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METAL PLATING OF PLASTICS

Trent D. Buckman, Berkeley, Calif., assignor to Shell Oil Company, New York, N.Y., a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

Organic polymer substrates are conditioned for electroless deposition of metal coatings by impregnating their surface layer to a depth of at least about 5 microns with a metal such as copper or nickel, diffused into the surface layer from solution of a complex which contains said metal in zero-valent form dissolved in an organic solvent which has a dissolving or swelling action on the plastic.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to deposition of metal on organic polymers. More particularly, it relates to a novel economical method for sensitizing thermoplastics to electroless metal deposition from chemical plating solutions. The invention also relates to the novel articles resulting from said method.

Description of the prior art

Electroless metal deposition, also called electroless or chemical metal plating, refers to chemical deposition of an adherent metal coating on a non-conductive, semiconductive or conductive substrate in the absence of an external electric source.

It is desirable for many commercial purposes to apply metal coatings to plastic surfaces, e.g., in order to provide electrically conductive surfaces or surface paths, or to provide decorative or protective coatings.

The recent state of the art is detailed in a serially published survey "Electroplated Plastics—A Comprehensive Survey of the Current Position" by W. Goldie, in "Electroplating and Metal Finishing," vol. 18, (1965) 414–417, 428 (December), and vol. 19, (1966) 3–7 (January), 49–53 (February), 97–100 (March), 133–137 (April), 185–188 (May) et seq.

Although many kinds of plastics have been metal-plated on an experimental basis, only special plating grades of ABS polymers have enjoyed substantial commercial success to date as plating substrates, apparently due to the fact that the presence of polarnitrile groups facilitates production of metal coatings having the desired degree of adhesion.

Known published and proprietary commercial methods for electroless plating of non-conductive or semi-conductive surfaces comprise a large number of separate steps, as many as 20 to 30, generally including most or all of the following: various washes to clean the substrate surface; chemical or physical treatments to provide a controlled amount of surface irregularity or roughness, or a chemical modification of the surface layer of polymer; surface treatment by immersion in an aqueous "sensitizing bath" such as acidified stannous chloride; "seeding" or "catalyzing" by immersion in an "activating bath" from which there are deposited on the thermoplastic surface catalytic nucleating centers of a metal which catalyzes the deposition of the desired metal coating—the activating bath is generally an aqueous acidified solution of a noble metal halide, e.g., of gold, platinum or palladium, which is reduced to metal by stannous ions adsorbed on the substrate or by reducing agents contained in the subsequent electroless metal deposition bath; and thereafter electroless deposition of a continuous, conducting coating of a metal such as copper, nickel or cobalt by immersing the activated substrate in an electroless plating bath containing a salt of the metal to be plated and a suitable reducing agent in aqueous solution. Articles plated in this manner can then be electroplated, if desired, by known electroplating methods, with a wide variety of metals. In commercial practice, a number of further manipulations intervene, such as controlled rinses between the treating steps.

The conventional methods summarized above have numerous disadvantages which are well known to persons skilled in the art. These methods are expensive to use, due to the need for a large number of manipulative steps and for a number of separate treating baths which may require frequent replacement. Achievement of reproducible results is difficult in such complex processes. Plating of non-polar thermoplastics by the prior art methods is particularly difficult.

SUMMARY OF THE INVENTION

An improved method for preparing metal-plated thermoplastic substrates, described and claimed in copending application Ser. No. 634,483 of Blytas et al., filed Apr. 28, 1967, comprises the steps of impregnating the surface layer of a thermoplastic article with metal diffused into the surface from solution of a salt of the metal and thereafter reducing the metal in the substrate by contact with a suitable reducing solution; the resulting article is adapted to be metal-plated by electroless deposition of metal, which may then be followed by electroplating.

The present invention provides for impregnation of thermoplastic substrates with neutral metal atoms, introduced from solution of a complex of the metal in a suitable solvent; this invention, therefore, does not require a reducing step between the impregnation step and electroless plating.

It is the principal object of this invention to provide a simplified method for conditioning thermoplastic substrates for electroless deposition of metals from conventional electroless plating solutions. A further object is to provide a simple, effective, economical method for metal-plating plastic articles. Other objects will become apparent from the following description of the invention.

