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COMPOSITION AND PROCESS FOR CONDITIONING NORMALLY HYDROPHOBIC SURFACES OF ACRYLONITRILE - BUTADIENE - STYRENE TERPOLYMER

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ABSTRACT OF THE DISCLOSURE

Process for the chemical reduction metal plating of acrylonitrile-butadiene-styrene terpolymer characterized by having a relatively chemically unreactive hydrophobic terpolmer surface portion or portions requiring an excessively prolonged time for conditioning by orthophosphoric acid- and chromic acid-containing conditioning solutons to convert the terpolymer surface to a hydrophilic surface receptive to the aqueous solutions utilized in the chemical reduction metal plating process. A minor amount of an aliphatic hydrocarbon monocarboxylic acid having 2-3 carbon atoms per molecule is incorporated in the orthophosphoric acid- and chromic acid containing conditioning solution, prior to the conditioning of the terpolymer, to accelerate the conversion of the relatively chemically unreactive, hydrophobic surface portions of the acrylonitrile-butadiene-styrene terpolymer to hydrophilic surface portions.

This invention relates to conditioning the surface or surfaces of articles of acrylonitrile-butadiene-styrene terpolymer, and more particularly to a new and improved composition and process for rendering hydrophilic and hence receptive to chemical reduction metal plating process aqueous solutions the normally hydrophobic surfaces of preformed articles of acrylonitrile-butadiene-styrene terpolymer characterized by having one or more surface portions, which are relatively chemically unreactive with a conditioning aqueous solution comprising orthophosphoric acid and chromic acid.

In the preparation of acrylonitrile-butadiene-styrene terpolymer surfaces and substrates for chemical reduction metal plating, the terpolymer surfaces heretofore have been subjected to (1) a manual mechanical roughening of the surface, and also (2) treatment with an aqueous acid solution containing concentrated sulfuric acid and chromic acid (CrO_3) or a chromic acid-yielding compound. Exemplary of such acid solutions are the following aqueous soltuions:

Solution I

	Per gallon of water
CrO_3 ---------- oz--	10
H_2SO_4 ---------- fl. oz--	32

Solution II

$K_2Cr_2O_7$ ---------- g--	15
H_2SO_4 ---------- ml--	100
H_2O ---------- ml--	50

The contacting of the terpolymer surfaces with such treatment solutions has been typically effected at room temperature of the solution, and for a contact time of typically one to two minutes as required to produce the desired hydrophilic surface.

As an improvement over the manual mechanical roughening and sulfuric acid-chromic acid aqueous solution surface treatment of the terpolymer in preparation for the chemical reduction metal plating, aqueous acid solutions

containing orthophosphoric acid in addition to the chromic acid and with or without sulfuric acid, preferably in the absence of sulfuric acid, were found to give good results for conditioning terpolymer surfaces which were relatively chemically reactive with such acid solutions to render the polymer surfaces hydrophilic and receptive to chemical reduction metal plating process aqueous solutions and without the requirement of the prior mechanical roughening of the terpolymer surface. The use of orthophosphoric acid- and chromic acid-containing aqueous acid solutions free of or also containing sulfuric acid for conditioning acrylonitrile-butadiene - styrene copolymer and other polymer surfaces is disclosed and claimed in copending U.S. Patent application Ser. No. 550,624, filed May 17, 1966, and assigned to the same assignee as is this application. Application Ser. No. 550,624 is a continuation-in-part of U.S. Patent application Ser. No. 303,670, filed Aug. 21, 1963, now abandoned. The elimination of the prior mechanical roughening of the terpolymer, which was a manual operation as stated supra, was deemed especially of merit as it enables the employment of conventional automatic plating machines for the entire plating cycle.

