United States Patent Office 3,505,098 Patented Apr. 7, 1970

3,505,098

ELECTROPLATING OF POLYMERIC MATERIALS HAVING A POLYMERIC PRIMER COATING

Vernon F. Miller, Jenkintown, and Robert P. Fellmann, Levittown, Pa., assignors to Rohm & Haas Company, Philadelphia, Pa., a corporation of Delaware

No Drawing. Filed Oct. 24, 1966, Ser. No. 588,737
Int. Cl. B44d 1/14, 1/36; B32b 27/08
U.S. Cl. 117—71 1 Claim

ABSTRACT OF THE DISCLOSURE

The invention relates to the electroplating of polymeric materials to which have been applied a primer composition comprising a butadiene-containing polymer, and to articles produced by the electroplating process.

This invention relates to an improved method for plating a metal on polymeric materials. In particular, this invention relates to an improved method for selectively electroplating a metal, such as copper, nickel, zinc, cadmium, chromium or gold on polymeric substrates especially polyacrylic substrates.

Various methods have been used to plate a metal on plastic materials such as polyethylenes polypropylenes, polystyrenes, polyacetals, fluorocarbons, cellulosics, urea-formaldehydes phenol-formaldehydes and ABS (acrylonitrile-butadiene-styrene) resins. Three widely used methods for applying a decorative metallic or chrome-plated appearance to plastic materials are vacuum-evaporation, chemical or electroless deposition, and electroless deposition followed by a metal coating build-up formed by means of electroplating a suitable metal thereon. The primary disadvantage of the vacuum-evaporation and the electroless deposition methods is the thin film of metal obtained. The film attainable is limited to only a few millionths of an inch thick; this limitation is caused by process cost disadvantages. Consequently, the film must be protected by a clear organic lacquer. This combination of thin film and lacquer still exhibits relatively poor abrasion and weathering resistance. It has been found that electroplating a thick deposit of metal upon the thin, conducting electroless coating overcomes these disadvantages, if the thin metal coating has good adhesion. In addition, the use of bright electroplating baths obviates the need to buff the metal deposit so that brightness is obtainable at less cost. However, a serious limitation of the electroplating technique has been the inability to adhere adequately the thick metal electroplated coating and the conductive electroless coating to the plastic substrate. The adhesion is measured by a peel strength test described herein below. If the peel strength is substantially less than 5 pounds per inch width, then the coating is unsatisfactory even for decorative purposes.

U.S. Patent 2,351,940 discloses a method for electroplating copper on plastic surfaces that ordinarily will not retain an electrolytic deposit. Prior to the copper deposition, the surface is coated with a lacquer such as a nitrocellulose lacquer containing copper or pigment particles. This method entails certain disadvantages in that copper powder and pigment particles must be incorporated in the lacquer. These particles impart a rough, matte appearance to the finished metallic coating thereby causing an undesirable appearance.

U.S. Patent 2,458,032 discloses a method of cementing a metal film to polymethyl methacrylate by means of an adhesive comprising partially polymerized methyl methacrylate. In recent experiments by the inventors, attempts were made to overcome the problem of the poor metal-to-plastic bond by treating the polymeric substrate

with an ABS-type lacquer containing at least 15 percent butadiene by weight, viz, an acrylonitrile/butadiene/styrene resin such as Marbon Chemical's "Cycolac EP 3510" has been dissolved in a suitable organic solvent and sprayed selectively onto a polymeric substrate to act as a binder or primer for anchoring an electroplatable metal to the polyacrylic substrate. The use of this particular binder material entails certain serious disadvantages. It presents a hard relatively unimpregnable layer that requires a prolonged dwell time, usually 30 minutes or more, in the cold acid conditioner that is used in the preconditioning sequence prior to the electroplating step. This prolonged dwell time in the acid causes harmful acid attack on the substrate, not only at the location that is to be plated, but especially to the balance of the substrate that is not to be plated. This in turn requires a masking of the locations that are not to be plated; this masking requires the expenditure of more time and money on the plating process. The acid dwell time can be shortened by elevating the temperature of the acid bath, but damage to a polymeric substrate such as a polyacrylic substrate is especially severe when the temperature exceeds 27° C. over a period of from 3 to 5 minutes.

It is an object of this invention to provide a method for selectively plating a metal to a polymeric substrate wherein there is no need to mask those areas of the substrate that are not to be plated. Another object of this invention is to provide an economically feasible method for producing metallized polymeric materials having an improved metal-to-plastic bond. Still another object of this invention is to provide an improved binder material in the form of a smooth lacquer to firmly anchor a metal coating to a polymeric substrate. It is another object of this invention to provide a metallized polyacrylic material having improved wear and abrasion resistance. It is still another object of this invention to provide metallized polymeric materials having improved outdoor weather resistance.

