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METAL PLATING OF PLASTICS

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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 salt of said metal in an organic solvent which has a dissolving or swelling action on the plastic, followed by reduction in situ by means of contact with a reducing solution.

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, including non-polar crystalline plastics such as polyolefins, 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, semi-conductive or conductive substrate in the absence of an external electric source.

It is desirable for many commercial purposes to apply metal coatings to thermoplastic 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 present of polar nitrile 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

It is the principal object of this invention to provide a simplified method for conditioning thermoplastic substrates, including non-polar ones such as polyolefins, 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 copper or nickel, diffused into the surface layer from solution of a salt of said metal in a solvent which has a dissolving or swelling action on the thermoplastic polymer. The diffusion step is followed by contacting the substrate with a reducing solution capable of reducing cations of metal in the substrate surface layer to zero valence. Substrates which contain diffused metal in accordance 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 salt of copper or nickel in a solvent which has dissolving or swelling action on the polymer. Control conditions to cause diffusion of metal salt into the polymer surface layer only.

(2) Drying

Dry the treated substrate.

(3) Reduction

Reduce at least part of the metal ions in the substrate to zero valence by immersing the dried substrate in a reducing solution at reducing conditions.

(4) Washing

Remove remaining reducing solution by suitable wash, e.g., water.

(5) Electroless plating

Apply a continuous coating of copper or 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 an organic polymers which are capable of being swelled or dissolved by a solvent in which a suitable metal salt is soluble. Polymers for use in this invention include non-conducting thermoplastic addition polymers or condensation polymers, and elastomeric polymers.

This invention is of particular advantage in the plating of polymers which contain no polar groups, because these are particularly difficult to plate by known methods. The method of this invention is thus particularly advantageous in the plating of polyolefins such as polyethylene, polypropylene, and stereoregular polymers of higher olefins. Other suitable polymers comprise polyvinyl aromatics such as polystyrene and its copolymers; ABS (copolymer of acrylonitrile, butadiene and styrene); polymers and copolymers of acrylonitrile, vinyl chloride, vinyl acetate, and the like; acrylic polymers such as polymethyl methacrylate; and condensation polymers such as polyesters, polyamides, and polyester amides. 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 a metal salt, preferably of copper, into the surface layer of the substrate, followed by reduction to convert at least part of the metal ions to zero valence.

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. For example, in the case of polypropylene articles of ⅛ inch thickness containing some irregular strains, annealing in boiling water for 24 hours, prior to any contact with solvent, resulted in coating of improved evenness. Annealing is preferably carried out at a temperature within about 15° F. of the highest temperature employed in the subsequent processing 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 salt, as well as accomplising 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. For example, pretreating polypropylene with 50% aqueous sulfuric acid appeared to result in some improvement in the peel strength of the final product, as illustrated in Example 6.

The impregnation step and optional pretreating steps

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 salt into the surface layer of the substrate to a depth of at least 5μ and no more than about 200μ. Preferably the depth of penertation is about 5–80μ. 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.

It will be readily apparent that different solvents and different treating conditions will be required for different polymers. For example, impregnation of polystyrene can be readily accomplished by immersion for about 10 seconds or less at room temperature in a bath containing 20–25% w. of a suitable copper salt (cuprous trifluoroacetate) in benzene. Impregnation of polypropylene requires more severe conditions, e.g., immersion for about 30 seconds at 100–110° C. in a bath containing 8–15% w. of the same copper salt in xylene.

For best results, polypropylene impregnation should be carried out from an aromatic solvent bath at a temperature of at least about 110° C., suitably at from 110°–115° C.

In general, it is desirable to select the impregnation bath and conditions such that impregnation is completed in less than about 1⅔ minutes, preferably in less than 1 minute and more preferably in from about 5 to about 30 seconds. Suitable impregnating baths generally contain impregnating metal ions such as Cu^{+} or Cu^{++} in solution in concentrations from about 2% wt. to the upper solubility limit, or to about 20% wt. Relatively high concentrations of metal salt—e.g., saturated solutions—are preferred for the impregnation of easily solvent-attacked polymers such as polystyrene. Such high salt concentrations permit quick introduction of the desired amount of metal into the polymer surface layer and also desirably reduce the solvent-activity of the liquid. For less readily solvent-attacked polymers, such as polypropylene, it has been found desirable to employ lower metal salt concentrations in the impregnation step, e.g., from 5–16% metal, unless the polymer has been given a solvent-pretreat as described below, in which case relatively high metal salt concentrations are also suitable.

