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METHOD OF PLATING POLYARYLENE POLYETHERS, POLYCARBONATE OR POLYHYDROXYETHERS AND THE RESULTING ARTICLES

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Continuation-in-part of applications Ser. No. 481,402, Aug. 20, 1965, and Ser. No. 528,608, Feb. 18, 1966. This application July 14, 1966, Ser. No. 565,109
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U.S. Cl. 29—195 22 Claims

ABSTRACT OF THE DISCLOSURE

Method of preparing a thermoplastic polymeric surface from the group of polyarylene polyethers, polycarbonates or polyhydroxyethers by treatment with a fluid from the group of N,N-dimethylformamide, pyridine and substituted pyridine compounds or alkylene glycols having a particular solubility parameter of 8.7 to 10.7. The N,N-dimethylformamide may be applied in gas or vapor form. The metal plated polymer will exhibit a peel strength of greater than 5 lbs. per inch. The metal coatings may be chromium, nickel or copper.

This application is a continuation-in-part of applications Ser. No. 481,402, filed Aug. 20, 1965, and Ser. No. 528,608, filed Feb. 18, 1966, both now abandoned.

This invention relates to method for metal-plating aromatic polymers, to products produced thereby and, in particular to metal-plated articles of thermoplastic polyarylene polyethers characterized by excellent thermal properties.

Metallic coatings on engineering plastics such as polycarbonates, polyhydroxyethers and polyarylene polyethers have been used for electrical and decorative purposes as, for example, in printed circuit boards and ornamental decorations. Recently, there has been increasing commercial interest in functional uses, i.e., applications wherein metal coated plastic parts can replace all-metal parts. In addition to being more economical to manufacture, such metal coated plastic parts are superior to all-metal parts in many important respects. For example, chromium-plated plastics are more weather-resistant than chromium-plated metals since the plastic substrate is inherently non-corrosive; moreover, considerable weight can often be saved while still retaining a metallic appearance and feel.

In order to realize these advantages, however, it is necessary to provide a high level of adhesion between the metal coating and the engineering plastic substrate. If the requisite high level of adhesion is not obtained, the metal coating can blister or peel from the plastic substrate either when subjected to variations in temperature, due to the difference in thermal coefficient of expansion between metal and plastic, or to small strains, due to the difference in elastic modulus. It has heretofore been empirically established in the plating art that a minimum peel strength of about 5 pounds per inch is required to prevent this type of failure in most applications of metal-plated plastic parts.

The methods currently employed for depositing metal coatings on engineering plastic substrates usually involve the use of several treating and plating baths. Generally, the plastic substrate is first "conditioned" or treated in a strong oxidizing solution, e.g., chromic acid/sulfuric acid, and then "sensitized" in a solution of a reducing agent, e.g., stannous chloride. The substrate is thereafter "activated" by immersion in a dilute solution of a noble metal salt, e.g., palladium chloride, and then transferred

to a so-called "electroless plating" bath wherein the substrate receives a sufficiently conductive metal coating to permit subsequent electroplating by the conventional methods used for standard metal parts. Electroless plating solutions are metastable solutions of a metal salt, e.g., copper, nickel and the like, and a reducing agent, e.g., formaldehyde, hypophosphite, sodium borohydride, and the like, in which reduction of the metal ion is inhibited by complexing agents such as ammonia, hydroxycarboxylic acids, and the like. The primary purposes of the pre-treatments are to improve the metal-to-plastic adhesion and to assure that the deposition of metal from the electroless plating solution occurs on the surface of the plastic substrate in preference to the walls of the plating bath.

The basic problem, however, which arises when metal deposition techniques such as described hereinabove are applied to currently available plastic substrates is that low adhesion values are generally obtained. Typical metal to polymer adhesions are shown in Table I below.

Table I

Polymer:	Peel strength (lbs./in.)
Acetal	0.5
Acrylic	1.5
Polystyrene (high impact)	0.8
ABS—Standard grades	0.8–2.5
ABS—Plating grade	5.0–10.0

Thus, it can be seen that only one plastic resin—ABS (acrylonitrile/butadiene/styrene)—has heretofore been able to meet the generally accepted minimum application requirement of 5 pounds per inch peel strength.

The present invention provides metal-plated engineering plastic substrates exhibiting a minimum peel strength of at least about 5.0 pounds per inch, and preferably at least about 8.0 pounds per inch.

In a preferred embodiment, the present invention provides a metal-plated article of thermoplastic polyarylene polyether, preferably exhibiting a minimum peel strength of at least about 5 pounds per inch, capable of being used in applications which involve exposure to elevated temperature for short or prolonged periods of time. Such metal-plated polyarylene polyether articles are useful as plumbing fixtures such as faucets and the like, capable of conveying and handling extremely hot fluids without ill effect, as printed circuits capable of being used at temperatures as high as 149° C. and higher without effect to the electrical properties of the circuit, as a reflector in searchlights and projectors capable of withstanding elevated temperatures for prolonged periods of time, and the like. In addition, the metal-plated polyarylene polyether articles of this invention have excellent resistance to environmental attack by virtue of the superior physical properties of the polyarylene polyether substrate and the added resistance gained from the metal-plated covering. As such, the metal-plated polyarylene polyether articles of this invention can be used as automotive carburetors having the capability of resisting attack by motor fuels and physical distortion at temperatures generated in the use of carburetors.

Broadly, the process of this invention for improving the adhesion of metal platings to plastic substrates comprises the steps of treating aromatic polymers such as polyarylene polyethers, polycarbonates, polyhydroxyethers and the like with a fluid that promotes microscopic etching or crazing and submicroscopic alteration of the polymer surface which increases the surface area thereby increasing the number of polar sites, and thereafter metal-plating the so-treated polymer in the conventional manner as above described by conditioning (which step produces the microscopic etching or crazing and submicroscopic alteration), sensitizing, activating,

electroless plating and, finally, electroplating. The term "fluid" is intended to include both liquids and vapors.

The metal-plated plastic substrates or articles of this invention include metal-plated polyarylene polyethers and metal-plated aromatic polymeric substrates exhibiting a minimum peel strength of at least about 5.0 pounds per inch and preferably at least 8.0 pounds per inch.

In a preferred embodiment the adhesion of metal platings to thermoplastic polyarylene polyether substrates is improved by treating these polymers with vapors of N,N-dimethylformamide (DMF) prior to metal-plating as described above. The DMF vapors promote microscopic etching or crazing and submicroscopic alteration of the polymer surface and eliminate certain problems encountered in treating with liquid DMF. For instance, polymer specimens do not have to be heat annealed before treating with DMF vapor, whereas with liquid DMF the specimens have to be heat annealed to prevent cracking during the treatment. The necessity to rinse specimens after treating with liquid DMF is eliminated. In metal plating with a liquid DMF pretreatment, maximum adhesion, as evidenced by peel strength, is not developed upon plating but after a period of time, for example 24 hours. In using DMF vapor, maximum adhesion is obtained shortly after plating. Lastly, the time for treating with DMF vapor is approximately one-half that required when treating with liquid DMF.

Polyarylene polyethers used in the present invention are linear thermoplastic polymers having a basic structure composed of recurring units having the formula:

$$—O—E—O—E'—$$

wherein E is the residuum of the dihydric phenol and E' is the residuum of the benzenoid compound having an inert electron withdrawing group in at least one of the positions ortho and para to the valence bonds, and where both of said residua are valently bonded to the ether oxygens through aromatic carbon atoms.

The residua E and E' are characterized in this manner since they are conveniently prepared by the reaction of an alkali metal double salt of a dihydric phenol and a dihalobenzenoid compound having an electron withdrawing group as is described more fully herein.

The residuum E of the dihydric phenol can be, for instance, a mono-nuclear phenylene group as results from hydroquinone and resorcinol, or it may be a di- or polynuclear residuum. The residuum E can also be substituted with other inert nuclear substituents such as halogen, alkyl, alkoxy and like inert substituents.

It is preferred that the dihydric phenol be a weakly acidic dinuclear phenol such as, for example, the dihydroxy diphenyl alkanes or the nuclear halogenated derivatives thereof, which are commonly known as "bisphenols," such as, for example, the 2,2-bis-(4-hydroxyphenyl)propane, 1,1 - bis - (4-hydroxyphenyl)-2-phenylethane, bis - (4 - hydroxyphenyl)methane, or the chlorinated derivatives containing one or two chlorines on each aromatic ring. Other suitable dinuclear dihydric phenols are the bisphenols of a symmetrical or unsummetrical joining group as, for example, ether oxygen (—O—), carbonyl (—CO—), sulfide (—S—), sulfone ($—SO_2—$), or hydrocarbon residue in which the two phenolic nuclei are joined to the same or different carbon atoms of the residue such as, for example, the bisphenol of acetophenone, the bisphenol of benzophenone, the bisphenol of vinyl cyclohexene, the bisphenol of α-pinene, and the like bisphenols where the hydroxyphenyl groups are bound to the same or different carbon atoms of an organic linking group.