The electroplated polymeric materials of this invention may be used for metal substitute parts where high strength and heat resistance are not required. They may also be used for automobile parts (particularly selectively plated parts, such as tail-light lens assemblies having selectively plated bezels), appliances, and marine and plumbing hardware. In particular, they may be used for housings for automobile tail and back-up lights, heater housings, instrument panels, automobile radiator grills, door handles, headlights, wheel covers, rear view mirrors, radio and clock cover plates, glove compartments, control knobs, trim, seat hinge covers, faucet bonnets and handles, drain flanges, escutcheons, sink strainers, soap dispenser parts, laboratory hardware, thumb tacks, typewriter carriage arms, levers, pen barrels and a host of other molded items.

In accordance with this invention, the above objects are accomplished by applying a novel primer composition comprising a butadiene containing polymer to the plastic substrate to form a relatively soft coating thereon, before it is conditioned for electroplating. This primer composition promotes a strong metal-to-plastic bond in the electroplated substrate; this will be described more fully herein below.

It has been discovered that polymeric substrates coated with the primer composition of this invention unexpectedly need only a short dwell time in a conventional electroplating process acid conditioner. Surprisingly, strong metal-to-plastic bonds are obtained even when the dwell time is reduced to 5 minutes or less. Since the dwell time is shorter than what is normally required in an electroplating process, such as the Enthone or Mac Dermid processes, there is no need to increase the temperature of the

acid conditioner to the point where the plastic substrate would be severely damaged. In addition, the shortened dwell time prevents damage to the plastic substrate caused merely by prolonged exposure to the acid conditioner.

The primer composition of this invention comprises a polymer containing 20 to 90 percent by weight butadiene. A butadiene content of 35 to 70 percent by weight is preferred. The composition of the primer will vary according to the composition of the substrate that is to be plated. For example, it is advantageous to include in the butadiene polymer of the primer composition a monomer or mixture of monomers that will serve to compatibilize the primer with the substrate. This will enable the primer to adhere to the substrate. In the instance of a polymethyl methacrylate substrate, the compatibilizing monomer can be methyl methacrylate. If the substrate were polystyrene, then the compatibilizing monomer in the butadiene polymer would be styrene. It can be seen that the proportions by weight of the compatibilizing monomer will vary with the substrate, and the amount required to achieve adherence to the substrate will be the major consideration in determining the weight proportions of butadiene.

Representative of the polymeric substrates that may be primed for electroplating by the primer compositions of this invention are the polyacrylics, polyethylenes, polypropylenes, polystyrenes, ABS (acrylonitrile - butadiene - styrene) resins, polyvinyl chlorides, cellulose acetate butyrate, polyacetals, fluorocarbons, polycarbonates, polyphenylene oxides, polysulfones and other polymeric substrates where it is difficult to effect a strong metal-to-plastic bond. The preferred substrates are the polyacrylics, the ABS resins and cellulose acetate butyrate. The polyacrylic substrates may be homopolymers of an (C_{1-4})-alkyl ester of acrylic or methacrylic acid or copolymers of one or more of these esters with each other or with other copolymerizable monomeric materials, such as styrene, alpha-methyl styrene, acrylic acid, methacrylic acid, acrylonitrile, methacrylonitrile, vinyl chloride and vinylidene chloride.

The primer compositions of this invention may be applied to the polymeric substrate in a variety of ways. For example, they may be applied either in the form of an aqueous latex or as a lacquer or dispersion in an organic solvent system at any suitable concentration from 1% to 50% solids. The primer composition may be solubilized in a suitable organic solvent system, such as xylene and diacetone alcohol in equal parts by weight, to form a sprayable lacquer. Application may be by dipping the part in the primer, or painting the primer on the part with a brush. They may be applied by a flow-coating technique, wherein the part is placed in a tank and attached to a rotatable shaft positioned in front of nozzles that supply a stream of primer composition that is distributed smoothly upon the part when it is rotated. The primer composition may also be sprayed onto the part either as an aqueous latex or in the form of a lacquer wherein it is contained in an organic solvent system. The percentage of solids in the primer may range from 11 percent to 20 percent, while a range of 12 percent to 14 percent solids is preferred.

It has been found that a deposit of the primer composition having a thickness of not less than about 0.0006 inch gives good results. If the primer composition has a thickness of less than about 0.0006 inch, the acid conditioner used in the plating process may severely attack the coating or consume it, and cause poor adhesion.

The primer composition of this invention may be used to condition the polymeric substrates so as to make them receptive for complete surface plating or selective electroplating. Selective plating is a technique wherein only portions of the substrate are plated. The need for masking those portions of the substrate surface which are not to be plated is obviated because the dwell time in the acid conditioner is not sufficient to sensitize or to damage the substrate areas that have not been coated by the primer composition of this invention. For example, a polymethyl methacrylate substrate without special pretreatment cannot retain an adherent metal coating deposited thereon by means of a conventional electroplating technique; therefore, those areas that have not been coated with the primer composition of this invention will not have an adherent metal-to-plastic bond and can readily be stripped. Similarly, poor regional adhesion results when the substrate consists of an ABS resin that has been selectively coated with the primer composition of this invention. The dwell time in the acid conditioner is insufficient to sensitize the unprimed areas of the ABS substrate, so that any metal that is plated on these areas adheres so poorly to the substrate that it is readily stripped therefrom.

The primer composition of this invention as indicated supra may be a copolymer of butadiene and another copolymerizable monomeric material that is compatible with the substrate. The copolymer may be butadiene copolymerized with styrene, acrylonitrile, or any other compatibilizing monomer, such as vinyl or vinylidene halides, such as the chlorides; vinyl esters such as vinyl acetate, butyrate or benzoate; acrylic and α-alkyl acrylic acids, their alkyl esters, amides and nitriles such as acrylic or methacrylic acid, ethyl acrylate, octyl acrylate, methyl methacrylate, acrylamide, acrylonitrile; vinyl aromatic compounds such as the styrenes including styrene itself, chlorostyrene and ethyl styrene; vinyl naphthalene; alkyl esters of maleic and fumaric acid such as dimethyl maleate; vinyl alkyl ethers and vinyl alkyl ketones; vinyl pyridine and isobutylene.

The compatible monomer may be emulsion polymerized with an already-formed butadiene-styrene copolymer to provide graft or layer polymers. For example, the primer composition of this invention may be a composition formed by polymerization of a butadiene-styrene copolymer latex and a monomeric material solely or preponderantly of methyl methacrylate. In such an instance, 15 to 75 percent by weight of a butadiene-styrene copolymer are mixed with monomeric materials which comprise 85 to 25 percent by weight of monomeric methyl methacrylate, or monomeric methyl methacrylate to the extent of at least 55 percent and preferably as much as 75 percent by weight in admixture with another monomer which copolymerizes therewith, such as ethyl acrylate, acrylonitrile, vinylidene chloride, styrene and similar monoethylenically unsaturated compounds having a group with a formula $H_2C{=}C<$. The butadiene-styrene copolymer in the latex may comprise about 10 to 50 percent by weight of styrene and about 90 to 50 percent by weight of butadiene and the molecular weight thereof is within the range of about 25,000 to 1,500,000. Interpolymerization of the monomer or monomeric mixture with the copolymer solids suspended in water is brought about in the presence of a free-radical generating catalyst; a polymerization regulator which serves as a chain transfer agent at a temperature of the order of 15° to 80° C. may be optionally included. The interpolymerized product is then isolated by any suitable means such as spray drying, evaporation, or coagulation as by means of a calcium chloride solution. The isolated interpolymerized product is then dried using conventional drying techniques.

To assist those skilled in the art to practice the present invention, the following modes of operation are suggested by way of illustration, parts and percentages being by weight and the temperatures in degrees C. unless otherwise specifically noted.

FORMULATION OF THE PRIMER COMPOSITION

One hundred parts of latex formed by emulsion copolymerizing 75 parts of butadiene and 25 parts of styrene in the presence of a dispersing agent at a relatively low temperature of the order of 5° C., the solids content of the latex being 50 percent by weight and the molecular weight of the copolymer being of the order of 500,000, is diluted with 100 parts of water containing 1.5 parts of

sodium lauryl sulfate dissolved therein. The diluted latex is agitated until homogeneous. One hundred and fifty-one parts of methyl methacrylate monomer containing 0.3 part of paramenthane hydroperoxide and 1.32 parts of n-dodecyl mercaptan are added to the diluted latex slowly with stirring to obtain a uniform stable emulsion. The emulsion so obtained is maintained at 60° C. for 18 hours to effect essentially complete polymerization. Coagulation of solids is then brought about by slowly pouring the emulsion into 1500 parts of a 0.5 percent aqueous calcium chloride solution containing 1.0 part of 2,6-ditertiary-butyl-4-methyl phenol maintained at a temperature of 90° C. A dry powder is obtained by filtering, washing, and drying the coagulated polymer under vacuum. Sixty gms. of the powder are slowly added to a mixture of 200 gms. of xylene and 200 gms. of diacetone alcohol. The resultant formulation is then stirred or shaken and filtered to remove undissolved polymeric particles.

Example 1.—(A) Application of primer composition to substrate

The primer composition prepared as described supra is sprayed on four polymethyl methacrylate bars that had been solvent cleaned of all organic and inorganic contamination. The lacquer is sprayed only on the areas to be plated. The primed bars are then air dried for 5 minutes. A second spray coating is applied to provide on the coated areas of the bars a total coating layer thickness of about 0.0006 inch. The primed bars are then baked for 45 minutes at 66° C. to remove residual solvent and then cooled to room temperature.