The impregnation step is desirably controlled to produce at least about 0.02 gram of metal per square foot of treated surface and preferably about 0.08 gram per square foot. Amounts of about 0.25 g./ft.^{2} are satisfactory and the suitable range extends to 0.5 g./ft.^{2}. More metal may be introduced but is generally not required.

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 compound in a homogeneous, single phase, liquid system at the desired treating temperature.

Typical solvents for use with polystyrene are aromatics such as benzene and toluene, or substituted aromatics such as chlorobenzene or benzyl alcohol.

Solvents suitable for impregnation baths for polypropylene comprise aromatics and other cyclic hydrocarbons which remain liquid at the treating temperature of at least about 100° C., e.g., toluene, xylene, tetrahydronaphthalene and decahydronaphthalene; benzene could be employed under sufficient pressure to keep it liquid at the treating temperature.

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 has been found to permit greater latitude in the treatment of polystyrene with salts such as cuprous trifluoroacetate. In general, polar compounds 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 reduce the metal salt 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 was found 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 salts

The requirements for a suitable metal salt for use in this invention are that the salt must be soluble in the impregnation bath, capable of diffusing into the substrate, and capable of being reduced in the substrate to zero valence.

Preferred for use in the invention are organic cuprous and cupric salts. Also useful are salts of nickel, silver and cobalt.

A group of copper salts which are particularly useful are the fluoro- or oxy-cuprous salts of the general formula CuXA, wherein the moiety XA represents an anion in which X is an oxygen or fluorine atom and A is the remainder of the anion. In general, the anions of these salts are inorganic, organic or organo-inorganic acids, having equivalent weights of no more than about 1000 and preferably no more than 200. Representative suitable anions comprise fluoro-substituted carboxylates, e.g., trifluoroacetate; sulfate; benzene sulfonate; ethylsulfonate; fluorosulfonate; nitrate, difluorophosphate and acid phosphates; diamino phosphate, perfluoroborate; hexafluorophosphate; hexafluoroantimonate, and chloroalanate; these cuprous salts tend to disproportionate under the influence of moisture; the salts and their solutions must be handled in the absence of contact with the atmosphere or with water.

Other suitable copper salts are cuprous salts of carboxylic acids, e.g., cuprous formate, acetate, lactate, benzoate, salicylate and di-tert. butyl salicylate. Cuprous chloride has been successfully employed in propionitrile solution in the impregnation of ABS polymer.

Other suitable copper salts are cupric salts of carboxylic acids, e.g., the naphthenate, undecylenate, oleate, salicylate, and the di-tert. butyl salicylate.

Among the cuprous and cupric carboxylates, those of acids having an olefinic or aromatic group are preferred.

It will be understood that not all salts will give equally good results, due to difference in properties such as solubility relationships, diffusion rates, ease of reduction, relative ease of being leached out of the substrate and the like.

In the event that the impregnating metal salt is sensitive to components of the atmosphere, e.g., oxygen or moisture, it is necessary to carry out the first part of the process, from impregnation through reduction, in the absence of such components, e.g., in an inert gas atmosphere.

If desired, a rinse may be interposed between the impregnation and drying steps, suitably utilizing the same solvent as is employed in the impregnation bath.

The drying step

The drying step is not critical. Its purpose is to remove solvent which adheres to and which may be sorbed in or on the substrate, so that it will not interfere with the following reducing bath. Conditions to accomplish this may differ for different polymers and solvents, but are readily determined. For example, very short drying periods, e.g., 10–60 seconds at room temperature and atmospheric pressure, are sufficient for polystyrene impregnated with a benzene solution of cuprous trifluoroacetate, while longer periods, e.g., 4 to 15 minutes at room temperature and atmospheric pressure, or a short exposure to vacuum or to a hot gas stream, are preferred for polypropylene impregnated with a xylene solution of the same salt.

The reduction step

The components of the reducing solution and the conditions in the reduction step are selected to provide controlled reduction of at least a substantial part of the metal salt in the surface layer of the substrate to zero valence. It is not necessary to achieve complete reduction of all the metal salt in the substrate.

Components of the reducing bath

The solvent employed in the reducing bath should be relatively inert to the substrate, since relatively long contact times are generally required. The reducing agent should be sufficiently strong and present in sufficient concentration to reduce at least a substantial part of the metal ions in the substrate to zero valence.

The ease of reducibility of the particular salt impregnated in the substrate and the strength of bonding between the salt and substrate will affect the selection of suitable reducing agents.

