> O -----	20

This solution is utilized to condition synthetic hydrophobic organic polymer surfaces at a solution temperature in the range of 70 F.-170° F.

The considerable improvement attained by the present invention is shown by the following Examples 10-12.

## Example 10

Panels of acrylonitrile-butadiene-styrene copolymer each of dimensions of length 3½", width 3" and thickness ⅛" were conditioned by immersion in a bath of a solution containing, by weight, 53% of H<sub>2</sub>SO<sub>4</sub>, 22% of H<sub>3</sub>PO<sub>4</sub>, 1.7% of CrO<sub>3</sub> and 23.3% of H<sub>2</sub>O. The temperature of the solution was 150° F. and the immersion time was 5 minutes. The panels were then withdrawn from the conditioning solution, rinsed with water, followed by sensitizing by immersion in an aqueous SnCl<sub>2</sub> solution, water rinsing, activating by immersion in aqueous PdCl<sub>2</sub> solution, water rinsing, electroless copper plating by immersion in a chemical reduction copper plating bath and water rinsing.

The copper plate on the plated panels was then subjected to the "pull" test, i.e. the Jacquet Test, and the test showed an average bond strength of the copper plate to the substrate of 3½ lbs. per inch.

## Example 11

The procedure of Example 10 was repeated except that the conditioning solution contained, by weight, 70% H<sub>2</sub>SO<sub>4</sub>, 24% water, and 6% chromic acid, and was free of orthophosphoric acid.

The "pull" test, i.e. Jacquet Test, showed an average bond strength of the copper plate to the substrate of only 2½ lbs. per inch.

## Example 12

The procedure of Example 10 was repeated except that the conditioning solution contained, by weight, 94.5% of H<sub>3</sub>PO<sub>4</sub> and 5.5% of CrO<sub>3</sub>.

The "pull" test, i.e. Jacquet Test, showed an average bond strength of the copper plate to the substrate of 4½ lbs. per inch.

The considerable improvement in bond strength of the metal plate to the polymer substrate when the sulfuric acid-free conditioning solution containing orthophosphoric acid and chromic acid was utilized to condition the polymer panels prior to the electroless copper plating, is shown by the test results of Example 12 wherein an average pull test of 4½ lbs. per inch was obtained, as compared with the 2½ lbs. per inch and 3½ lbs. per inch pull test results obtained when utilizing the sulfuric acid-containing conditioning solutions of Examples 11 and 12, respectively. The considerable improvement in bond strength of the metal plate to the polymer substrate provided by the presence of the orthophosphoric acid in the conditioning solution herein, is shown by the test result of Example 10 wherein the average pull test result of 3½ lbs. per inch was obtained, as compared with the orthophosphoric acid-free solution of Example 11 wherein an average pull test of only 2½ lbs. per inch was obtained.

In the foregoing Examples 1-12 inclusive, the sulfuric



acid was 66° Bé. acid (98%  $\text{H}_2\text{SO}_4$ ), the orthophosphoric acid was  $\text{H}_3\text{PO}_4$  of 85%  $\text{H}_3\text{PO}_4$  concentration, and the  $\text{CrO}_3$  was commercial flake  $\text{CrO}_3$ .

The "pull" test, i.e. Jacquet Test, is a commonly used industrial test for adhesion of metals to plastics. In the test, a relatively thin metallic strip, which in the test runs herein was the electroless copper plating or coating, is pulled at a 90° angle from the underlying plastic or polymer substrate. The force required, either to initiate or sustain at a steady rate, peeling of the metal from the polymer is recorded as the numerical value for the test. In Examples 10-12 herein, the results of the pull test are given in lbs. per inch which means it required the specified number of pounds to pull a 1 inch wide strip of the metal of 2 mils thickness at a 90° angle from the underlying plastic or polymer substrate.

The following Example 13 is illustrative of a complete processing cycle including the conditioning of this invention, for surfaces of preformed articles of acrylonitrile-butadiene-styrene copolymers, phenolformaldehyde polymers, polyvinyl chloride, polyvinylidene chloride, polystyrenes, butadiene-styrene copolymers, styrene-acrylonitrile copolymers, polymethyl methacrylate and methyl methacrylate-styrene copolymers. The use of the processing cycle of Example 13 on surfaces of preformed articles of the polymers and copolymers mentioned immediately above, was found to result in no or virtually no degradation of the polymer surface due to the conditioning procedure.

#### Example 13

(1) Non-silicated aqueous alkaline cleaner containing borax, sodium pyrophosphate, and an anionic wetting agent as aqueous solution at cleaner concentration of 60 g./l. of water; cleaner solution temperature 140° F., cleaner contact time 2-3 minutes; cold water rinse.

(2) Conditioning solution of any of Examples 1-9 herein; conditioning solution temperature of 140° F.; conditioning solution contact time 5 minutes; cold water rinse.

(3)  $\text{SnCl}_2$ -containing sensitizer solution at room temperature; sensitizer solution contact time 1 minute; cold water rinse.