Such dinuclear phenols can be characterized as having the structure:

$$HO(\overset{(Y)_r}{\underset{|}{Ar}}—R—\overset{(Y_1)_z}{\underset{|}{Ar}})OH$$

wherein Ar is an aromatic group and preferably is a phenylene group, Y and Y_1 can be the same or different inert substituent groups as alkyl groups having from 1 to 4 carbon atoms, halogen atoms, i.e. fluorine, chlorine, bromine, or iodine, or alkoxy radicals having from 1 to 4 carbon atoms, r and z are integers having a value of from 0 to 4, inclusive, and R is representative of a bond between aromatic carbon atoms as in dihydroxydiphenyl, or is a divalent radical, including for example, inorganic radicals as —CO—, —O—, —S—, —S—S—, $—SO_2—$, and divalent organic hydrocarbon radicals such as alkylene, alkylidene, cycloadiphatic, or the halogen, alkyl, aryl or like substituted alkylene, alkylidene and cycloaliphatic radicals as well as alkalicyclic, alkarylene and aromatic radicals and a ring fused to both Ar groups.

Examples of specific dihydric polynuclear phenols include among others: the bis-(hydroxyphenyl)alkanes such as

2,2-bis-(4-hydroxyphenyl)propane,
2,4'-dihydroxydiphenylmethane, bis-(2-hydroxyphenyl)methane,
bis-(4-hydroxyphenyl)methane,
bis-(4-hydroxy-2,6-dimethyl-3-methoxyphenyl) methane,
1,1-bis-(4-hydroxyphenyl)-ethane,
1,2-bis-(4-hydroxyphenyl)ethane,
1,1-bis-(4-hydroxy-2-chlorophenyl)ethane,
1,1-bis-(3-methyl-4-hydroxyphenyl)propane,
1,3-bis-(3-methyl-4-hydroxyphenyl)propane,
2,2-bis-(3-phenyl-4-hydroxyphenyl)propane,
2,2-bis-(3-isopropyl-4-hydroxyphenyl)propane,
2,2-bis-(2-isopropyl-4-hydroxyphenyl)propane,
2,2-bis-(4-hydroxynaphthyl)propane,
2,2-bis-(4-hydroxyphenyl)pentane,
3,3-bis-(4-hydroxyphenyl)pentane,
2,2-bis-(4-hydroxyphenyl)heptane,
bis-(4-hydroxyphenyl)phenylmethane,
2,2-bis-(4-hydroxyphenyl)-1-phenylpropane,
2,2-bis-(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane

and the like;

Di(hydroxyphenyl)sulfones such as bis-(4 - hydroxyphenyl)sulfone, 2,4' - dihydroxydiphenyl sulfone, 5'-chloro-2,4'-dihydroxydiphenyl sulfone, 5'-chloro-4,4'-dihydroxydiphenyl sulfone, and the like;

Di(hydroxyphenyl)ethers such as bis - (4 - hydroxyphenyl)ether, the 4,3'-, 4,2'-, 2,2'-, 2,3'-dihydroxydiphenyl ethers, 4,4'-dihydroxy-2,6-dimethyldiphenyl ether, bis - (4 - hydroxy - 3 - isobutylphenyl)ether, bis - (4-hydroxy - 3 - isopropylphenyl)ether, bis - (4-hydroxy-3-chlorophenyl)ether, bis-(4-hydroxy-3-fluorophenyl)ether, bis-(4-hydroxy-3-bromophenyl)ether, bis - (4 - hydroxynaphthyl)ether, bis-(4 - hydroxy-3-chloro-naphthyl)ether, 4,4'-dihydroxy-3,6-dimethoxydiphenyl ether, 4,4' - dihydroxy-2,5-diethoxydiphenyl ether, and like materials.

It is also contemplated to use a mixture of two or more different dihydric phenols to accomplish the same ends as above. Thus when referred to above the E residuum in the polymer structure can actually be the same or different aromatic residua.

As used herein, the E term defined as being the "residuum of the dihydric phenol" refers to the residue of the dihydric phenol after the removal of the two aromatic hydroxyl groups. Thus it is readily seen that polyarylene polyethers contain recurring groups of the residuum of the dihydric phenol and the residuum of the benzenoid compound bonded through aromatic ether oxygen atoms.

The residuum E' of the benzenoid compound can be from any dihalobenzenoid compound or mixture of dihalobenzenoid compounds which compound or compounds have the two halogens bonded to benzene rings having an electron withdrawing group in at least one of the positions ortho and para to the halogen group. The dihalobenzenoid compound can be either mononuclear

where the halogens are attached to the same benzenoid ring or polynuclear where they are attached to different benzenoid rings, as long as there is the activating electron withdrawing group in the ortho or para position of that benzenoid nucleus.

Any of the halogens may be the reactive halogen substituents on the benzenoid compounds, fluorine and chlorine substituted benzenoid reactants being preferred.

Any electron withdrawing group can be employed as the activator group in the dihalobenzenoid compounds. Preferred are the strong activating groups such as the sulfone group (—SO_2—) bonding two halogen substituted benzenoid nuclei as in the 4,4′-dichlorodiphenyl sulfone and 4,4′-difluorodiphenyl sulfone, although such other strong withdrawing groups hereinafter mentioned can also be used with ease. It is further preferred that the ring contain no electron supplying groups on the same benzenoid nucleus as the halogen; however, the presence of other groups on the nucleus or in the residuum of the compound can be tolerated. Preferably, all of the substituents on the benzenoid nucleaus are either hydrogen (zero electron withdrawing), or other groups having a positive sigma* value as set forth in J. F. Bunnett in Chem. Rev., 49, 273 (1951) and Quart. Rev., 12, 1 (1958).

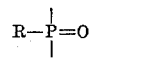
The electron withdrawing group of the dihalobenzenoid compound can function either through the resonance of the aromatic ring, as indicated by those groups having a high sigma* value, i.e., above about +0.7, or by induction as in perfluoro compounds and like electron sinks.

Preferably the activating group should have a high sigma* value, preferably above 1.0, although sufficient activity is evidenced in those groups having a sigma* value above 0.7.

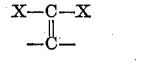
The activating group can be basically either of two types:

(a) Monovalent groups that activate one or more halogens on the same ring as a nitro group, phenylsulfone, or alkylsulfone, cyano, trifluoromethyl, nitroso, and herero nitrogen as in pyridine.

(b) Divalent groups which can activate displacement of halogens on two different rings, such as the sulfone group —SO_2—; the carbonyl group —CO—; the vinyl group —CH=CH—; the sulfoxide group —SO—; the azo- group —N=N—; the saturated fluorocarbon groups —CF_2—CF_2—; organic phosphine oxides



where R is a hydrocarbon group, and the ethylidene group



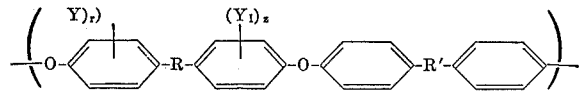
where X can be hydrogen or halogen or which can activate halogens on the same ring such as with difluorobenzoquinone, 1,4- or 1,5- or 1,8-difluoroanthraquinone.

If desired, the polymers may be made with mixtures of two or more dihalobenzenoind compounds each of which has this structure, and which may have different electron withdrawing groups. Thus the E′ residuum of the benzenoid compounds in the polymer structure may be the same or different.

It is also seen that as used herein, the E′ term defined as being the "residuum of the benzenoid compound" refers to the aromatic or benzenoid residue of the compound after the removal of the halogen atoms of the benzenoid nucleus.

From the foregoing, it is evident that preferred linear thermoplastic polyarylene polyethers are those wherein E is the residuum of a dinuclear dihydric phenol and E′ is the residuum of a dinuclear benzenoid compound.