The objects of this invention are achieved by the method of impregnating the surface layer of a clean thermoplastic substrate to a depth of at least about 5 microns (μ) with a metal such as nickel, diffused into the surface layer from solution of a complex containing said metal in zero-valent form, dissolved in a solvent which has a dissolving or swelling action on the thermoplastic polymer. Substrates which contain diffused metal in accordane with this invention are capable of being metal-plated by contact with electroless chemical plating solutions of the prior art, followed, if desired, by conventional electroplating of the chemically metal-plated substrate.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A typical embodiment of the invention is illustrated by the following schematic flow diagram:

(1) IMPREGNATION

Immerse a clean thermoplastic substrate in a solution of a complex of zero-valent nickel in a solvent which has dissolving or swelling action on the polymer. Control conditions to cause diffusion of metal into the polymer surface layer only. Remove from solution. Drying is optional.

(2) ELECTROLESS PLATING

Apply a continuous coating of nickel by immersing the substrate in an electroless plating solution.

The method of this invention is applicable to polymer substrates in any shape. For example, it can be employed to impregnate and coat finely divided particles of polymer, fibers or films of polymer, molded articles and extruded shapes. The method is especially adapted for plating articles of substantial thickness—e.g., 50 mils and greater. The metal impregnation affects only a few mils of the outer surface, thus leaving the bulk of the article unaffected, permitting it to retain the physical and chemical properties of the polymer, e.g., its strength and stability.

A substantial advantage of the invention is that it permits metal coating of run-of-the-mill polymers rather than requiring the use of special polymer formulations.

The process of this invention is applicable to any organic polymers which are capable of being swelled or dissolved by a solvent in which a suitable metal complex is soluble. Polymers for use in this invention may be nonconducting addition polymers or condensation polymers, and elastomeric polymers.

This invention is suitable for treating any thermoplastic polymers which are subject to being swelled or dissolved by a solvent at conditions at which a complex of a zero-valent metal can exist in the solvent-polymer system and diffuse into the thermoplastic substrate. polymers which are readily treated according to this invention are those which are subject to swelling or dissolution at relatively mild conditions at which zero-valent metal complexes tend to be most stable.

Suitable polymers comprise polyvinyl aromatic such as polystyrene and its copolymers; ABS (copolymer of acrylonitrile, butadiene and styrene); polymers and copolymers of acrylonitrile, vinyl chloride, vinylacetate, and the like; acrylic polymers such as polymethyl methacrylate; and condensation polymers such as polyesters, polyamides, and polyester amides. The method may be applied to polyolefins such as polyethylene, polypropylene and other polymers of alpha-monoolefins, provided relatively stable metal complexes are employed which do not degrade rapidly at the elevated temperatures required for impregnation of these polyolefins. Suitable elastomers comprise copolymers of butadiene and styrene (SBR), polybutadiene, rubbery ethylene-propylene copolymers (EPR) and the like provided they are capable of being swollen by a solvent.

One of the outstanding features of this invention is that it does away with the multiple sensitizing and activation solutions employed in the prior art processes for preparing non-conductive substrates for electroless plating. Instead, this process uses a relatively simple absorption of metal atoms, suitably nickel, into the surface layer of the substrate.

OPTIONAL PRETREATMENT STEPS

In general, the best plating results are obtained when there are no significant irregular internal strains in the substrates. Substrates containing internal strains due to the method of preparation are preferably first annealed, e.g., by immersion in boiling water for 24 hours, prior to any contact with solvent. Annealing is preferably carried out at a temperature within about 15° F. of the highest temperature employed in the subsequent process steps.

The substrates, prior to impregnation in accordance with this invention, should be reasonably clean. No elaborate special cleaning procedures are required.

In the case of substrates which are relatively resistant to solvent penetration, such as isotactic polypropylene, it may be of advantage to pretreat the substrate with an active solvent prior to the impregnation step. This appears to make its surface layer more receptive to the metal as well as accomplishing a simple cleansing function. Such pretreat is suitably carried out at about the same temperature and with the same solvent employed in the impregnation step, by a dip lasting a few seconds. Such pretreatment may also be accomplished by exposure to solvent vapor. Other treatments which make the substrate more receptive to impregnation or improve adhesion of the metal coating may be employed.

A heating step may intervene between the impregnation and plating steps. Such heating may be of advantage if a metal complex of relatively high stability has been employed in impregnation. Heating in such case should be at about the decomposition temperature of the complex.

THE IMPREGNATION STEP

It is essential that the impregnation bath have some solvent or swelling action on the substrate, since it is only from such a solution that the metal salt will penetrate into the surface layer.

In the impregnation step, treating conditions and solution components are selected to provide penetration of metal into the surface layer of the substrate to a depth of at least 5μ and no more than about 200μ. Preferably the depth of penetration is about $5–80\mu$. Deeper metal penetration into the substrate would provide no advantages in the process of this invention and may be of disadvantage because the more intensive solvent action required to achieve such penetration may damage the surface of the substrate, and the larger amount of metal in the polymer may affect its physical or chemical properties in an undesirable manner. Different solvents and different treating conditions may be required for different polymers.

In general, it is desirable to select the impregnation bath and conditions such that impregnation is completed in about 1⅔ minutes, preferably in from 1 second to 1 minute and most preferably in from about 5 to about 30 seconds.

COMPONENTS OF THE IMPREGNATION BATHS—SOLVENTS

Effective solvents for use in this process are those which have the required swelling or solvent action on the substrate to be impregnated and are capable of dissolving the desired metal complex in a homogeneous, single phase, liquid system at the desired treating temperature.

Typical solvents for use in this invention are aromatics such as benzene and toluene, alicyclic hydrocarbons, and substituted aromatics such as chlorobenzene or benzyl alcohol.

Mixed solvent systems are sometimes of advantage. For example, in the treatment of polystyrene it may be desirable to add from 3–50%, and suitably from 10–20%, of a polar organic compound. Such addition may permit greater latitude in the treatment of polystyrene with metal complexes. In general, polar compound which are desirable for use with aromatics in the impregnation of polystyrene are compounds which have a dielectric constant in excess of 10 and which do not attack the metal complex in the impregnating bath. Suitable compounds include propylene carbonate, ethylene carbonate and various acetals, lactones and nitriles.

For impregnation of ABS polymers from aromatic impregnating baths, it may be desirable to include an amount of a lower aliphatic nitrile, e.g., acetonitrile or propionitrile, in excess of about 1%, e.g., about 2% by weight of the solution, in benzene. Other nitriles and other aromatics can also be employed in the impregnation of ABS. Even pure nitriles can be used for ABS or other polyarylonitrile-containing polymers.

For impregnation of polymethyl methacrylate a suitable solvent composition consists of benzene with 1–2% by weight dichloroethane Other aromatics containing minor proportions of other chlorinated hydrocarbons can be employed Other solvents suitable for impregnation baths for polymethyl methacrylate include methyl methacrylate monomer and other organic esters.

COMPONENTS OF THE IMPREGNATION BATHS—METAL COMPPLEXES

The requirements for a suitable complex of zero-valent metal for use in this invention are that the complex must be soluble and reasonably stable in the impregnation bath at impregnation conditions, must be capable of diffusing into the substrate and must be sufficiently weak or else capable of decomposing or being decomposed in the substrate so that its metal atom will be available for interaction with the electroless metal plating bath

Metals which form zero-valent metal complexes that may be suitable for use in this invention are nickel, iron, chromium, cobalt, molybdenum, rhodium, palladium and platinum Complexing ligands which may be employed in producing complexes for use in this invention are phosphines, arsines, olefins, quinones, carbon monoxide and nitriles.

A typical zero-valent metal complex for use in impregnating polymers such as polystyrene or ABS in accordance with this invention is bis(cyclooctadienyl) nickel. Other illustrative complexes are cyclododecatriene nickel, diallylnickel, acrylonitrile nickel, nickel carbonyl, triphenylphosphene-cobalt complexes, cobalt carbonyl and dibenzene chromium.

It will be understood that not all metal complexes will give equally good results, due to difference in properties such as solubility relationships, diffusion rates, stability and the like.

In the event that the impregnating metal complex is sensitive to components of the atmosphere, e.g., oxygen or moisture, it is necessary to carry out the impregnation in the absence of such components, e.g., in an inert gas atmosphere.

APPLYING CONTINUOUS METAL COATING

After impregnation as described, a thin adherent continuous metal coating can be applied to the substrate by immersion in an electroless chemical plating bath.

Metals which may be applied in this manner include nickel, copper, gold, silver, cobalt, and mixtures such as nickel-copper and nickel-cobalt.

The chemically metal-coated substrate may then be subjected to electroplating in the conventional manner, either to apply a thicker coating of copper or nickel or to apply a protective or decorative coating of metals such as chromium, copper, nickel, tin, cadmium, cobalt, silver, gold, platinum-group metals etc.

Both electroless plating and electroplating are well known processes. Detailed descriptions of electroless plating and electroplating including formulations of plating baths and conditions for conducting such plating, are found in reference works such as "Modern Electroplating" by F. A. Lowenheim, John Wiley and Sons, 1963, 2nd edition, and in references cited therein. Electroless plating, including suitable formulations of plating baths for copper, nickel, silver and gold is also described by Goldie, supra, vol. 19, pp. 6–8.