The reducing bath is usually capable of dissolving the metal salt being reduced and is therefore capable of leaching metal salt out of the substrate. In relatively polar substrates, e.g., polystyrene, there is sufficient bonding between the substrate and the metal salt to prevent substantial leaching during the reducing step. In non-polar substrates, such as polypropylene, it is important to control conditions during reduction so as to prevent excessive leaching before the desired amount of reduction has taken place in the substrate. This can be accomplished by adopting relatively drastic reduction conditions, for example, higher temperature and higher concentration, at which reduction occurs faster than leaching. For example, reduction in polystyrene is satisfactory using 2–3% w. hydrazine in isopropyl alcohol at 25° C., while reduction in polypropylene is preferably carried out at about 60° C. with 4–8% hydrazine in isopropyl alcohol.

A preferred reducing agent for use in this invention is hydrazine (N_2H_2). Others which have been successfully employed to reduce cuprous salts in substrates are aluminum triisopropyl and benzaldehyde. Other reducing agents can be selected from those kown in the art, e.g., those described in "Electroless Copper Plating" by E. B. Saubestre in Proceedings of the American Electroplaters Society, vol. 46, pp. 264–276 (1959).

A preferred solvent for the hydrazine reducing bath is anhydrous isopropyl alcohol. Hydrazine may also be employed in propylene carbonate, water, or other solvents which do not attack the hydrazine or the substrate.

Washing

On completion of the reduction step, the article is removed from the reducing bath and rinsed or washed to remove any adhering or sorbed components which might interfere with the following plating bath. In most cases water is a suitable wash or rinse medium. It may be deionized or distilled; two or more successive washes or rinses may be employed, as required to remove potential plating contaminants to the desired extent.

Applying continuous metal coating

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

For practical reasons, copper is usually the preferred metal applied by electroless coating; nickel is next preferred. Nickel requires much higher temperatures (80° C. or more) for electroless plating. Copper is deposited at room temperature. Also, copper is solderable which is important, for example, in electronic applications. Other metals which may be applied in this manner include 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.

EXAMPLES

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 weight 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 ⅛ inch thick sheet of the polymer being tested.

An indication of the effectiveness of the plating is the "peel strength" of the plate, which is determined on samples which have been coated to a total thickness of about 3 mil with ductile copper. The peel strength test employed in these examples consisted of placing the sample in a special jig on an Instron tensile testing machine and pulling a 1 inch wide strip of the metal layer at an angle of 90° from the surface, utilizing a cross-head speed of 1 inch per minute. Peel strength is reported in pounds per inch of width (lbs./in.).

Example 1

Coupons of commercial high impact polystyrene containing a small amount of SBR (conventional styrene-butadiene rubber) are dipped in an impregnating bath consisting of 25% cuprous trifluoroacetate in benzene at room temperature. The samples are withdrawn from the bath, dried in a still nitrogen atmosphere at room temperature for 30 seconds and then immersed for 10 minutes in a 3% solution of hydrazine in anhydrous isopropyl alcohol at room temperature. The samples are withdrawn from the reducing bath, washed three times with distilled water, and then plated in a conventional electroless bath having the following typical compositions:

	G./l.
$CuSO_4$	3.3
HCHO	8
NaOH	4
Rochelle salt	17
Na_2CO_3	1.6
$NiCl_2$ (optional)	1.5

The samples are kept in the electroless plating bath until at least a conductive continuous layer of copper has been plated out. A layer of less than one mil in thickness is sufficient. The samples may then be further plated by conventional electroplating with additional copper or other metals.

Samples prepared as above, electroplated with copper to 3 mil total thickness, have a plating peel strength of about 5 lbs./in.

Example 2

The procedure of Example 1 is repeated except that the impregnation bath consists of 25% cuprous trifluoroacetate in a mixed solvent of 80% benzene and 20% propylenecarbonate.

Samples produced utilizing this impregnation bath have an improved plating peel strength, in the range of 6–8 lbs./in.

Example 3

Substituting coupons of crystal grade polystyrene for the high impact polystyrene in Examples 1 and 2 results in plated articles having a plating peel strength of ½ to 1 lb./in. less in each case.

Example 4

Coupons of commercial isotactic polypropylene are immersed in a 10% solution of cuprous trifluoroacetate in xylene in 110° C. for 30 seconds. The samples are withdrawn and maintained 5 to 10 minutes in a still nitrogen atmosphere at room temperature. The dry samples are immersed at 60° C. for at least 5 minutes in a reducing bath consisting of 5% hydrazine in isopropyl alcohol. The samples are then washed three times with water and plated in the manner described in Example 1.