These preferred polymers then are composed of recurring units having the formula



wherein R represents a member of the group consisting of a bond between aromatic carbon atoms and a divalent connecting radical and R′ represents a member of the group consisting of sulfone, carbonyl, vinyl, sulfoxide, azo, saturated fluorocarbon, organic phosphine oxide and ethylidene groups and Y and Y_1 each represent inert substituent groups selected from the group consisting of halogen, alkyl groups having from 1 to 4 carbon atoms and alkoxy groups having from 1 to 4 carbon atoms and where *r* and *z* are integers having a value from 0 to 4 inclusive. Even more preferred are the thermoplastic polyarylene polyethers of the above formula wherein *r* and *z* are zero, R is divalent connecting radical R″—C—R″ represents a member of the group consisting of hydrogen, lower alkyl, lower aryl, and the halogen substituted groups thereof, and R′ is a sulfone group.

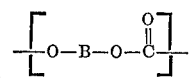
Thermoplastic polyarylene polyethers described herein can be prepared as described in Belgian Pat. 650,476 in a substantially equimolar one-step reaction of a double alkali metal salt of a dihydric phenol with a dihalobenzenoid compound in the presence of specific liquid organic sulfoxide or sulfone solvents under substantially anhydrous conditions. Any alkali metal salt of the dihydric phenol can be used as the one reactant.

Thermoplastic polyarylene polyethers described herein can also be prepared as described in Example 1 hereof and in the aforementioned Belgian patent, in a two-step process in which a dihydric phenol is first converted in situ in a primary reaction solvent to the alkali metal salt by the reaction with the alkali metal, the alkali metal hydride, alkali metal hydroxide, alkali metal alkoxide or the alkali metal alkyl compounds.

Thermoplastic polyarylene polyethers as described herein are characterized by high molecular weights indicated by reduced viscosity in indicated solvents. For purposes of the present invention, it is preferred that thermoplastic polyarylene polyethers have a reduced viscosity above about 0.35 and most preferably above about 0.4. The manner of determining reduced viscosity is detailed infra.

For purposes of providing metal-plated articles having good thermal properties, useful polyarylene polyethers have a heat distortion temperature at 18.6 kg./cm.^{2} of at least about 149° C.

The aromatic carbonate polymers used in the present invention may be prepared by reacting a dihydric phenol with a carbonate precursor such as phosgene, a haloformate, or a carbonate ester. Generally speaking, such carbonate polymers can be typified as possessing recurring structural units of the formula



where B is a divalent aromatic radical of the dihydric phenol employed in the polymer producing reaction. The dihydric phenols which may be employed to provide such aromatic carbonate polymers are mononuclear or polynuclear aromatic compounds, containing as functional groups, 2 hydroxy radicals, each of which is attached directly to a carbon atom of an aromatic nucleus. Typical dihydric phenols are

2,2-bis-(4-hydroxyphenyl)propane,
hydroquinone,
resorcinol,
2,2-bis-(4-hydroxyphenyl)pentane,
2,4-dihydroxy diphenyl methane,
bis-(2-hydroxyphenyl)methane,

bis-(4-hydroxyphenyl)methane,
bis-(4-hydroxy-5-nitrophenyl)methane,
1,1-bis-(4-hydroxyphenyl)-ethane,
3,3-bis-(4-hydroxyphenyl)pentane,
2,2'-dihydroxydiphenyl,
2,6-dihydroxy naphthalene,
bis-(4-hydroxyphenyl)sulfone,
2,4'-dihydroxydiphenyl sulfone,
5'-chloro-2,4'-dihydroxy-diphenyl sulfone,
bis-(4-hydroxyphenyl)diphenyl disulfone,
4,4'-dihydroxydiphenyl ether,
4,4'-dihydroxy-3,3'-dichlorodiphenyl ether, and
4,4'-dihydroxy-2,5-diethoxydiphenyl ether.

A variety of additional dihydrophenols which may be employed to provide such carbonate polymers are disclosed in U.S. Pat. 2,999,835. It is, of course, possible to employ two or more different dihydric phenols, or a dihydric phenol in combination with a glycol, an hydroxy terminated polyester, or a dibasic acid in the event a carbonate copolymer rather than a homopolymer is desired for use in the preparation of the mixtures of the invention.

When a carbonate ester is used as the carbonate precursor in the polymer forming reaction, the materials are reacted at temperatures of from 100° C. or higher for times varying from 1 to 15 hours. Under such conditions ester interchange occurs between the carbonate ester and the dihydric phenol used. The ester interchange is advantageously consummated at reduced pressures of the order of from about 10 to about 100 mm. of mercury, preferably in an inert atmosphere, such as nitrogen or argon, for example.

Although the polymer forming reaction may be conducted in the absence of a catalyst, one may, if desired employ the usual ester exchange catalysts, such as, for example, metallic lithium, potassium, calcium and magnesium. Additional catalysts and variations in the exchange methods are discussed in Groggins, Unit Processes in Organic Synthesis (4th edition, McGraw-Hill Book Company, 1952), pages 616 to 620. The amount of such catalyst, if used, is usually small, ranging from about 0.001 to about 0.1%, based on the moles of the dihydric phenol employed.

The carbonate ester useful in this connection may be aliphatic or aromatic in nature, although aromatic esters, such as diphenyl carbonate, are preferred. Additional examples of carbonate esters which may be used are dimethyl carbonate, diethyl carbonate, phenyl methyl carbonate, phenyltolyl carbonate and di(tolyl) carbonate.

A preferred method for preparing the carbonate polymers suitable for use in this invention involves the use of a carbonyl halide, such as phosgene, as the carbonate precursor. This method involves passing phosgene gas into a reaction mixture containing the dihydric phenol and an acid acceptor such as a tertiary amine (e.g., pyridine, dimethylaniline, quinoline, etc.). The acid acceptor may be used undiluted or diluted with inert organic solvents as, for example, methylene chloride, chlorobenzene, or 1,2-dichloroethane. Tertiary amines are advantageous since they are good solvents as well as acid acceptors during the reaction.

The temperature at which the carbonyl halide reaction proceeds may vary from below 0° C. to about 100° C. The reaction proceeds satisfactorily at temperatures from room temperature (25° C.) to 50° C. Since the reaction is exothermic, the rate of phosgene addition may be used to control the temperature of the reaction temperature. The amount of phosgene required will generally depend upon the amount of dihydric phenol present. Generally speaking, one mole of phosgene will react with one mole of the dihydric phenol used to provide the polymer and two moles of HCl. Two moles of HCl are in turn "attached" by the acid acceptor present. The foregoing are herein referred to as stoichiometric or theoretical amounts.

Another method for preparing the carbonate polymer comprises adding phosgene to an alkaline aqueous suspension of the dihydric phenol used. This is preferably done in the presence of inert solvents such as methylene chloride, 1,2-dichloroethane and the like.

Quaternary ammonium compounds may be employed to catalyze the reaction.

A third method for preparing such carbonate polymers involves the phosgenation of an agitated suspension of the anhydrous alkali salts of the dihydric phenol used in a non-aqueous medium such as benzene, chlorobenzene and toluene. The reaction is illustrated by the addition of phosgene to a slurry of the sodium salt of 2,2-bis-(4-hydroxyphenyl)propane in an inert polymer solvent such as chlorobenzene. The organic solvent should preferably be a polymer solvent but need not necessarily be a good solbent for the reactants.

Generally speaking a haloformate such as the bishaloformate of 2,2-bis-(4-hydroxyphenyl)propane may be substituted for phosgene as the carbonate precursor in any of the methods described above.

In each of the above solution methods of preparation, the carbonate polymer emerges from the reaction in either a true or pseudo solution whether aqueous base or pyridine is used as an acid acceptor. The polymer may be precipitated from the solution by adding a polymer nonsolvent, such as heptane or isopropanol. Alternatively, the polymer solution may be heated to evaporate the solvent.

A preferred method for preparing the polycarbonates useful in the practice of this invention comprises passing a carbonyl halide, such as phosgene, into a slurry comprising a suspension of solid particles in a single liquid phase, the suspension of solid particles comprising a dihydric phenol and at least two moles, per mole of dihydric phenol, of at least one acid acceptor selected from the group consisting of a hydroxide, a carbonate and a phosphate of an alkali or an alkaline earth metal, and the single liquid phase comprising an inert organic liquid which is a solvent for the carbonate polymer, but a non-solvent for the dihydric phenol and the acid acceptor, to form a reaction mixture having a solid phase and a single liquid phase comprising a solution of the carbonate polymer in the inert organic liquid, and separating the liquid phase from the solid phase.

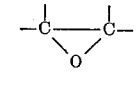
Polyhydroxyethers used in this invention are linear thermoplastic polymers having the general formula

$$\text{+O—D—O—D'+}_n$$

wherein D is the residuum of a dihydric phenol, D' is a hydroxyl containing residuum of an epoxide, and n represents the degree of polymerization and is at least 30 and is preferably 80 or more. Polyhydroxyethers having a melt flow of less than about 7.0 determined as hereinafter described are preferred.