A very common electroplating succession is to electroplate with "leveling copper," then with nickel, then with chromium. The thicknesses usually applied are in the order Cu>Ni>Cr.

The invention is illustrated, but is not to be considered limited by the following examples. Parts and percentages in the examples and throughout the specification are by weights unless otherwise indicated. "Room temperature" is about 25° C. The illustrative experiments are carried out, unless otherwise stated, on 2 inch by 2 inch coupons cut from about 1/8 inch thick sheet of the polymer being tested.

EXAMPLE 1

Coupons of commercial crystal grade polystyrene are dipped for 1 second in an impregnating bath consisting of about 5% bis(cyclooctadienyl) nickel in toluene at room temperature. The impregnating bath is maintained in an inert atmosphere in a "dry box." The samples are withdrawn from the bath, dried in a still nitrogen atmosphere at room temperature for a few seconds and then plated at 87° C. in a conventional electroless nickel plating bath having the following typical compositions:

	G./l.
Nickel chloride	30
Sodium glycollate	50
Sodium hypophosphite	10

A conductive continuous layer of nickel is plated out on the samples in less than 1 minute. A layer of less than one mil in thickness is sufficient. The electrolessly deposited nickel film adhered satisfactorily to the sample.

The samples may be further plated by conventional electroplating with additional nickel or other metals.

EXAMPLE 2

Samples of commercial ABS polymer, both of a plating grade and of a non-plating grade, are impregnated by being immersed for about 1 second in a solution of about 5% of bis(cyclooctadienyl)nickel in toluene containing 2–5% acetonitrile. The procedure of Example 1 is then repeated. A satisfactory nickel plating is deposited on the samples.

What is claimed is:

1. A method of producing a metal-coated article of an organic polymeric composition selected from the group consisting of polyvinyl aromatic polymers and copolymers; copolymers of acrylonitrile, butadiene and styrene; polymers and copolymers of acrylonitrile or vinyl chloride and of vinyl acetate; acrylate polymers; polyesters; polyamides; polyesteramides; polyolefins; and elastomeric hydrocarbon polymers; comprising the steps of impregnating a substrate of said polymeric composition to a depth in the range from 5 to 200 microns with a metal selected from the group consisting of nickel, iron, chromium, cobalt, molybdenum, rhodium, palladium, and platinum, by contact of said substrate with a solution of a zero-valent complex of said metal in a solvent capable of exerting a swelling or dissolving action on said substrate, and coating the resulting metal-containing substrate with a metal by contact with an electroless chemical plating bath.

2. The method of plating an article of an organic polymeric composition selected from the group consisting of polyvinyl aromatic polymers and copolymers; copolymers of acrylonitrile, butadiene and styrene; polymers and copolymers of acrylonitrile or vinyl chloride and of vinyl acetate; acrylate polymers; polyesters; polyamides; polyesteramides; polyolefins; and elastomeric hydrocarbon polymers; said article being at least 50 mil in thickness, which comprises:

(a) contacting the surface of said article which is to be plated with an impregnating solution comprising a zero-valent complex of a metal selected from the group consisting of nickel, iron, chromium, cobalt, molybdenum, rhodium, palladium and platinum, dissolved in a solvent capable of exerting a swelling or dissolving action on said polymeric composition, until said metal has penetrated the surface of said article to a depth of from 5 to 200 microns;

(b) removing the article from contact with said solution; and

(c) immersing the washed article in an electroless plating solution, whereby a metal coating is deposited on said surface.

3. The method according to claim 2 wherein:

said polymeric composition is predominantly polystyrene;

said impregnating solution comprises essentially a complex of zero-valent nickel in an aromatic hydrocarbon solvent;

said contact with impregnating solution takes place at about room temperature and lasts no more than 10 seconds;

said electroless plating solution is a nickel-plating solution.

4. The method according to claim 3 wherein said complex is bis(cyclooctadienyl) nickel.

5. The method according to claim 2 wherein:

said polymeric composition is predominantly a copolymer of acrylonitrile, butadiene and styrene, and

said impregnating solution comprises essentially a com-

plex of zero-valent nickel in a solvent comprising from 1 to 100% by weight of a lower aliphatic nitrile admixed with from 99 to 0% of aromatic hydrocarbons.

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MURRAY KATZ, Primary Examiner

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