(4)  $\text{PdCl}_2$ -containing activator solution at room temperature; activator solution contact time 1 minute; cold water rinse.

(5) Electroless copper plating bath at room temperature; plating bath contact time 20 minutes; cold water rinse.

(6) Acid copper electroplating at room temperature of acid copper bath.

(7) Final plate as desired.

Metal-plated plastic or polymer articles preparable by this invention include those for use in the automotive industry, for instance decorative or garnish moldings for automobiles; and in the home appliance field, for instance housings for appliances for use in the kitchen, e.g. housings for food mixers.

What is claimed is:

1. A process for imparting a hydrophilic property and receptivity for metal plating to a normally hydrophobic surface, which comprises contacting a normally hydrophobic surface of a preformed solid article of a synthetic hydrophobic organic polymeric material wherein the polymeric material is selected from the group consisting of acrylonitrile-butadiene-styrene copolymers, phenol-formaldehyde resins, vinyl polymers, polystyrenes, butadiene-styrene copolymers, styrene-acrylonitrile copolymers and acrylic polymers with an acid solution comprising orthophosphoric acid and chromic acid in a weight ratio in the weight ratio range of about 8.5:1 to about

95:1 respectively until the hydrophobic surface is converted to a hydrophilic surface receptive to chemical reduction metal plating process aqueous solutions and readily bondable to chemical reduction metal plating.

2. The process of claim 1 wherein the normally hydrophobic surface is cleaned by immersion in a non-silicated alkaline aqueous liquid cleaner composition prior to contacting the surface with the conditioning solution.

3. The process of claim 1 wherein the polymeric material is an acrylonitrile-butadiene-styrene copolymer.

4. The process of claim 1 wherein the polymeric material is a phenol-formaldehyde resin.

5. The process of claim 1 wherein the polymeric material is a vinyl polymer.

6. The process of claim 1 wherein the polymeric material is a polystyrene.

7. The process of claim 1 wherein the polymeric material is an acrylic polymer.

8. The process of claim 1 further characterized in that subsequent to the acid solution contacting, the hydrophilic surface is water rinsed, sensitized by contacting the surface with a sensitizer aqueous solution, water rinsed, activated by contacting the surface with an activator aqueous solution, water rinsed, and electrolessly metal plated by contacting the activated surface with an electroless metal plating solution.

9. The process of claim 8 wherein the sensitizing is effected by immersing the surface in a  $\text{SnCl}_2$ -containing sensitizer aqueous solution, the activating by immersing the surface in a  $\text{PdCl}_2$ -containing activator aqueous solution, and the electroless metal plating by immersing the activated surface in an electroless metal plating solution.

10. The process of claim 1 wherein the acid solution contains water as an additional ingredient in amount up to about 30 weight percent of the total solution.

11. The process of claim 10 wherein the acid solution contains sulfuric acid as an additional ingredient, the weight ratio of the sulfuric acid to the orthophosphoric acid in the acid solution being in the weight ratio range of about 0.1:1 to about 5:1 respectively, and the weight ratio of the orthophosphoric acid to chromic acid being in the weight ratio range of about 10:1 to about 95:1 respectively, the water being present in such acid solution in amount of about 5-30 weight percent of the total solution.

12. The process of claim 1 wherein the acid solution is free of sulfuric acid.

13. The process of claim 12 wherein the hydrophilic polymer surface is immersed in the acid solution for a time in the range of from 15 seconds to 30 minutes.

14. The process of claim 12 wherein the temperature of the acid solution during the immersing is in the range of 60° F.-170° F.

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ALFRED L. LEAVITT, Primary Examiner

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U.S. Cl. X.R.

117-71, 138.8, 160



**UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION**

Patent No. 3,471,313

October 7, 1969

Edward B. Saubestre et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 21, "9:1" should read -- 95:1 --. Column 3, line 61, "hydrophilic" should read -- hydrophic --. line 25, "ingredients-" should read -- ingredients, --; line 32, "1.0:1" should read -- 0.1:1 --. Column 7, line 64, "reglazing" should read -- deglazing --. Column 8, line 66, "12" should read -- 10 --.

Signed and sealed this 19th day of May 1970.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

**WILLIAM E. SCHUYLER, JR.**

Commissioner of Patents

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,471,313 Dated October 7, 1969

Inventor(s) E. B. Saubestre and W. M. Emons, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 21, "9:1" should read -- 95:1 --.  
Column 3, line 61, "hydrophilic" should read -- hydrophobic --.  
Column 5, line 32, "1.0:1" should read -- 0.1:1 --.  
Column 7, line 64, "reglazing" should read -- deglazing --.  
Column 8, line 66, "12" should read -- 10 --.

This certificate supersedes Certificate of Correction issued May 19, 1970.

Signed and sealed this 11th day of August 1970.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

WILLIAM E. SCHUYLER, JR.  
Commissioner of Patents