The peel strength of the plating of the samples is 5 lbs./in.

Example 5

Samples of commercial isotactic polypropylene are immersed in a xylene bath at 100° C. for 30 seconds to one minute. The samples are then impregnated and further treated as in Example 4. The plating peel strength of the resulting products is over 5 lbs./in.

Pretreating the samples in xylene permits successful impregnation with an impregnating bath having a higher concentration of cuprous trifluoroacetate, e.g., 15–20% than that desirable for the procedure of Example 4. Substituting such a more concentrated impregnating bath for that of Example 4 results in still further improvement in peel strength of the plated polypropylene.

Example 6

Samples of commercial isotactic polypropylene are pretreated by immersion in 50% aqueous sulfuric acid at 80° C. for about one minute. The samples are then washed with water to remove adhering acid completely, and are further treated by the procedure of Example 4. The resulting plated polypropylene has peel strengths in the range of 5–6 lbs./in.

Example 7

In the plating of polystyrene according to the general procedure of Example 1, the impregnating and reducing baths are replaced, respectively, with a saturated solution of cupric naphthenate and 5 to 8% w. solution of hydra-

zine in anhydrous isopropyl alcohol. The samples are maintained in the reducing bath for about 20 minutes at room temperature or for about 10 minutes at about 45–50° C. The plated samples have peel strengths in excess of 2 lbs./in.

Example 8

Samples of commercial ABS polymer, both of a plating grade and of a non-plating grade, are impregnated by being immersed for 5 to 10 seconds in a solution of 10% w. cuprous chloride in acetonitrile. The samples are dried for 3 to 5 minutes in a still nitrogen atmosphere at room temperature and then immersed in a reducing solution of 2–3% hydrazine in isopropyl alcohol. The samples are then washed three times with distilled water and plated according to the procedure of Example 1. The plated samples have plating peel strengths of over 2 lbs./in. Similar results are obtained with samples impregnated with 10% cuprous trifluoroacetate in benzene containing 2% acetonitrile.

Omission of acetonitrile from the plating bath results in insufficient impregnation under otherwise identical conditions.

Example 9

Samples of commercial polymethyl methacrylate are impregnated, being immersed for about 60 seconds in a bath consisting of 20% cuprous trifluoroacetate in benzene containing 2% ethylene dichloride. The samples are withdrawn, dried in a still nitrogen atmosphere for at least 30 seconds and immersed in a reducing bath of 2–4% hydrazine for 10–20 minutes. The samples are then washed three times with water and plated according to the procedure of Example 1. The peel strength of the plating is more than 2 lbs./in. Similar results are obtained with an impregnating solution of 20% cuprous trifluoroacetate in methyl methacrylate.

Example 10

A strip of styrene-butadiene rubber is successfully plated with flexible copper plating by following the procedure of Example 1, except for substitution of 5–10% aqueous N_2H_2 solution as the reduction bath.

Example 11

Injection molded 2½ inch x 2½ inch x ⅛ inch plaques are prepared from isotactic polypropylene and from blends of isotactic polypropylene with 20% SBR (conventional styrene-butadiene rubber containing 23.5% styrene) and with 17% rubbery polyisobutylene, respectively. The samples are annealed 12 to 24 hours in boiling water. The samples are then dried, dipped about 10 seconds in reagent grade xylene at 110° C., removed and dipped 5 seconds in an impregnation bath consisting of 30% w. solution of cupric undecylenate in xylene, at 110° C. The samples are withdrawn from the impregnation bath, allowed to dry in air at room temperature, and then immersed 30 minutes in a reducing bath consisting of 6% hydrazine in anhydrous isopropyl alcohol. They are withdrawn from the reducing bath and washed several minutes in running water at 40° to 50° C. to remove reducing agent and any loose copper particles, and then placed in a chemical copper plating bath such as that of Example 1. Conductive coatings are deposited in less than 2 hours of immersion. The samples are then electroplated with ductile copper to a total thickness of 3 mils and the peel strength determined. Peel strengths are in the range from 5 to 6 lbs./in.; samples of the SBR-containing compositions generally have somewhat higher peel strengths than samples of 100% polypropylene, while polyisobutylene-containing compositions show no improvement in peel strength over straight polypropylene.