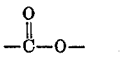
The residuum D of the dihydric phenol in the polyhydroxyether formula is the same as the dihydric phenol residuum E in the polyarylene polyether recurring unit formula described above.

The epoxide contributing the hydroxyl containing residuum D' can be a monoepoxide or diepoxide. By "epoxide" is meant a compound containing an oxirane group, i.e., oxygen bonded to two vicinal aliphtaic carbon atoms, thus,

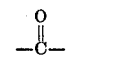


A monoepoxide contains one such oxirane group and provides a residuum D' containing a single hydroxyl group; a diepoxide contains two such oxirane groups and provides a residuum D' containing two hydroxyl groups. Saturated epoxides, by which term is meant diepoxides free of ethylenic unsaturated, i.e., —C=C— and acetylenic unsaturation, i.e., —C≡C—, are preferred. Particularly preferred are halogen substituted saturated monoepoxides, i.e., the epiahalohydrin and saturated diepoxides

which contain solely carbon, hydrogen and oxygen, especially those wherein the vicinal or adjacent carbon atoms form part of an aliphatic hydrocarbon chain. The oxygen in such diepoxides can be, in addition to oxirane oxygen,



carbonyl oxygen



and the like.

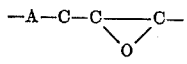
Specific examples of monoepoxides include epihalohydrins such as epichlorohydrin, epibromohydrin, 1,2-epoxy-1-methyl-3-chloropropane, 1,2-epoxy-1-butyl-3-chloropropane, 1,2-epoxy-2-methyl-3-fluoropropane, and the like.

Illustrative diepoxides include

diethylene glycol bis(3,4-epoxycyclohexane-carboxylate),
bis(3,4-epoxycyclohexylmethyl)adipate,
bis(3,4-epoxycyclohexylmethyl)phthalate,
6-methyl-3,4-epoxycyclohexylmethyl-6-methyl-3,4-epoxycyclohexane-carboxylate,
2-chloro-3,4-epoxycyclohexylmethyl-2-chloro-3,4-epoxycyclohexanaecarboxylate,
diglycidyl ether,
bis(2,3-epoxycyclopentyl)ether,
1-,5-pentanediol bis(6-methyl-3,4-epoxycyclohexylmethyl)ether,
bis(2,3-epoxy-2-ethylhexyl)adipate
diglycidyl maleate,
diglycidyl phthalate,
3-oxatetracyclo[4.4.0.$1^{7,10}$.$0^{2,4}$]undec-8-yl 2,3-epoxypropyl ether,
bis(2,3-epoxycyclopentyl)sulfone,
bis(3,4-epoxyhexoxypropyl)sulfone,
2,2'-sulfonyldiethyl-bis(2,3-epoxycyclopentanecarboxylate),
3-oxatetracyclo[4.4.0.$1^{7,10}$.$0^{2,4}$]undec-8-yl 2,3-epoxybutyrate,
4-pentenal-di(6-methyl-3,4-epoxycyclohexylmethyl) acetal,
ethylene glycol bis(9,10-epoxystearate),
diglycidyl carbonate,
bis(2,3-epoxybutylphenyl)2-ethylhexyl phosphate,
diepoxydioxane,
butadiene dioxide and
2,3-dimethylbutadiene dioxide.

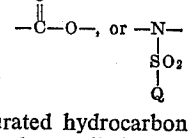
The preferred diepoxides are those wherein each of the oxirane groups is connected to an electron donating substituent which is not immediately connected to the carbon atoms of that oxirane group.

Such diepoxides have the grouping



wherein A is an electron donating substituent such as —O—,

—S—, —SO—, —SO_2—,



where Q is a saturated hydrocarbon radical such as an alkyl, cycloalkyl, aryl or aralkyl radical.

A single monoepoxide or diepoxide or a mixture of at least two monoepoxides or diepoxides can be employed in preparing thermoplastic polyhydroxyethers and the terms "monoepoxide" and "diepoxide" are intended to include a mixture of at least two monoepoxides or diepoxides, respectively.

Melt flow of each of the thermoplastic polyhydroxyethers was determined by weighing in grams the amount of polyhydroxyether which, at a temperature of 220° C. and under a pressure of 44 p.s.i., flowed through an orifice having a diameter of 0.825" and a length of 0.315" over a ten minute period. Four such determinations were made and the average of the four determinations is reported as decigrams per minute under a pressure of 44 p.s.i. and at 220° C.

Thermoplastic polyhydroxyethers used in the present invention can be further modified by being reacted with a variety of crosslinking agents such as, among others organic isocyanates, e.g., toluene diisocyanates, dianisidine diisocyanates, polyethylene polyisocyanate, toluene diisocyanate terminated polybutylene glycol, and phenol blocked polyisocyanate and the like; methylol containing compounds, e.g., 2,4,6-trimethylolphenol, polymethylolated bisphenol sulfone, dimethylol-p-tert-butylphenol, dimethylol - p - methylphenol butylphenol-formaldehyde resin, nonylphenol formaldehyde resin, butylated melamine-formaldehyde resin and the like; epoxy compounds e.g., the diglycidyl ether of 2,2,-bis(4-hydroxyphenyl) propane, 2,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexanecarboxylate and the like; aldehydes e.g., glyoxal, dialdehyde starch, formaldehyde copolymers and the like; formals e.g., dibutyl formal, di-(2-chloromethyl)formal and the like; dicarboxylic acid anhydrides, e.g., maleic anhydrides, phthalic anhydride and the like; acids e.g., glutaric acid, sebacic acid, isophthalic acid, phosphoric acid; chloroformates, e.g., diglycol chloroformate of 2,2-bis(4-hydroxyphenyl)propane and the like; silanes e.g., ethyltrichlorosilane, diphenyl dichlorosilane, tetraethyl ortho silicate and the like; metal organic salts e.g., tetrabutyl titanate, aluminum acetyl acetonate, zinc acetyl acetonate, zirconium acetyl acetonnate and the like; ureas e.g., dimethyl ether of dimethylol urea; inorganic esters e.g., dimethyl sulfate; acyl chlorides, e.g., succinyl chlorides and the like; inorganic polychlorides, e.g., zinc chloride, aluminum trichloride and the like; esters, e.g., glycol deformate, glycol dipropionate triglycol di-(2-ethyl hexanoate) and the like; as well as trichloroacetaldehyde glyoxalic acid, and epichlorohydrin and similar compounds having mixed functional groups.

Also useful in this invention are thermoplastic polyhydroxyethers modified without crosslinking by esterification with an acyl group obtained from any one of a variety of acylating agents containing but one secondary hydroxyl reactive group e.g., organic acids, inorganic acids and the acid derivatives such as acid halides and anhydrides having the general formula GZ wherein G is an inorganic or organic acid radical such as acetyl, benzoyl, stearyl, formyl, propionyl, chloroacetyl, o-chlorobenzyl, p-tolenesulfonyl, mercaptoacetyl, diphenylphosphinyl, nitrate and like groups and Z is (a) halogen, i.e., fluorine, chlorine, bromine, and iodine where the acylating agent is an acid halide; (b) a G' group, G' being a radical as listed above and free of any substituents reactive with secondary hydroxyl groups where the acylating agent is an acid anhydride; (c) an OH group wherein the acylating agent is an acid, either inorganic or organic; and a G" group where G" is any hydrocarbon group free of aliphatic unsaturation such as alkyl, cycloalkyl, aryl or aralkyl groups or a substituted hydrocarbon group free of substituents reactive with secondary hydroxyl groups where the acylating agent is an acid ester. Other acylating agents include hexachloro-2-cyclopentenone, soya fatty acids and tall oil acids.

Other aromatic polymers include polyphenylene ethers of the type described in U.S. Pat. 3,134,753 which is incorporated herein by reference.

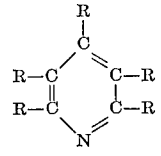
As indicated previously, fluids useful in the present invention for improving the adhesion of metal platings to aromatic polymers promote a microscopic etching or crazing and submicroscopic alterations of the polymer

substrates. This etching manifests itself by a generally hazy appearance to the naked eye rather than a cracked or spider-webbed appearance.

Suitable fluids that will promote the microscopic etching and submicroscopic alteration of aromatic polymer substrates include N,N-dimethylformamide

$$(HCON(CH_3)_2)$$

pyridines having the formula



wherein R is hydrogen or an inert substituent such as methyl, halo (F, Cl, Br or I), methoxy, aryl aryloxy, or wherein two R's form a fused aromatic ring which may contain hetero nitrogen atoms, and alkylene glycols which are liquid at elevated temperatures, e.g. 190° C., and have a solubility parameter (Plastics, 26, 290 (1961)) of from about 8.7 to about 10.7 such as dipropylene glycol and ethylene glycols having an average molecular weight of up to about 6000 which can be represented by the formula $HO(CH_2CH_2O)_nH$ wherein n is an integer having a value of at least 1.

Fluids useful in the present invention can also be described as water miscible, oxidation resistant Lewis bases that are believed to promote a breakdown in molecular weight and the formation of carboxyl groups in those instances where aliphatic groups are present in the polymer chain at the surface of the aromatic polymer substrate in the presence of a strong acid such as sulfuric acid and a strong oxidizing agent such as chromic acid or chrominum trioxide. It is believed when carboxyl groups are formed, their presence plays some role in improving the adhesion of metal platings to aromatic polymer substrates. Thus there is observed a physical effect (microscopic etching) as well as a chemical effect (submicroscopic alteration, that is, a breakdown in molecular weight and, in some cases, the formation of carboxyl groups) on the aromatic polymer substrates.

The fact that these particular fluids improve the adhesion of metal platings is unexpected because other even similar and homologous fluids have been found to have no effect on the adhesion of metal platings. These include formamide, N-methyl formamide, N,N-diethylformamide, methyl ethyl ketone, N,N-dimethylacetamide, dioxane, methylene chloride, tetrahydrofuran, benzene, toluene, nitrobenzene, aniline, phenol, anisole, cyclohexanone, trichloroethylene, 2 - pyrrolidone, N-methyl-2-pyrrolidone, morpholine, glycerine and α-pinene. With the foregoing fluids, electroless plated copper was easily pulled off with Scotch Tape indicating a peel strength of less than 1 lb./in. which is far less than the commercially acceptable level of 5 lb./in.

Aromatic polymer substrates can be treated with the aforementioned adhesion promoting fluids by immersion, dipping, spraying, and like techniques. The temperature of the fluid during treatment is not narrowly critical. Generally room temperatures (about 23° C.) are employed with N,N-dimethylformamide and the pyridines but temperatures just above the freezing point up to the boiling point of the particular fluid can be used if desired. DMF vapors are generated at about 83–86° C. With the alkylene glycols, elevated temperatures within about 50° C. or above the heat distortion point (ASTM D–6137–59T) of the aromatic polymer are preferred. The duration of the liquid treatment is not narrowly critical and should be sufficient to produce peel strengths of at least about 5 lb./in.

Polymer substrates for metal plating can be prepared in the form of self-supporting sheets by extrusion, injection, compression molding and like techniques, or can be fabricated into any desired shape by injection, compression, or blow molding, or by thermoforming and like techniques. Once the substrate is formed and treated with an adhesion promoting fluid as described above, conventional methods are employed to plate metal layers thereon. Generally, the substrate is cleaned, treated as described above, immersed in a conditioner (strong oxidizing solution) which may be a bath of fuming sulfuric acid (oleum); fuming sulfuric acid/chromium trioxide; sulfuric acid/phosphoric acid/chromic trioxide; or sulfuric acid/chromium trioxide with agitation to microscopically etch and submicroscopically alterate the substrate as described above to provide for good adhesion of the metal plated layers, rinsed in water (not when using DMF vapor), immersed in a bath containing stannous chloride or other stannous salt, rinsed in water, immersed in a bath to provide catalytic nucleating centers of a salt of a metal catalytic to the deposition of the desired electroplated metal deposit such as silver nitrate or the chloride of gold, palladium, or platinum, the ions of these metals being reduced to catalytic metal nucleating centers by the stannous ions adsorbed on the substrate and/or by reducing agents contained in the electroless metal deposition bath, rinsed in water, depositing the desired metal such as copper, nickel, or cobalt by treating the catalyzed surface with a salt of the desired metal plus a reducing agent therefor, and thereafter electroplating to deposit the desired metal layer.

Cleaning the polymer substrate can be accomplished by conventional cleaning methods such as mechanical cleaning, scrubbing, organic cleaners, alkaline or acid cleaners, wetting agents and pickling baths.

Particles of metals catalyze the electroless chemical reduction deposition of a desired metal on a polyarylene polyether substrate. For example, the following metals are catalytic to the deposition of nickel and cobalt: copper, beryllium, aluminum, carbon, tungsten, tellurium, nickel, gold, germanium, silicon, molybdenum, selenium, iron, tin, and palladium. These metals are also catalytic to the deposition of copper, lead, platinum, rhodium, ruthenium, osmium, iridium, iron, cobalt, carbon, silver, nickel, aluminum, gold, palladium, and magnesium. Cobalt, nickel, and iron can be used to catalyze the deposition of chromium.

One suitable process includes cleaning a polymer substrate, treating with an adhesion promoting fluid, microscopically etching and submicroscopically altering as described above. The substrate is then sensitized with stannous chloride which is adsorbed on the surface. After rinsing, next comes activation to make the treated substrate catalytic by immersion in a bath containing a salt of a precious metal such as palladium chloride. After rinsing, electroless metal deposition is accomplished by immersion in an electroless copper bath containing a copper salt, complexing agents to keep copper in solution and a reducing agent. This is followed by conventional electroplating to deposit adherent layers of copper, nickel and chromium.

The following examples are intended to further illustrate the present invention without limiting the same in any manner. All parts and percentages are by weight unless indicated otherwise.

Reduced viscosity (RV) was determined by dissolving a 0.2 gram sample of thermoplastic polyarylene polyether in chloroform contained in a 100 ml. volumetric flask so that the resultant solution measured exactly 100 ml. at 25° C. in a constant temperature bath. The viscosity of 3 ml. of the solution which had been filtered through a sintered glass funnel was determined in an Ostwald or similar type viscometer at 25° C. Reduced viscosity values were obtained from the equation:

$$\text{Reduced viscosity} = \frac{t_s - t_o}{c \cdot t_o}$$

wherein:

t_o is the efflux time of the pure solvent

t_s is the efflux time of the polymer solution

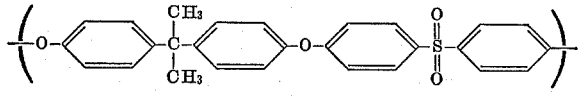
c is the concentration of the polymer solution expressed in terms of grams of polymer per 100 ml. of solution

EXAMPLE 1

Preparation of thermoplastic polyarylene polyether

In a 250 ml. flask equipped with a stirrer, thermometer, a water cooled condenser and a Dean-Stark moisture trap filled with benzene, there were placed 11.42 grams of 2,2 - bis - (4-hydroxyphenyl)propane (0.05 mole), 13.1 grams of a 42.8% potassium hydroxide solution (0.1 mole KOH), 50 ml. of dimethylsulfoxide and 6 ml. benzene and the system purged with nitrogen to maintain an inert atmosphere over the reaction mixture. The mixture was refluxed for 3 to 4 hours, continously removing the water contained in the reaction mixture as an azeotrope with benzene and distilling off enough of the latter to give a refluxing mixture at 130–135° C. consisting of the dipotassium salt of the 2,2-bis-(4-hydroxyphenyl)propane and dimethylsulfoxide essentially free of water. The mixture was cooled and 14.35 grams (0.05 mole) of 4,4'-dichlorodiphenylsulfone was added followed by 40 ml. of anhydrous dimethylsulfoxide, all under nitrogen pressure. The mixture was heated to 130° and held at 130–140° with good stirring for 4–5 hours. The viscous, orange solution was poured into 300 ml. water, rapidly circulating in a Waring Blendor, and the finely divided white polymer was filtered and then dried in a vacuum oven at 100° for 16 hours. The yield was 22.2 g. (100%) and the reaction was 99% complete based on a titration for residual base.

The polymer had the basic structure



EXAMPLE 2

Preparation of thermoplastic polyhydroxyether

Thermoplastic polyhydroxyether was prepared by the reaction of equimolar amounts of 2,2-bis(4-hydroxyphenyl)propane and epichlorohydrin together with sodium hydroxide. Equipment used was provided with a sealed stirrer, thermometer, and reflux condenser. There was placed therein:

2,2 - bis(4 - hydroxyphenyl)propane—114.5 parts (0.5 mole)
Epichlorohydrin (99.1%) pure—46.8 parts (0.5 mole)
Ethanol—96.0 parts
Butanol—10.0 parts
Sodium hydroxide (97.5%) pure—22.6 parts
Water—70.0 parts

The above mixture was stirred at room temperature for 16 hours to accomplish the initial coupling reaction. The mixture was then heated at 80° C. for an hour. Sixty parts of a 7:3 mixture of toluene:butanol was added. Heating of the mixture at 80° C. was continued another two hours. There was added an additional 50 parts of the 7:3 toluene:butanol mixture and 4.5 parts of phenol. The contents of the vessel were heated at 80° C. (reflux) for 2½ hours. Upon cooling, the reaction mixture was cut with 200 parts of the 7:3 toluene:butanol mixture. One hundred parts of water was added and agitated with the contents to dissolve salts present in the reaction mixture. The vessel contents were allowed to settle for ten minutes during which time a lower brine phase formed. This phase was separated by decantation. The upper polymer containing solution phase was washed successively with two 160 part portions of water containing 4.5% butanol. The washed polymer solution was acidified by stirring the solution with a mixture of 1 part of 85% phosphoric acid with 100 parts of water (pH=2) for one hour. The upper polymer solution phase was again separated by decantation and water washed with four successive 200 part portions of water containing 4.5% butanol. The washed polymer was then coagulated in 1,000 parts of isopropanol, filtered, and dried. There was obtained a thermoplastic polyhydroxyether of 2,2-bis(4-hydroxyphenol)propane and epichlorohydrin having a melt flow of 7.0 decigrams per minute.

EXAMPLE 3

Preparation of aromatic polycarbonate polymer

A slurry is prepared by stirring the following materials in a reaction vessel; 114 parts 2,2-bis-(4-hydroxyphenyl) propane, 129.6 parts calcium hydroxide, and 760 parts methylene chloride.

The slurry is heated to about 40° C. at which time heating is discontinued. Phosgene is added to the stirred slurry at a rate of about 0.82 part per minute for about 55 minutes and thereafter at 0.08 part per minute for an additional 90 minutes. The heat generated by the reaction maintains the slurry at a temperature of 38–40° C., i.e. the reflux temperature of the methylene chloride. After the reaction subsides, air is blown through the reaction mixture to cool it and free it of any excess phosgene. The cool slurry is diluted with methylene chloride, centrifuged, and the solid phase removed. The single liquid phase, consisting of a solution of the carbonate polymer in the methylene chloride, is filtered, and the carbonate polymer precipitated by adding heptane to the solution. The polymer is separated from the mixture by filtration and drying at 125° C. The intrinsic viscosity (ASTM D-1601-61) measured in dioxane at 30° C. of the polymer is 0.54, which corresponds to a molecular weight of about 35,000 (weight average).

EXAMPLES 4–13

The following solutions were used in these examples:

(1) Alkaline cleaner—PC451 [1] 6 oz./gal. H_2O
(2) Fuming sulfuric acid (oleum)
(3) Neutralizer—AD–480 [1] 8 oz./gal.
(4) Stannous chloride sensitizer 432 [1]—1 part/15 parts H_2O/1 part conc. HCl (by vol.)
(5) Palladium chloride activator 440 [1]—1 part/15 parts H_2O (by vol.)
(6) Electroless copper—1 part CU 400A [1]/1 part CU 400B [1]/1 part H_2O (by vol.)
(7) Electroplating bath—28 to 32 oz. $CuSO_4$/gal., 6–8 oz. H_2SO_4/gal. by wt., UBAC #1 [2] 0.2–0.6%/vol.

General procedure

(1) 2" x ⅛" injection molded discs of polyarylene polyether as described in Example 1 were annealed 4 hours at 170° C.
(2) Alkaline cleaner—4 mins. at 70° C.
(3) Rinse in water—1–2 mins. at room temperature, about 23° C. (RT).
(4) Neutralize—½ min. at room temperature.
(5) Rinse in water—1–2 mins. at room temperature.
(6) Fuming sulfuric acid (oleum) 15, 20 and 30% SO_3 based on $H_2SO_4+SO_3$ 1–30 minutes at room temperature.
(7) Rinse—1–2 mins. at room temperature.
(8) Alkaline cleaner—4 mins. at 70° C.
(9) Rinse in water—1–2 mins. at room temperature.
(10) Neutralize—½ min. at room temperature.
(11) Rinse in water—1–2 mins. at room temperature.
(12) Sensitize—1 min. at room temperature.
(13) Rinse in water—1–2 mins. at room temperature.
(14) Activate—1 min. at room temperature.
(15) Rinse in water—1–2 mins. at room temperature.
(16) Electroless copper—10 mins. at room temperature.
(17) Rinse in water—2 mins. at room temperature.
(18) Aged overnight in air at room temperature.

[1] Enthone Inc., New Haven, Conn.
[2] Udylite Corp., Detroit (a brightener).

(19) Electroplate—50–60 amps/ft.^{2} 43–45 mins.
(20) Rinse in water—2 mins. at room temperature.
(21) Bake at 87° C. for 165 mins.

EXAMPLE 4

A 4" x 3" x ⅛" injection molded polyarylene polyether plaque (0.50 RV) was electroplated with a 2 mil coating of copper following steps 1 and 6–21 of the general procedure. Etching time was 10 minutes with 20% oleum. Adhesion of the copper to the plaque was determined by measuring the peel strength of a one-inch strip of metal plate pulled from the substrate at an angle of 90°. Peel strength was 7.3 lbs./in.

EXAMPLE 5

Example 4 was duplicated except 20% oleum containing 1% CrO_3 was used as the etchant. Peel strength was 7.5 lbs./in.

EXAMPLE 6

Example 4 was duplicated except etching time was 30 mins. Peel strength was 5.9 lbs./in.

EXAMPLE 7

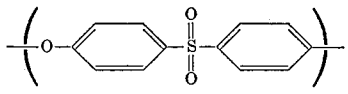
Two inch x ⅛" round injection molded polyarylene polyether discs (RV—.52) were electroplated using steps 1–21 of the general procedure. The discs were etched for 10 minutes in 20% oleum. Peel strength was 5.5 lbs./in.

EXAMPLE 8

Example 7 was duplicated except the disc was etched 30 minutes in 30% oleum. Peel strength was 7.6–10.8 lbs./in.

EXAMPLE 9

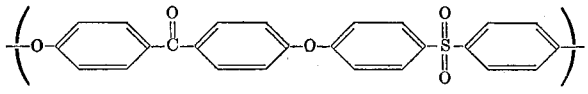
Thermoplastic polyarylene polyether having the formula



is prepared from 4,4'-dihydroxydiphenyl sulfone and 4,4'-dichlorodiphenyl sulfone according to the procedure in Example 1. This polymer is molded into a plaque and electroplated as in Example 4. Peel strength is in excess of 5lbs./in.

EXAMPLE 10

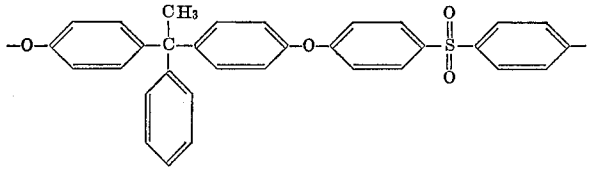
Theromplastic polyarylene polyether having the formula



is prepared from the bisphenol of benzophenone and 4,4'-dichlorodiphenylsulfone according to the procedure in Example 1. This polymer is molded into a plaque and electroplated as in Example 7. Peel strength is in excess of 5 lbs./in.

EXAMPLE 11

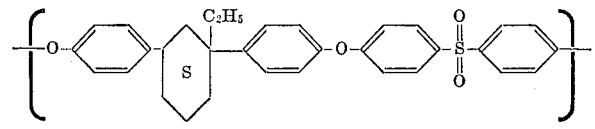
Thermoplastic polyarylene polyether having the formula



is prepared from the bisphenol of acetophenone and 4,4'-dichlorodiphenylsulfone according to the procedure in Example 1. This polymer is molded into a plaque and electroplated as in Example 7. Peel strength is in excess of 5 lbs./in.

EXAMPLE 12

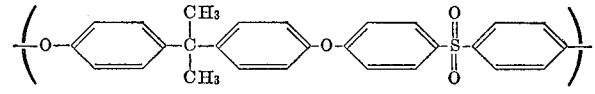
Thermoplastic polyarylene polyether having the formula



was prepared from the bisphenol of vinyl cyclohexene (prepared by an acid catalyzed condensation of 2 moles of phenol with one mole of vinyl cyclohexene) and 4,4'-dichlorodiphenylsulfone according to the procedure in Example 1. This polymer is molded into a plaque and electroplated as in Example 4. Peel strength is in excess of 5 lbs./in.

EXAMPLE 13

Thermoplastic polyarylene polyether having the formula



is prepared from 2,2-bis-(4-hydroxyphenyl)propane and 4,4'-difluorobenzophenone according to the procedure in Example 1. This polymer is molded into a plaque and electroplated as in Example 7. Peel strength is in excess of 5 lbs./in.

The following examples illustrate the use of an adhesion promoting liquid.

EXAMPLE 14

A 2" round x ⅛" injection molded disc of polyarylene polyether prepared as described in Example 1 was annealed by placing it in a 165° C. oven for four hours. Upon removal the sample was allowed to cool to room temperature. It was then immersed in a solution consisting of 93 cc. N,N-dimethylformamide and 7 cc. distilled water for 2 minutes, after rinsing in water for 1 minute it was immersed for 5 minutes in the acid etching bath designated Enthone 470 (Enthone, Inc., New Haven, Conn.) which was heated to 70° C. The sample was rinsed in water and then treated in the following solutions:

(1) Alkaline cleaner, PC–452 [1] (6 oz./gal.—4 mins. at 80° C.
(2) Neutralizer, AD–480 [1] (8 oz./gal.)—½ min. at room temperature.
(3) Stannous chloride 432 [1]—1 part to 14 parts water to 1 part conc. HCl—1 min. at room temperature.
(4) Palladium chloride 440 [1]—1 part to 15 parts water—1 min. at room temperature.
(5) Electroless copper—1 part CU–400A [1], 1 part CU–400 B [1], 1 part water—10 min. at room temperature.
(6) Distilled water—15 mins. at 80° C.

Following each of steps 1–5, the sample was rinsed for one minute in circulating tap water. The electroplating bath consisted of 28–32 oz./gal. $CuSO_4$, 6–8 oz. (wt.)/gal. H_2SO_4, 0.2–0.6%/vol. UBAC #1 (Udylite Corporation, Detroit).

The sample was electroplated with 2 mils of copper in 30 minutes using a current density of 75 amps/sq./ft. Peel strength was 16 lbs./in.

EXAMPLE 15

The same procedure as described in Example 14 was followed except that the organic solution consisted of 92 cc. pyridine and 8 cc. water and etching time was 15 minutes. Peel strength was 11 lbs./in.

[1] Enthone, Inc.

Control

The same procedure as described in Example 14 was followed except that the organic solution consisted of 93 cc. dimethylacetamide and 7 cc. water immersion time in this solution was two minutes; etching time was 3 minutes. Peel strength was less than 1 lb./in.

EXAMPLE 16

A 2" x ⅛" annealed (4 hrs. at 165° C.) disc of polyarylene polyether prepared as described in Example 1 was immersed for 4 minutes in hot (182° C.) polyethylene glycol having an average molecular weight of 400. After removal the sample was rinsed in water and immersed for 10 minutes in a hot (80° C.) solution of:

	Percent wt.
H_2SO_4	29
CrO_3	29
H_2O	42

The sample was rinsed, electroless plated and then electroplated with copper following the steps described in Example 14. Peel strength was 14 lbs./in.

EXAMPLE 17

Example 16 was followed except the sample was treated for 1 hour in hot (160° C.) dipropylene glycol. Peel strength was 14 lbs./in.

EXAMPLE 18

A 2" x ⅛" unannealed disc of bisphenol A polycarbonate prepared as described in Example 3 was immersed for ½ minute in a solution consisting of 93 cc. N,N-dimethylformamide and 7 cc. distilled water. After removal the disc was rinsed in isopropanol for 1½ minutes and allowed to air dry for 4 minutes. The disc was immersed for 10 minutes in the acid etching bath Enthone 470. Following rinsing in water it was treated in solutions 3–5 of Example 14 and electroplated as in Example 14. Peel strength was 13 lbs./in.

EXAMPLE 19

The same procedure as described in Example 18 was followed except that the polymer disc was bisphenol A polyhydroxyether prepared as described in Example 2 and the adhesion promoting liquid treatment consisted of immersion for 2 minutes in a solution consisting of 75 cc. N,N-dimethylformamide and 25 cc. distilled water. Peel strength was 12 lbs./in.

EXAMPLE 20

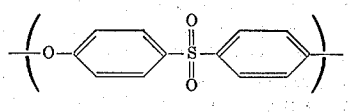
The same procedure as described in Example 16 is followed except that the polymer disc is bisphenol A polycarbonate prepared as described in Example 3 and the polyethylene glycol bath is at a temperature of 135° C. Peel strength is in excess of 5 lbs./in.

EXAMPLE 21

The same procedure as described in Example 16 is followed except that the polymer disc is bisphenol A polyhydroxyether prepared as described in Example 2 and the polyethylene glycol bath is at a temperature of 90° C. Peel strength is in excess of 5 lbs./in.

EXAMPLE 22

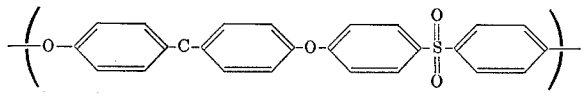
Thermoplastic polyarylene polyether having the formula



is prepared from 4,4'-dihydroxydiphenyl sulfone and 4,4'-dichlorodiphenyl sulfone according to the procedure in Example 1. This polymer is molded into a plaque and electroplated as in Example 14. Peel strength is in excess of 5 lbs./in.

EXAMPLE 23

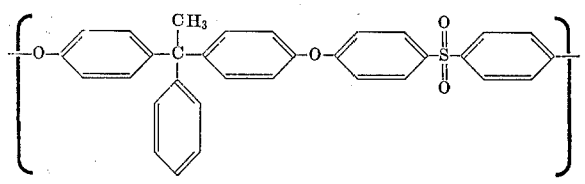
Thermoplastic polyarylene polyether having the formula



is prepared from the bisphenol of benzophenone and 4,4'-dichlorodiphenylsulfone according to the procedure in Example 1. This polymer is molded into a plaque and electroplated as in Example 14. Peel strength is in excess of 5 lbs./in.

EXAMPLE 24

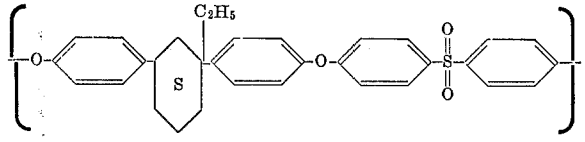
Thermoplastic polyarylene polyether having the formula



is prepared from the bisphenol of acetophenone and 4,4'-dichlorodiphenylsulfone according to the procedure in Example 1. This polymer is molded into a plaque and electroplated as in Example 16. Peel strength is in excess of 8 lbs./in.

EXAMPLE 25

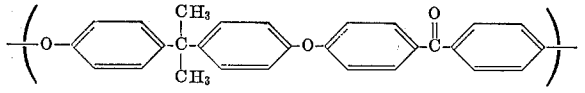
Thermoplastic polyarylene polyether having the formula



was prepared from the bisphenol of vinyl cyclohexene (prepared by an acid catalyzed condensation of 2 moles of phenol with one mole of vinyl cyclohexene) and 4,4'-dichlorodiphenylsulfone according to the procedure in Example 1. This polymer is molded into a plaque and electroplated as in Example 15. Peel strength is in excess of 5 lbs./in.

EXAMPLE 26

Thermoplastic polyarylene polyether having the formula



is prepared from 2,2'-bis-(4-hydroxyphenyl)propane and 4,4'-difluorobenzophenone according to the procedure in Example 1. This polymer is molded into a plaque and electroplated as in Example 17. Peel strength is in excess of 8 lbs./in.

EXAMPLE 27

A 12" diameter x 13" high stainless steel pot was fitted with copper cooling coils that sat on top of the open end of the pot. About a ½ inch layer of DMF was charged to the pot and heated to 83–86° C. at which temperature vapors were clearly evident. Four inch injection molded polyarylene polyether discs prepared as described in Example 1 (unannealed) were suspended in the vapors for various periods of time and then immersed in an acid conditioner for various periods of time. The discs were then plated according to the procedure described below.

The acid conditioner was composed of the following

	Percent
H_2SO_4 (96%)	55.9
H_3PO_4 (85–87%)	10.4
CrO_3	3.0
H_2O	30.7

The plating procedure was as follows:

(1) Immerse the parts in the acid conditioner for three minutes at 67° C.; agitate during conditioning and rinse thoroughly with water.

(2) Sensitize the conditioned parts by immersion in Enthone Enplate [1] 432 sensitizer for one minute at 22 to 25° C.; rinse thoroughly with water.

(3) Activate the part surfaces by immersion in Enthone Enplate [1] 440 activator for one minute at 22 to 25° C.; rinse thoroughly with water.

(4) Plate the parts with copper using a ten minute immersion in Enthone Enplate [1] CU–400 electroless copper at 22 to 25° C.; rinse thoroughly with water.

(5) Electroplate as described in Example 14.

The following results were obtained:

Vapor Pretreatment, mins.	Acid Conditioning, mins. at 70° C.	Peel Strength, lbs./in.
2	3	9
4	3	14–15
6	3	19–20
4	2	10
4	4	16–18
4	5	17

EXAMPLE 28

A 12" diameter x 17" high stainless steel pot was fitted with a stainless steel lid and a thermometer which extended from the bottom of the pot out through a hole in the lid. About a ½ inch layer of N,N-dimethylformamide was charged to the pot and heated to 50° C. A 4" x ⅛" unannealed injection molded disc of polyarylene polyether as in Example 27 was suspended in the vapors (with the lid on) for three minutes. It was then immersed in the acid conditioner described in Example 27 for two minutes following which it was rinsed in 68° C. tap water.

The sample was rendered conductive by immersion in:

(1) Sensitizer 432 [1]—1 part 432, 1 part conc. HCl, 14 parts distilled water—1 min.

(2) Activator 440 [1]—1 part 440, 15 parts distilled water—1 min.

(3) Electroless nickel NI–410 [1]—2 parts NI–410A, 1 part NI–410B, 13 parts distilled water; 5 mins. at 80° C.

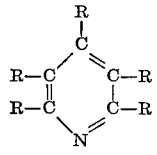
One minute water rinses at 68° C. followed each step.

The sample was then electroplated with 2 mils of semi-bright nickel. Peel strength was 13 lbs./in. one hr. after electroplating with 24 lbs./in. after 16 hrs.

[1] Endthone, Inc.

I claim:

1. Process for increasing the adhesion of metal platings to thermoplastic aromatic polymeric substrates which comprises treating an aromatic polymeric substrate selected from the group of polyarylene polyethers, polycarbonates and polyhydroxyethers with a fluid selected from the group of N,N-dimethylformamide, compounds having the formula



wherein R is hydrogen or an inert substituent, and alkylene glycols having a solubility parameter (Plastics and 26, 90, (1961)) of from about 8.7 to about 10.7, conditioning the treated substrate with a strong oxidizing solution and thereafter metal plating the conditioned substrate.

2. Process of claim 1 wherein said compound is pyridine.

3. Process of claim 1 wherein said alkylene glycol is an ethylene glycol having an average molecular weight of up to about 6000.

4. The process of claim 1 wherein said alkylene glycol is dipropylene glycol.

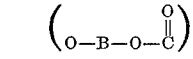
5. Process of claim 1 wherein said polyarylene polyether is composed of recurring units having the formula

$$\text{-(O—E—O—E')-}$$

wherein E is the residuum of a dihydric phenol and E' is the residuum of a benzenoid compound having an inert electron withdrawingg roup in at least one of the positions ortho and para to the valence bonds, and where both of said residua are valently bonded to the ether oxygens through aromatic carbon atoms.

6. Process of claim 5 wherein said fluid is vaporous N,N-dimethylformamide.

7. Process of claim 1 wherein said polycarbonate is composed of recurring units having the formula



wherein B is a divalent aromatic radical.

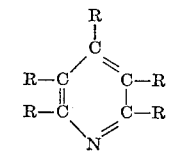
8. Process of claim 1 wherein said polyhydroxyether has the general formula

$$(O—D—O—D')_n$$

wherein D is the residuum of a dihydric phenol, D' is a hydroxyl containing residuum of an epoxide, and *n* is at least 30.

9. Process as defined in claim 1 wherein said treated substrate is conditioned by immersing said substrate in an oxidizing solution selected from the group consisting of aqueous solutions of chromic acid in inorganic acids and aqueous solutions of chromic acid, said solutions being at least about 85 percent saturated with respect to chromic acid at the use temperature of the oxidizing solution.

10. Process for increasing the adresion of metal platings to aromatic polymeric substrates which comprises treating a thermoplastic aromatic polymeric substrate selected from the group of polyarylene polyethers, polycarbonates and polyhydroxyethers with a fluid selected from the group of N,N-dimethylformamide, compounds having the formula



wherein R is hydrogen or an inert substituent, and alkylene glycols having a solubility parameter (Plastics, 26, 90 (1961)) of from about 8.7 to 10.7, conditioning the treated substrate within a strong oxidizing solution, immersing the conditioned substrate in a solution of reducing agent to sensitize said substrate, immersing the sensitized substrate in a solution of a noble metal salt to activate said substrate, immersing said activated substrate in an electroless metal plating solution to deposit a conductive metal film thereon, and thereafter electroplating said polymer.

11. Process of claim 10 wherein said fluid is vaporous N,N-dimethylformamide.

12. An article of manufacture made in accordance with the process of claim 1.

13. An article of manufacture made in accordance with the process of claim 5.

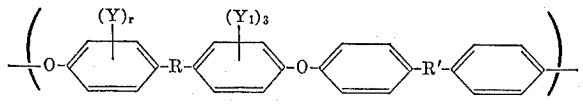
14. An article of manufacture made in accordance with the process of claim 6.

15. An article of manufacture made in accordance with the process of claim 7.

16. An article of manufacture made in accordance with the process of claim 8.

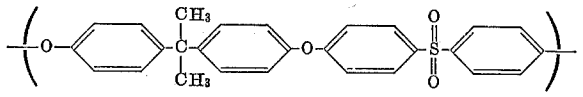
17. An article of manufacture made in accordance with the process of claim 9.

18. An article of manufacture made in accordance with claim 1 werein said substrate is a polyarylene polyether composed of recurring units having the formula:

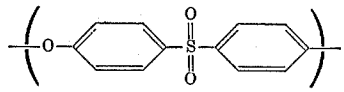


wherein R represents a member of the group consisting of a bond between aromatic carbon atoms and a divalent connecting radical and R′ represents a member of the group consisting of sulfone, carbonyl, vinyl, sulfoxide, azo, saturated fluorocarbon, organic phosphine oxide and ethylidene groups and Y and Y_1 each represent inert substituent groups selected from the group consisting of halogen, alkyl groups having from 1 to 4 carbon atoms and alkoxy groups having from 1 to 4 carbon atoms and where *r* and *z* are integers having a value of from 0 to 4 inclusive.

19. An article of manufacture made in accordance with claim 1 wherein said substrate is a polyarylene polyether composed of recurring units having the formula:



20. An article of manufatcure made in accordance with claim 1 wherein said substrate is a polyarylene polyether composed of recurring units having the formula:



21. An article of manufacture made in accordance with claim 1 in the form of a reflector wherein said substrate is comprised of a linear thermoplastic polyarylene polyether composed of recurring units having the formula:

—O—E—O—E′—

wherein E is the residuum of a dihydric phenol and E′ is the residuum of a benzenoid compound having an inert electron withdrawing group in at least one of the positions ortho and para to the valence bonds, and where both of said residua are valently bonded to the ether oxygens through aromatic carbon atoms and said metal plating is applied to a reflecting surface of said reflector and is comprised of an electroless metallic deposit and a second metallic deposit applied thereto by electroplating.

22. An article of manufacture made in accordance with claim 1 wherein said substrate is a linear thermoplastic polyarylene polyether composed of recurring units having the formula:

—O—E—O—E′—

wherein E is the residuum of a dihydric phenol and E′ is the residuum of a benzenoid compound having an inert electron withdrawing group in at least one of the positions ortho and para to the valence bonds, and where both of said residua are valently bonded to the ether oxygens through aromatic carbon atoms and said metal plating is in the form of a printed electrical circuit comprised of an electroless metallic deposit and a second metallic deposit applied thereto by electroplating.

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JOHN H. MACK, Primary Examiner

W. B. VAN SISE, Assistant Examiner

U.S. Cl. X.R.

117—47, 138.8; 156—2; 204—15, 20, 30

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,518,067 Dated June 30, 1970

Inventor(s) Bruce P. Barth

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

Column 4, line 12; "cycloadiphatic" should read --cycloaliphatic--
Column 6, line 27; "specifIc" should read --specific--
Column 8, line 16; "bent" should read --vent--
Column 9, line 4; after "oxirane oxygen" add --ether oxygen -O-,oxycarbonyl oxygen--
Column 10, line 75; "alternations" should read --alteration--
Column 14, line 36; "PC4511" should read --PC452*--
Column 15, line 1; "45" should read --35--
Column 20, line 10; "withdrawingg roup" should read --withdrawing group--
Column 20, line 36; "adresion" should read --adhesion--

Signed and sealed this 29th day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334.