Although the orthophosphoric-and chromic acid-containing aqueous solutions with or without the sulfuric acid gave good results in conditioning the relatively chemically reactive hydrophobic acrylonitrile-butadiene-styrene terpolymer surfaces to render same hydrophilic and readily bondable to chemical reduction metal plating, such solutions are not especially favorable and leave considerable room for improvement for conditioning acrylontrile-butadiene-styrene terpolymer surfaces having surface portions which are relatively chemically unreactive with the orthophosphoric acid-and chromic acid-containing aqueous solutions also containing or free of the sulfuric acid. The relatively chemically unreactive surface portions of such terpolymer are usually small portions thereof of microscopic size and surrounded partially or completely by the relatively chemically reactive terpolymer surface portions, due to the presence of such unreactive terpolymer surface portions, excessively prolonged time periods of conditioning are required for converting these chemically unreactive normally hydrophobic terpolymer surface portions to hydrophilic surfaces receptive to the chemical reduction metal plating aqueous solutions and readily bondable to the metal plating by a uniformly firmly adherent bond. Thus, for example, an orthophosphoric acid-and chromic acid-containing aqueous solution also containing sulfuric acid required only ten minutes for conditioning an entirely relatively chemically reactive surface of acrylonitrile-butadiene-styrene terpolymer to render same hydrophilic and readily bondable to a chemical reduction copper plating by a uniformly firmly adherent bond, but such aqueous acid solution required 50 minutes to obtain such results in conditioning an acrylonitrile-butaidene-styrene terpolymer surface having relatively chemically unreactive, normally hydrophobic terpolymer surface portions surrounded by relatively chemically reactive terpolymer surface portions.

Although we do not wish to be bound by theory, it appears the presence of the relatively chemically unreactive surface portion or portions on the acrylonitrile-butadiene-styrene terpolymer article or substrate is due to nonuniform molding conditions during the formation of the shaped terpolymer article or articles, and/or orientation of the terpolymer molecule chains with bundles of terpolymer molecule chains extending to the terpolymer surface in highly disoriented fashion and hence the relatively unreactive surface portions, and other terpolymer molecule chains extending to the terpolymer surface in highly oriented fashion providing the relatively chemically reactive terpolymer surface portions.

A principal object of this invention is to provide a new and improved composition and process for conditioning or converting the normally hydrophobic surface or surfaces of performed articles of acrylonitile-butadiene-styrene terpolymer characterized by having one or more surface portions which are relatively chemically unreactive with the prior conditioning aqueous solutions containing orthophosphoric acid and chromic acid, to hydrophilic surfaces receptive to chemical reduction metal plating process aqueous solutions and readily bondable to the electroless metal plating, film or deposit.

Additional objects and advantages will be apparent as the invention is hereinafter described.

In accordance with the present invention, it has now been found that by adding or incorporating an aliphatic hydrocarbon monocarboxylic acid having 2–3 carbon atoms per molecule into the orthophosphoric acid- and chromic acid-containing conditioning solutions, conditioning solutions are obtained which convert the normally hydrophobic, relatively chemically unreactive surface portions of the acrylonitrile-butadiene-styrene terpolymer to hydrophilic surfaces in a much shorter time than was previously required, besides converting the terpolymer hydrophilic surface portions of normal chemical reactivity with the orthophosphoric acid- and chromic acid-containing aqueous solutions to hydrophilic surface portions with good results and within the same time period. Conditioning aqueous solutions of this invention containing the aliphatic hydrocarbon monocarboxylic acid herein, which acid was unsubstituted on the aliphatic hydrocarbon portion or moiety thereof, in addition to the orthophosphoric and chromic acids, have required as little as $\frac{1}{10}$th of the time required by the conditioning aqueous solutions free of the aliphatic hydrocarbon monocarboxylic acid for converting the hydrophobic relatively chemically unreactive surface portions with the orthophosphoric acid and chromic acid-containing conditioning solutions to hydrophilic surfaces readily bondable to chemical reduction metal plating. Acetic acid gave especially good results herein. Propionic acid is also utilizable herein.

By the term "relatively chemically unreactive" or "chemically unreactive" as utilized herein in referring to the acrylonitrile-butadiene-styrene terpolymer portion or portions on such terpolymer surface is meant a portion or portions of such terpolymer on the terpolymer surface which requires a relatively long time to be conditioned by contact with a conditioning aqueous solution comprising orthophosphoric acid and chromic acid in the presence or obsence of sulfuric acid, to convert the normally hydrophobic terpolymer surface to a hydrophilic surface which is readily bondable to an electroless metal plating. Such conversion of the hydrophobic surface to the hydrophilic surface is believed to be an oxidative conversion of such surface. Such "chemically unreactive" terpolymer portion or portions is contrasted with the "relatively chemically reactive" surface portions of such terpolymer or such terpolymer surface portions of "normal chemical reactivity" which requires a considerably shorter time than do the "chemically unreactive" terpolymer portions, to be conditioned by contact with a conditioning aqueous solution comprising orthophosphoric acid and chromic acid in the presence or absence of sulfuric acid, to convert the normally hydrophobic terpolymer surface to a hydrophilic surface which is readily bondable to an electroless metal plating.

The addition of nitrous acid, HCN or formic acid instead of acetic or propionic acid to the orthophosphoric acid- and chromic acid-containing conditioning solutions was found not to accelerate the conditioning of the hydrophobic, relatively chemically unreactive surface portions of the terpolymer.

The aliphatic hydrocarbon monocarboxylic acid is utilized in the conditioning solutions or baths herein in a minor amount, sufficient to accelerate the conversion of

the relatively chemically inactive surface portion or portions of the terpolymer to a hydrophilic surface portion or portions readily bondable to a chemical reduction metal plating by a firmly adherent bond, i.e. a bond showing a Jacquet or pull test result of greater than five pounds per inch. Preferably the monocarboxylic acid is employed in the conditioning solution or bath in amount, by weight, of about 0.1%–10% (based on total product conditioning solution). With the use of much more than 10 weight percent of the aliphatic hydrocarbon monocarboxylic acid, the conditioning solution may etch deeply the terpolymer surface including that relatively chemically unreactive and that of normal reactivity with conditioning aqueous solutions comprising orthophosphoric acid chromic acids.

In addition to the mixture of aliphatic hydrocarbon monocarboxylic acid, orthophosphoric acid, chromic acid and water, the conditioning aqueous solutions herein can contain sulfuric acid as an ingredient of such solution or mixture. However, it is preferred that the conditioning solution be free of sulfuric acid, as it was found that the sulfuric acid-free conditioning solutions resulted in appreciably stronger bond strengths of the metal plating to the terpolymer surface.

The terpolymer surface or substrate can be contacted with the conditioning liquid composition herein at room temperature with good results. Elevated temperatures of the conditioning liquid up to about 160° F. can also be employed. Temperatures of the conditioning liquid within a range of about 100° F.–140° F., are preferred for conditioning the relatively chemically unreactive surface portion of the terpolymer.

The conditioning time herein for converting the hydrophobic terpolymer surface including the chemically unreactive terpolymer surface portion or portions to a hydrophilic surface will usually range from about 5–10 minutes. In general the time of conditioning the polymer surface is that sufficient to convert the normally hydrophobic terpolymer surface of a hydrophilic surface which is readily bondable to the chemical reduction metal plating by a uniformly firmly adherent bond.

Although we do not wish to be bound by theory, it appears the hydrophilic terpolymer surface produced herein has open chemical bonds on the terpolymer surface which serve as reactive sites at which bonding of the metal plating to the polymer readily occurs.

The acetic acid accelerating agent herein is preferably glacial acetic acid.

In the sulfuric acid-orthophosphoric acid-chromic acid-acetic acid-containing aqueous conditioning solutions herein, the sulfuric acid is preferably present therein in amount of about 40%–80%, the orthophosphoric acid preferably in amount of about 5%–40%, the chromic acid preferably in amount of about 1%–7%, the aliphatic hydrocarbon monocarboxylic acid preferably in amount of about 0.1%–10%, and the total water, i.e. added as such and together with acid ingredients, in amount preferably of about 10%–35%, all percentages being by weight. In the aqueous conditioning solutions herein containing orthophosphoric acid, chromic acid and acetic acid but free of sulfuric acid, the orthophosphoric acid is preferably present therein in amount of about 65%–90%, the chromic acid preferably in amount of about 2%–8%, the aliphatic hydrocarbon monocarboxylic acid in amount preferably of about .1%–10%, and the total water in amount of about 5%–20%, all percentages being by weight.

The sulfuric acid is preferably a concentrated acid, typically of 98% H_2SO_4 concentration; the orthophosphoric acid is preferably a concentrated acid, typically of 85% H_3PO_4 concentration, the chromic acid (CrO_3) is preferably a commercial flake CrO_3, the acetic acid is preferably a concentrated acid such as glacial acetic acid, and the propionic acid when utilized in place of the acetic acid is preferably a concentrated acid, typically of acid concentration of 100%.

Prior to conditioning the polymer or plastic substrate or surface, the substrate or surface, if not already clean, i.e. free of foreign material, dirt, debris, etc., is preferably cleaned, or instance by being immersed in a conventional alkaline cleaner, preferably a non-silicated alkaline cleaner. Exemplary of such alkaline cleaners is the following:

Borax	g./l.	30
Sodium pyrophosphate	g./l.	30
Anionic wetter	g./l.	0.1

The anionic wetter was a conventional anionic surface active wetting agent obtained in commerce. After cleaning, the polymer substrate or surface is rinsed in water.

The cleaned polymer surface or substrate is then conditioned by contacting the surface with the conditioning liquid composition as hereinbefore described, usually by immersing the substrate or surface therein, to render the normally hydrophobic polymer surface hydrophilic and hence receptive to chemical reduction metal plating process aqueous solutions, and readily bondable to metal plating. After conditioning, the polymer surface or substrate is rinsed thoroughly with water.

The conditioned polymer surface is then sensitized by contacting same with a sensitizer solution in known manner, usually by immersing the polymer surface or substrate in the sensitizer solution. A typical sensitizer solution follows:

Sensitizer solution

$SnCl_2$	g.	10
HCl	ml.	40
H_2O	ml.	1000

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

The sensitized polymer surface is then activated by being contacted with an activator solution in known manner, usually by immersing the sensitized surface therein. While not intended to be restrictive, the following activator solution has been found to be highly suitable.

Activator Solution

$PdCl_2$	g.	1
HCl	ml.	10
H_2O	gallon	1

After activation, the polymer surface is rinsed thoroughly with water.

Alternatively, the polymer surface or surfaces can first be activated followed by sensitization.

The activated polymer surface is then electrolessly metal plated with, for example, metallic copper or nickel, by contacting the activated surface or surfaces with a suitable chemical reduction metal plating solution or bath, usually by immersing the activated surface or surfaces in such bath. Exemplary of the chemical reduction metal plating baths are the following:

Electroless Copper Bath

Copper sulfate	g./l.	29
Sodium carbonate	g./l.	25
Rochelle salt	g./l.	140
Versene T	g./l.	17
Sodium hydroxide	g./l.	40
Formaldehyde (37% solution)	g./l.	166
pH		11.5
Temperature	° F.	70

"Versene T" is a soluble salt of ethylenediamine tetraacetic acid.

Electroless Nickel Bath

Nickel chloride	g./l.	30
Sodium glycolate	g./l.	50
Sodium hypophosphite	g./l.	10
NaOH, to adjust pH to pH 5.5–6.		
Temperature	° F.	150

Plating is continued with the foregoing electroless metal baths until the polymer substrate or surface is completely or substantially completely electrically conductive. Alternatively the activated polymer substrate or surface can be plated with silver, utilizing chemical reduction silver plating baths until the substrate is completely or substantially completely electrically conductive following the teachings of U.S. Patent 2,976,180 to Brookshire or the disclosure of T. M. Rodgers in "Handbook of Practical Electroplating," Macmillan (1960), pages 63–65.

The conductive polymer surface or substrate can then be electroplated with, for instance, nickel or copper in conventional nickel or copper electroplating baths. If the substrate or surface is to have a final bright decorative finish, the electroplating solution should contain a brightener or brighteners, which are readily obtainable in commerce.

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

The following examples of conditioning compositions of the present invention are illustrative and not restrictive.

Example 1

	Percent by weight
H_2SO_4	40.0
H_3PO_4	35.5
CH_3COOH	4.0
CrO_3	3.0
H_2O	17.5

Example 2

H_2SO_4	53.0
H_3PO_4	18.0
CH_3COOH	4.0
CrO_3	1.7
H_2O	23.3

Example 3

H_2SO_4	71.3
H_3PO_4	20.0
CH_3COOH	2.0
CrO_3	1.7
H_2O	5.0

Example 4

H_2SO_4	50.0
H_3PO_4	40.0
CH_3COOH	3.0
CrO_3	1.7
H_2O	5.3

Example 5

H_2SO_4	53.0
H_3PO_4	20.0
CH_3COOH	2.0
CrO_3	1.0
H_2O	24.0

In the conditioning solutions of foregoing Examples 1–5 and 9–16 hereinafter set forth, the H_2SO_4 is acid of 98% H_2SO_4 concentration, the H_3PO_4 is acid of 85% H_3PO_4 concentration, the CrO_3 is a commercial flake CrO_3, and the CH_3COOH is glacial acetic acid. In Examples 6–8 which follow, the CrO_3 and CH_3COOH is a commercial flake CrO_3 and glacial acetic acid respectively, and the H_3PO_4 is anhydrous orthophosphoric acid, i.e. acid of 100% H_3PO_4 concentration.

Example 6

	Percent by weight
H_3PO_4	80.0
CH_3COOH	2.0
CrO_3	8.0
H_2O	10.0

Example 7

	Percent by weight
H_3PO_4	75.0
CH_3COOH	5.0
CrO_3	6.0
H_2O	14.0

Example 8

H_3PO_4	65.0
CH_3COOH	4.0
CrO_3	7.0
H_2O	24.0

A plurality of injection molded panels of acrylonitrile-butadiene-styrene terpolymer were conditioned by immersion in an acetic acid-containing conditioning solution or bath of Examples 1–8 supra, with all eight baths of such examples utilized separately to condition a separate group of such terpolymer panels. The temperature of the conditioning solutions or baths was about 150° F. A plurality of articles of such terpolymer of similar shape and dimensions as those conditioned in the baths of Examples 1–8 were separately conditioned by immersion in one of the acetic acid-free conditioning baths of Examples 9–16 which follow, with all such baths being utilized separately to condition a separate group of such terpolymer panels under similar conditions of bath temperature as utilized with the baths of Examples 1–8. Such acetic acid-free conditioning baths were:

Example 9

	Percent by weight
H_2SO_4	40.0
H_3PO_4	39.5
CrO_3	3.0
H_2O	17.5

Example 10

H_2SO_4	53.0
H_3PO_4	22.0
CrO_3	1.7
H_2O	23.3

Example 11

H_2SO_4	71.3
H_3PO_4	22.0
CrO_3	1.7
H_2O	5.0

Example 12

H_2SO_4	53.0
H_3PO_4	40.0
CrO_3	1.7
H_2O	5.3

Example 13

H_2SO_4	53.0
H_3PO_4	22.0
CrO_3	1.0
H_2O	24.0

Example 14

H_2SO_4	5
H_3PO_4	80
CrO_3	5
H_2O	10

Example 15

H_3PO_4	94.5
CrO_3	5.5

Example 16

H_3PO_4	90
CrO_3	5
H_2O	5

After the conditioning, the terpolymer panels were withdrawn from their respective bath of Examples 1–8 and 9–16 respectively, thoroughly rinsed with water, then sensitized by immersion in an aqueous $SnCl_2$ solution followed by a thorough water rinsing, activated by immersion in aqueous $PdCl_2$ solution, again thoroughly water rinsed, electrolessly copper plated by immersion in a chemical reduction copper plating bath, and again thoroughly water rinsed after electroless copper plating was completed and withdrawal from the plating bath. The table of data which follows sets forth the time required by the conditioning bath of each of foregoing Examples 1–16 to properly condition the terpolymer for the plating:

Example:	Time required to properly condition the terpolymer surface (minutes)
1	5–10
2	5–10
3	5–10
4	5–10
5	5–10
6	5–10
7	5–10
8	5–10
9	35–50
10	35–50
11	35–50
12	35–50
13	35–50
14	35–50
15	35–50
16	35–50

By the second column heading "Time Required to Properly Condition the Terpolymer Surface" in the foregoing table is meant the time necessary to maintain the terpolymer articles immersed in the particular conditioning bath so as to ultimately obtain a uniformly firmly adherent bonding of the electroless copper plating to the terpolymer surface, having a Jacquet or "pull" test in excess of 5.

As shown by the table of test results supra, the acetic acid-containing conditioning baths of Examples 1–8 of this invention exhibited a considerably faster rate of conditioning of the acrylonitrile-butadiene-styrene terpolymer panels than did the acetic acid-free conditioning baths of Examples 9–16. Thus, the acetic acid-containing baths of Examples 1–8 required as little as $\frac{1}{10}$th the time to properly condition the terpolymer surfaces as did the acetic acid-free baths of Examples 9–16. The slowness of the conditioning of the terpolymer surfaces utilizing the acetic acid-free baths was attributed to the presence of relatively chemically unreactive portions of terpolymer on the terpolymer surface which, due to the absence of the acetic acid, required a longer time to properly condition than the terpolymer portions of normal chemical reactivity with the conditioning solutions comprising orthophosphoric acid and chromic acid.

Additional examples of the conditioning solutions or baths herein are set forth below:

Example 17

	Percent by weight
H_3PO_4	75.0
CH_3CH_2COOH	5.0
CrO_3	6.0
H_2O	14.0

Example 18

H_2SO_4	40.0
H_3PO_4	35.5
CH_3CH_2COOH	4.0
CrO_3	3.0
H_2O	17.5

Acrylonitrile-butadiene-styrene terpolymers, or "ABS" terpolymers, are utilized in many areas of industry and are of considerable importance in the automotive, appliance and building hardware industries. The terpolymers

exhibit a good balance of properties including chemical resistance, dimensional stability, heat resistance, toughness, rigidity, dielectric properties, and ease of processing and machining. Metal plated formed articles of such terpolymer provided by this invention are utilizable, for example, as garnish molding, gear shift or automatic transmission selector lever knobs and window crank handles in the automotive industry, as appliance housings or casings in the home appliance field, and as pull handles in the building hardware industry.

The preformed terpolymer article, object or structure treated by this invention may be the formed or shaped, e.g. injection molded, extruded or otherwise formed or shaped, terpolymer article as such or the formed or shaped terpolymer article or structure which is bonded or secured to a layer or substrate of a different material, for instance a base metal, a different polymer or plastic, a refractory ceramic or a glass.

In addition to providing hydrophilic surfaces of the acrylonitrile-butadiene-styrene terpolymer which are receptive to the aqueous solutions of the chemical reduction metal plating process, the present invention has utility for providing hydrophilic surfaces on the normally hydrophobic terpolymer which are receptive to printing inks, adhesives and glues.

What is claimed is:

1. In a process for the chemical reduction plating of a metal deposit onto the normally hydrophobic surface of an acrylonitrile-butadiene-styrene terpolymer characterized by at least a portion of the hydrophobic terpolymer surface being relatively chemically unreactive with a conditioning aqueous solution comprising orthophosphoric acid and chromic acid involving converting the normally hydrophobic terpolymer surface destined to be electrolessly metal plated to a hydrophilic surface receptive to chemical reduction metal plating process aqueous solutions by contacting the hydrophobic terpolymer surface with said conditioning solution for a time sufficient to effect such conversion, activating the hyrophilic terpolymer surface, and then electrolessly metal plating the activated terpolymer surface by contacting the activated surface with an aqueous chemical reduction metal plating solution for a time sufficient to deposit thereon a metal plating of the desired thickness, the improvement which comprises prior to contacting the hydrophobic terpolymer surface with the conditioning solution, incorporating into said conditioning solution a minor amount, sufficient to accelerate appreciably the conversion of the relatively chemical unreactive hydrophobic terpolymer surface portion to a hydrophilic surface portion, of an aliphatic hydrocarbon monocarboxylic acid having 2–3 carbon atoms per molecule.

2. The process of claim 1 wherein the monocarboxylic acid is acetic acid.

3. The process of claim 1 wherein the monocarboxylic acid is present in said conditioning solution in amount, by weight, from about 0.1%–10% by weight.

4. The process of claim 1 wherein the polymer surface is sensitized subsequent to being converted to a hydrophilic surface and prior to being activated.

5. The process of claim 1 wherein the temperature of the conditioning solution during the conditioning of the polymer surface is in the range from room temperature to about 160° F.

6. The process of claim 1 wherein the polymer surface is contacted with the conditioning aqueous solution for a time in the range from about 5–10 minutes.

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MURRAY KATZ, Primary Examiner

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