(B) Selectively electroplating the primed substrate

The selectively primed bars of Example 1(A) are immersed for 2 to 5 minutes in a cold chromic acid containing complex acid mixture.[1] the bars are then rinsed in running water immersed in an alkaline bath for about ½ minute to neutralize any residual acid. The bars are then immersed in a $SnCl_2$ sensitizing solution for about 1 minute wherein a readily oxidized metallic salt is adsorbed on the primed surfaces of the bars. The bars are then rinsed and immersed in a palladium activator solution for about 1 minute wherein a precious metal salt is deposited on the surface by reaction with the sensitizer. The bars are then immersed in an electroless copper solution for about 10 to 30 minutes to chemically deposit a dense conductive copper film on the primed surfaces of the bars. Finally, the bars are placed in a bright copper acid electroplating bath and a layer of about 0.5 to 1.5 mils thickness of copper is electrolytically deposited on the bars. The electroplating is carried out for about 30 minutes at a current density of 0.4 amp./sq. in.

A final plating of nickel, chromium, brass, gold or any of the other electroplatable metals may be applied in addition to the copper.

Peel tests are conducted on the four bars of polymethyl methacrylate that were selectively electroplated with copper according to Example 1 above. The peel strength is a measure of the metal-to-plastic bond strength, and is expressed in terms of the number of pounds of force per inch width required to pull the plated metal from the surface of the substrate. The peel test is carried out by cutting through the copper plating with a knife to make a strip ½ inch wide (or 1 inch wide if the test bar width permits). One end of the copper plating is raised by means of the knife blade. To facilitate peeling the metal from the bar, a ½ inch wide strip of 3M Scotch Filament Tape is pressed along the strip. The end of the strip of metal and tape is gripped in the jaws of a tensile tester and the bar is held while the strip is peeled away at an angle of 90 degrees to the surface of the bar. The crosshead is run at a speed of 1 inch per minute. The average pull in pounds is taken from the chart and the peel strength is calculated in pounds per inch of copper width. The four bars exhibited peel strengths of 7.3 lb./in., 9.3 lb./in., 7.9 lb./in. and 7.7 lb./in.

[1] The cold chromic acid containing complex acid mixture is disclosed on page 65 of the "The Iron Age," Aug. 11, 1966.

Example 2

Cellulose acetate butyrate bars are used instead of the polymethyl methacrylate bars of Example 1. The primer composition of Example 1 is applied in the same manner as in Example 1, and selectively electroplated in the same manner. The peel strength is greater than 5 lb./in. width.

Example 3

Acrylonitrile-butadiene-styrene resin bars are used as the polymeric substrate in place of the substrate in Example 2. The operations of Examples 1 and 2 are carried out in the same way. Peel strengths of greater than 5 lb./in. width and comparable with that of Example 1 are obtained.

Example 4

Polyphenylene oxide bars are substituted for the substrates of Example 3 and treated in the same fashion. Peel strengths of greater than 5 lb./in. width and comparable with that of Example 1 are obtained.

What is claimed is:

1. An article of manufacture comprising a polymeric substrate having on the surface thereof a graft or layer polymer consisting essentially of:
   (a) 15 to 75 weight percent styrene-butadiene copolymer components wherein the styrene constitutes 10 to 50 weight percent of said styrene-butadiene copolymer, and
   (b) 85 to 25 weight percent respectively of polymer components formed of a monomeric material consisting of:
      (1) 100 to 55 weight percent of methyl methacrylate, and
      (2) 0 to 45 weight percent respectively of another monoethylenically unsaturated monomer having a $H_2C{=}C<$ group,

and, superimposed on the primer layer, an electroplated layer of a metallic material.

References Cited

UNITED STATES PATENTS

2,680,695	6/1954	Judd	117—71 X
3,149,997	9/1964	Tamburro	117—138.8 X
3,152,004	10/1964	Screnock et al.	117—138.8 X
3,216,825	11/1965	Caldwell	117—138.8 X
3,224,896	12/1965	Quinn et al.	117—138.8 X
3,226,312	12/1965	Lamm et al.	117—161 X
3,305,460	2/1967	Lacy	117—71 X
2,857,360	10/1958	Feuer	260—879

FOREIGN PATENTS

728,103	2/1966	Canada.

OTHER REFERENCES

Golding, Polymers and Resins, Van Nostrand, 1959, pp. 500–501.

WILLIAM D. MARTIN, Primary Examiner

J. E. MILLER, Jr., Assistant Examiner

U.S. Cl. X.R.

117—76, 138.8, 145, 161, 160