We claim:

1. A method of producing a metal-coated article of organic polymeric composition, comprising the steps of

(a) impregnating a metal-free substrate of said polymeric composition to a depth of 5 to 200 microns with a reducible copper salt by contact of said substrate with a solution of 2 to 20% by weight of said salt in an organic solvent capable of exerting a swelling or dissolving action on said substrate;

(b) reducing at least a substantial proportion of metal cations in the resulting impregnated substrate to zero valence; and

(c) coating the resulting metal-containing substrate with a metal by contact with an electroless chemical plating bath.

2. A method of plating an article of organic polymeric composition, at least 50 mil in thickness, which comprises:

(a) contacting the surface of said article which is to be plated and which is metal-free with an impregnating solution comprising 2 to 20% by weight of reducible copper salt dissolved in an organic solvent capable of exerting a swelling or dissolving action on said polymeric composition, until said salt has penetrated the surface of said article to a depth of from 5 to 200 microns;

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

(c) contacting the impregnated article with a reducing solution adapted to reduce the metal ions of said salt in said polymeric composition until at least a substantial part of said metal ions has been reduced to zero valence;

(d) removing the article from contact with said reducing solution and washing off adhering solution;

(e) and thereafter 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 impregnating solution consists essentially of an aromatic hydrocarbon solvent and an organic cuprous or cupric salt capable of dissolving in said solvent and of diffusing into said polymeric composition.

4. The method according to claim 3 wherein said metal salt is selected from the group consisting of fluorocuprous and oxycuprous salts having the formula CuXA, wherein X is an oxygen or fluorine atom and A is an anion of an organic acid having an equivalent weight no more than 1000, and cuprous and cupric salts of carboxylic acids having an olefinic or aromatic group.

5. The method according to claim claim 2 wherein

said polymeric composition is predominantly polystyrene;

said impregnating solution comprises essentially a reducible organic copper salt and an aromatic hydrocarbon solvent;

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

said reducing solution comprises essentially hydrazine and an inert solvent; and

said contact with reducing solution takes place at about room temperature.

6. The method according to claim 5 wherein said impregnating solution consists of a reducible organic copper salt, an aromatic hydrocarbon solvent, and from 3 to 50% of a polar organic compound having a dielectric constant greater than 10 which does not reduce the copper salt in the impregnating bath.

7. The method according to claim 5 wherein said impregnating solution consists of a reducible organic copper salt in benzene containing from 10 to 20% by weight of ethylene carbonate or propylene carbonate.

8. The method according to claim 5 wherein said impregnating solution consists of from about 20% to 25% by weight of cuprous trifluoroacetate in benzene, and said reducing solution consists of about 2% to about 3% by weight of hydrazine in isopropyl alcohol.

9. The method according to claim 2 wherein

said polymeric composition is predominantly polypropylene;

said impregnating solution comprises essentially a reducible organic copper salt and an aromatic hydrocarbon solvent;

said contact with impregnating solution takes place at a temperature of at least about 100° C. and lasts from 5 to 100 seconds;

said reducing solution comprises essentially hydrazine in an inert solvent; and

said contact with reducing solution takes place at a temperature of at least about 60° C.

10. The method according to claim **9** wherein said impregnating solution consists of from about 8% to about 15% cuprous trifluoroacetate in xylene and said reducing solution consists of about 4% to about 8% by weight hydrazine in isopropyl alcohol.

11. The method according to claim **9** wherein, immediately prior to said contact with impregnating solution, said surface which is to be plated is contacted at a temperature of at least about 100° C. with an aromatic hydrocarbon solvent.

12. The method according to claim **11** wherein said contact with said impregnating solution takes place at a temperature of at least 110° C.

13. 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 reducible organic copper salt in a solvent comprising from 1 to 100% by weight of a lower aliphatic nitrile admixed with from 99 to 0% of aromatic hydrocarbons.

14. The method according to claim **2** wherein

said polymeric composition is predominantly polymethyl methacrylate and

said impregnating solution comprises essentially a reducible organic copper salt in a solvent comprising a major proportion of aromatic hydrocarbon and a minor proportion of a chlorinated hydrocarbon.

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U.S. Cl. X.R.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,524,754 Dated August 18, 1970

Inventor(s) George C. Blytas-Edward R. Bell-Robert S. Slott

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

In the heading, the name of the patentee SLOTT is corrected to read "ROBERT S. SLOTT".

SIGNED AND SEALED NOV. 3, 1970

SIGNED AND
SEALED
NOV. 3, 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents