

PROCESS FOR PREPARING COATED ARTICLES

This invention relates to electronically-conductive polymers, and more particularly to composite articles or polymer blends containing electronically-conductive polymers.

It is known to prepare coated articles by electrostatic painting methods. In such methods, a paint or coating is charged or ionized and sprayed on a grounded article, and the electrostatic attraction between the paint or coating and a grounded, conductive article results in a more efficient painting process with less wasted paint material, and thicker and more consistent paint coverage, particularly when the article has a complex shape. When articles fabricated from metals are painted, the metal, which is inherently conductive, is easily grounded and efficiently painted. In recent years, there has been an emphasis on the use of polymeric materials in the manufacture of articles, particularly in applications requiring reductions in weight and improved corrosion resistance, such as automotive applications. However, polymers typically used in such processes are insufficiently conductive to efficiently obtain a satisfactory paint thickness and coverage when the article is electrostatically painted.

One method that has been used to prepare electrostatically-coated polymers is to employ compositions containing conductive fibers, such as described in European Patent Application No. 363,103. However, adding such large amounts of fibrous fillers to a polymer can adversely affect both the polymer's physical properties and paint finish. U.S. Patent No. 5,188,783 discloses a method for making electrostatically-coated articles from composites containing ion-conductive polymers. However, such articles may be less conductive than desirable for use in electrostatic coating processes.

PCT Publication No. WO 94/07612 discloses a process for preparing electrostatically-paintable polyurethane compositions by the incorporation of ion-conductive metal salts. However, the conductivity of such compositions may be less than desirable for certain electrostatic painting processes.

In one aspect, this invention is a process for preparing a coated article which includes the step of electromotively coating an article having a conductivity of at least about 10^{-14} Siemens/cm (S/cm), which is molded or extruded from a liquid composition which comprises a mixture of (a) a thermoplastic polymer, reaction components for the preparation of a thermoset polymer, or a mixture thereof and (b) an electronically-conductive charge transfer complex or inherently semi-conducting polymer different from (a).

It has been discovered that the process of the invention provides a means by which electromotively-coated polymer articles may be conveniently prepared. These and other advantages of the invention will be apparent from the description which follows.

The term "electronically-conductive charge transfer complex" as used herein refers to two organic or inorganic molar species, or combinations thereof, which are

sufficiently associated to result in a partial or total transfer of electrons between the species. Such complexes may be formed, for example, via hydrogen bonds or ionic bonds, such as polyaniline association with lithium. Suitable electronically-conductive charge transfer complexes for use in the process of the invention include (1) any polymer with extended
5 pi-conjugated groups, which has been rendered conductive with a charge transfer or redox agent to provide a conductivity of at least about 10^{-12} S/cm, and (2) pi-stacking compounds.

The polymers with extended pi-conjugated groups are referred to hereafter collectively as "intrinsically-conductive polymers," or "ICPs." The process of rendering the polymer conductive is referred to herein as "doping." ICPs which have been rendered
10 conductive and have not been rendered conductive are referred to herein as "doped" ICPs and "undoped" ICPs, respectively. The compounds and polymers which may be used in such doping processes to render the ICPs conductive are referred to herein as "dopants." Polymers useful as component (a) of the composition are referred to herein as "matrix" polymers, even though they may comprise substantially less than 50 percent of the polymers present in the
15 composition. The compositions comprised of components (a) and (b) are referred to herein as "composites."

Examples of pi-stacking compounds include tetrathiotetracene, metallophthalocyanines, tetracyano-p-quinodimethane, tetrathiofulvalene, tetracyano-p-quinodimethane-tetrathiofulvalene, N-methylphenazinium-tetracyano-p-quinodimethane,
20 and mixtures thereof.

Examples of suitable ICPs include polyanilines, polyacetylenes, poly-p-phenylenes, polypyrroles, polythiophenes, poly(phenylene sulfide), polyindole, derivatives thereof, such as poly(3-alkylthiophene) and poly(o-methoxy aniline), and mixtures thereof. Preferably, the ICP is a polyaniline, polypyrrole, or polythiophene, but is most preferably a polyaniline. However,
25 the choice of ICP may also depend on its compatibility with the particular thermoplastic or thermoset matrix polymer (component (a)), as discussed below. For example, polypyrrole is especially compatible with polymers with which it can form hydrogen bonds along its backbone; polyalkylthiophenes are particularly compatible with polyolefins and polystyrene; and polyacetylenes are particularly compatible with polyolefins.

The polymeric form of the ICP may be used to prepare the composites useful in the process of the invention, either by blending the ICP with the matrix polymer, or polymerizing the matrix polymer *in situ* from a dispersion of the corresponding monomer in the ICP. Alternatively, the monomeric form of the ICP may be dissolved or dispersed in the matrix polymer and the ICP polymerized *in situ*, or both the ICP and matrix polymer may be
35 polymerized together *in situ*. In another embodiment of the invention, a graft-copolymer of a thermoplastic polymer and nitrogen-containing compound may be utilized as the component (b). An example of a method for preparing such a copolymer is illustrated in U.S. Patent No.

5,278,241. Examples of suitable inherently semi-conducting polymers include undoped polythiophene.

The optimum amount of component (b) used to prepare the composite will typically depend on the conductivity of the electronically-conductive complex or semi-conducting polymer, the relative cost of such complex or polymer, and the desired conductivity and physical properties of the article which is to be electromotively-coated. Component (b) is preferably present in an amount, based on the weight of the composite, of at least 0.1 percent; but no more than 25 percent, more preferably no more than 20 percent, and most preferably no more than 10 percent. However, if a high molecular weight dopant is utilized, a greater amount of the component (b) may be necessary to provide a desired conductivity, since the undoped ICP would represent a proportionately smaller part of the component (b). Similarly, if component (b) is prepared as a graft copolymer of an ICP and an insulating polymer, a greater amount of the component (b) may be necessary to provide a desired conductivity, since the conductive portion of the polymer would be proportionately smaller.

The ICP may be doped by any suitable method prior to being utilized in the preparation of the composite. Of course, the effectiveness of the various doping methods and the conductivity of the doped ICP obtained thereby will vary depending on the doping method, the particular ICP, the particular dopant, and the point in the fabrication process at which the ICP is doped. The ICP may be doped, for example, by mixing a solution or dispersion of a dopant with the ICP either in solution or with the ICP in the solid state, contacting a solid ICP with a solid dopant (solid state doping), or by contacting a solid ICP with a dopant in vapor form.

The amount of dopant to be used in the preparation of the doped ICP and the composite will depend on several factors, including the desired conductivity of the ICP and the composite, the physical, thermal, and/or solution processing characteristics of components (a) and (b), as well as their compatibility with each other. In general, a polyaniline ICP will reach a maximum conductivity when it is supplied in an amount sufficient to dope about 50 mole percent of the available sites. Other types of ICPs will typically reach a maximum conductivity at a somewhat lower level of doping such as, for example, 30 mole percent of the available sites for polypyrroles and polythiophenes. The amount of dopant necessary to reach the maximum conductivity for the ICP will depend on (1) the particular ICP utilized (2) its chemical purity and (3) the distribution of the dopant within the ICP matrix. Preferably, the amount of dopant utilized does not greatly exceed the amount which is needed to dope the polymer for cost reasons, and because the excess dopant may have a tendency to leach out of the composite containing the doped polymer and excess dopant.

Polyaniline can occur in several different forms such as leucoemeraldine, protoemeraldine, emeraldine, nigraniline, and pernigraniline, depending on the ratio of amine groups to imine groups present in the backbone of the polymer. The emeraldine salt

form of polyaniline, in which about 50 percent of the nitrogen atoms are contained in imine groups, is a very conductive and stable form of polyaniline, when doped.

Examples of suitable dopants for polyaniline include any salt, compound, or polymer capable of introducing a positively charged site on the polyaniline, including both
5 partial and full charge transfer such as, Lewis acids, Lowry-Brønsted acids, and the alkali metal, alkaline earth metal, ammonium, phosphonium, and transition metal salts thereof; and other redox agents having a sufficiently oxidizing oxidative couple to dope the polyaniline; alkyl or aryl halides; and acid anhydrides.

Examples of suitable Lewis acids and Lowry-Brønsted acids include those
10 described in U.S. Patent No. 5,160,457, the "functionalized protonic acids" described in U.S. Patent No. 5,232,631 and the "polymeric dopants" described in U.S. Patent No. 5,378,402. Specific examples include hydrogen chloride, sulfuric acid, nitric acid, HClO_4 , HBF_4 , HPF_6 , HF , phosphoric acids, picric acid, m-nitrobenzoic acids, dichloroacetic acid, selenic acid, boronic acid, organic sulfonic acids, inorganic clusters of polyoxometallates, and higher molecular
15 weight polymers having terminal or pendant carboxylic, nitric, phosphoric, or sulfonic acid groups, salts, esters, and diesters thereof, or mixtures thereof.

Other examples of dopants include ethylene/acrylic acid copolymers; polyacrylic acid; ethylene/methacrylic acid copolymers; carboxylic acid- or sulfonic acid-capped polystyrene, polyalkylene oxides, and polyesters; and graft copolymers of polyethylene or
20 polypropylene and acrylic acid or maleic anhydride as well as mixtures thereof; sulfonated polycarbonates, sulfonated ethylene-propylene-diene terpolymers (EPDM), sulfonated polystyrene, sulfonated ethylene-styrene copolymers, polyvinylsulfonic acid, sulfonated poly(phenylene oxide), and sulfonated polyesters such as polyethylene terephthalate; as well as the alkali metal, alkaline earth metal, transition metal, ammonium, and phosphonium salts
25 of such acids, preferably the lithium, manganese, and zinc salts of such acids. Examples of suitable alkylation agents include those corresponding to the formula R-X , wherein R is a C_{1-5} alkyl group or aryl group, and X is Cl, Br, or I. Examples of suitable acid anhydrides include maleic anhydride and phthalic anhydride.

ICPs other than polyaniline may be doped with transition metal salts such as,
30 CuCl_2 , CeCl_3 , FeCl_3 , and $\text{Fe}_2(\text{SO}_4)_3$, or other redox agent having a sufficiently oxidizing oxidative couple to dope the ICP, such as AsF_5 , NOPF_6 , I_2 , Br_2 , or Cl_2 . The doped ICP preferably has a conductivity of at least 10^{-12} S/cm, more preferably at least 10^{-6} S/cm, and most preferably at least about 1 S/cm.

Suitable thermoplastic polymers for use in the process of the invention preferably
35 have a glass transition temperature in the range of from -100°C to 300°C . Examples of such polymers include polyolefin polymers and copolymers such as polypropylene, polyethylene, poly(4-methylpentene), and poly(ethylene-vinyl acetate); styrenic polymers and copolymers such as polystyrene, syndiotactic polystyrene, poly(styrene-acrylonitrile) or poly(styrene-maleic

anhydride); polysulfones; polyethersulfones; poly(vinyl chloride); aliphatic or aromatic polyesters such as poly(ethylene terephthalate) or poly(butylene terephthalate); aromatic or aliphatic polyamides such as nylon 6, nylon 6,6 and nylon 12; polyacetal; polycarbonate; thermoplastic polyurethanes; modified polyphenylene oxide; polyhydroxy ethers; 5 polyphenylene sulfide; poly(ether ketones); poly(methyl methacrylate); as well as mixtures thereof. Suitable polyolefins also include high and low density polyethylenes and polypropylene, linear low density polyethylene and polypropylene, and homogeneous random partly crystalline ethylene- α -olefin copolymers having a narrow molecular weight distribution, as described by Elston in U.S. Patent No. 3,645,992, and elastic substantially linear olefin 10 polymers (available from DuPont Dow Elastomers L.L.C as ENGAGE™ polyolefins) as disclosed, for example, by Lai et al. in U.S. Patent No. 5,272,236.

The thermoplastic polymer may also be a physical blend of the above-mentioned polymers or it can take the form of an impact-modified polymer containing a discrete rubbery phase dispersed within the thermoplastic polymer itself. An example of the latter is a material 15 commonly referred to as a thermoplastic polyolefin (TPO), which is a blend of polypropylene and ethylene-propylene (EPR) or ethylene-propylene-diene (EPDM) rubber commonly used in automotive applications. Other examples include poly(styrene-acrylonitrile) copolymer modified with polybutadiene rubber, commonly referred to as ABS, which is frequently used in automotive applications, and blends of ABS and other polymers, such as polycarbonate. In 20 addition, the thermoplastic polymer may contain additive materials such as antioxidants, UV stabilizers, plasticizers, mineral fillers, mold release agents, or a combination of such additives.

The thermoplastic polymer should possess a molecular weight high enough to impart physical properties to the composite that are desired for the particular end-use application. For example, for automotive applications, the polymer should be selected to 25 provide sufficient tensile and impact strength over a range of temperatures, heat and chemical resistance, elongation, and stiffness. The relationship between polymer molecular weight and resulting physical properties varies with the class of polymers considered, however, thermoplastic polymers with molecular weights in excess of about 30,000 typically afford molded or fabricated articles with these desirable property attributes. In addition, the 30 thermoplastic matrix polymer preferably possesses sufficient thermal stability to permit the use of melt fabrication as a means of preparing the blend with the electronically-conductive charge transfer complex or semi-conducting polymer. Most of the above-mentioned thermoplastic polymers which are commercially available can be melt processed at temperatures where the amount of polymer degradation, if any, is not sufficient to substantially affect the polymer's 35 physical properties.

Examples of suitable thermoset polymers include polyureas, polyurethanes, polyepoxides, polymers used to prepare sheet molding compound (SMC) and bulk molding compound (BMC), including unsaturated polyesters and vinyl ester resins, and mixtures

thereof, including combinations of epoxy resins and polyurethane elastomers. Polymers useful for the preparation of sheet molding compound and bulk molding compound are described, for example, in Kia et al., *Sheet Molding Compounds: Science and Technology* (Hanser/Gardner Publications, 1993). The electronically-conductive charge transfer complex, inherently semi-conducting polymer, or monomer or other precursor for the preparation of either may be incorporated into either reaction component of a two-component or multi-component reaction for the preparation of such polymers, so long as they do not significantly interfere with the subsequent reaction of the components which form the thermoset polymer. For example, if the polymer is a polyurethane or polyurea polymer, and the ICP is polyaniline, the polyaniline is preferably added to the isocyanate-reactive component. Examples of polyurethane/polyurea reaction components, as well as processes for the preparation of such polymers, are described, for example, in PCT Application No. WO 94/07612 and U.S. Patent No. 5,055,544. Alternatively, the thermosetting composition used to prepare the composite may be a one-component composition, such as a reactive hot melt adhesive.

In addition to components (a) and (b), the composite may additionally comprise other materials, such as, conductive fillers such as carbon, graphite, and metallic fibers or whiskers, as well as non-conductive fillers, pigments, surfactants, plasticizers, mold release agents, antioxidants, and UV stabilizers. Preferably, the matrix polymer of the composite is present in an amount, based on the weight of the composite, of at least 10 percent, and more preferably at least 20 percent.

The conducting thermoplastic composites described above may be prepared by any suitable method for preparing a uniform mixture of components (a) and (b). For example, such mixture may be prepared by adding a doped ICP to the matrix polymer and then blending the two in a suitable solvent, by melt-processing the polymers (a) and (b) together at temperatures above the glass transition temperatures of one of the polymers. It may also be more convenient in some cases to prepare the composite by first preparing a blend or master batch having a relatively high concentration of component (a), extruded pellets of which may then be mixed with pellets of component (b). The final polymer composite would thereafter be prepared at the point at which the pellet mixture is thermally processed and used to manufacture the end-use article. Mixtures containing thermoset polymers may be prepared by incorporating component (b) into any component of a multi-component thermoset system, as described above.

The electronically-conducting charge transfer complex or inherently semi-conductive polymer is preferably selected to be chemically/physically stable under the processing conditions used to fabricate the article to be subsequently electromotively-coated. For example, component (b) must be thermally stable at the processing temperature if it is to be melt processed, or must be sufficiently soluble or dispersible if a solution processing fabrication technique is utilized.

When combining doped ICPs with the matrix polymer to form the composite, a compatibilizing agent may be utilized to improve the compatibility and/or blending characteristics of the polymers in order to produce a uniform blend of a conductive material which has the most cost-effective amount of ICP necessary to achieve a particular conductivity, and which also has suitable physical properties, such as Young's modulus and impact properties. The term "compatible" as used herein refers to the tendency of the mixture to not undergo gross phase separation from the time the blend is molded or extruded into an article up until the conductive properties of the article are utilized, but also refers to the ability of the blend components to not significantly chemically react with or otherwise degrade each other's physical or conductive properties, and the ability of the ICP to remain relatively uniformly dispersed with the matrix polymer.

The conductivity of the composite used in the process of the invention is preferably at least 10^{-12} S/cm, more preferably at least 10^{-8} S/cm, and most preferably at least 10^{-5} S/cm. However, the most preferred conductivity for a particular composite will of course depend on the particular electromotive coating process employed, including the particular equipment utilized to carry out the process, as well as the cost and physical property requirements of the composite. For example, electrodeposition coating and electroplating processes may require a higher conductivity (such as 10^{-3} to 100 S/cm) than electrostatic coating processes. The conductivity of the composite directly affects the coating thickness and uniformity obtainable in an electromotive coating process, as well as the efficiency of the process, under a given set of coating process conditions. As the conductivity increases, thicker coatings as well as less waste of the coating material may be observed. Once a "target" conductivity for a particular coating process is identified, the degree of "improvement" in conductivity for a matrix polymer which is necessary to achieve the target conductivity will depend on its inherent electronic conductivity, since some polymers are naturally more insulating than others. Many polymers commonly used commercially in structural applications have conductivities of less than 10^{-14} S/cm. The specific conductivity values given herein are intended to represent the local conductivity of the composite at the point at which it is measured, unless otherwise noted, since the conductivity of the composite may not be completely uniform across the entire sample.

Component (b) is preferably employed in an amount sufficient to increase the electronic conductivity of a composition which is the same in all respects except that it does not contain component (b), by at least a factor of 10, in S/cm. The electronically-conductive charge transfer complex or inherently semi-conducting polymer is preferably used in an amount sufficient to increase the average conductivity of the composite by a factor of 10^4 , and most preferably by a factor of 10^8 , relative to the same composite prepared in the absence of the complex or semi-conducting polymer. Of course, it is necessary for the complex or semi-conducting polymer to be more electronically-conductive than the matrix polymer for this to

occur, but the polymer may possess some degree of electronic conductivity without the complex or semi-conducting polymer, as discussed above, or the composite may contain other conductive fillers, such as carbon particles or fibers.

The composites described above for use in the process of the invention may
5 possess advantageous physical properties, such as tensile strength, elongation, room temperature impact strength, and/or low temperature strength, relative to other plastic materials having substances incorporated therein in amounts sufficient to increase their conductivity, particularly for a given target conductivity above about 10^{-5} S/cm. Low temperature impact resistance of a material may be determined using ASTM Method
10 No. 3763-8 6(1995) carried out on a DYNATUP™ impact testing machine (Model No. 8000) at a temperature of about -29°C. Tensile strength properties of the composites may be tested according to ASTM Method No. D638-876 (1988).

The composite may be molded or extruded into an article and electromotively-coated using any suitable technique. For example, thermoplastic composites may be fabricated
15 by thermal processing techniques, such as extrusion, pultrusion, compression molding, injection molding, blow molding, and co-injection molding. Thermoset materials may be fabricated by reaction injection molding techniques, for example, or processes typically employed in the preparation and molding of SMC and BMC, such as compression molding. Once fabricated, the electronically-conductive article can be painted or coated on at least one
20 of its surfaces using any suitable electromotive coating process. The term "electromotive coating process" as used herein refers to any coating process wherein an electrical potential exists between the substrate being coated and the coating material. Examples of electromotive coating processes include electrostatic coating of ligands or powders, electrodeposition ("E-Coat") processes, electromotive vapor deposition, and electroplating
25 processes. The article may be painted or coated with any suitable water-based or organic-based composition (or water/organic mixture), including conductive primer compositions which further enhance the electronic conductivity of the article, or with a solventless organic composition by a powder coating or vapor deposition method.

The coated articles prepared by the process of the invention are useful in any
30 application for coated plastic articles, but are particularly useful as components in applications where the use of a lightweight non-corrosive material is desirable, such as automotive and other transportation applications, as well as static-dissipation and shielding applications.

The following examples are given to illustrate the invention and should not be interpreted as limiting it in any way. Unless stated otherwise, all parts and percentages are
35 given by weight.

Example 1

A blend containing 400 g of polypropylene (PRO-FAX™ 6323, available from Himont), 170 g of ethylene/octene elastomer (ENGAGE™ 8100) and 110 g of VERSICON™ (an

organic sulfonic acid-doped polyaniline having a molecular weight of 60,000 to 90,000 and a conductivity of about 1.5 S/cm, available from Allied Signal) was compounded on a Welding Engineers 20 mm twin-screw extruder at 200 rpm using the following temperature settings:
Zone 1 = 180°C; Zone 2 = 190°C; Zone 3 = 195°C; Zone 4 = 200°C; Zone 5 = 205°C;
5 Zone 6 = 210°C; Zone 7 = 210°C; Die = 200°C.

The extruded blend was cooled in a water bath and pelletized. A 4 inch by 8 inch by 0.125 inch plaque was compression molded at 200°C for 5 minutes. The same blend containing polypropylene and ethylene/octene elastomer without VERSICON™ was also compounded and compression molded as a control sample. The plaques were electrostatically
10 painted using the following procedure.

The plaques were rinsed for 60 seconds at 77°C in a phosphoric acid based detergent (ISW 32, available from DuBois Chemical Corp.), followed by a 30-second deionized water rinse at 71°C, a 30-second rinse at 71°C in ISW 33, a phosphoric acid based painting conditioning agent (available from DuBois Chemical Corp.), a 30-second ambient temperature
15 deionized water rinse, and a 15-second ambient temperature deionized water rinse.

The plaques were dried with forced air followed by a 30-minute drying in an electric air circulating oven at 71°C. The plaques were cooled to room temperature before painting.

Two coats of paint (CBC9753 White, manufactured by Pittsburg Paint and Glass)
20 were applied to the panels using a SPRAYMATION™ Model 310160 automatic panel sprayer using a Binds Model 80A electrostatic spray gun (63 B fluid dip, N63 air cap, 111-1271 fluid needle). The panels were painted using an 850 inch/minute gun traverse speed, a 2-inch spray gun index with 50 percent fan overlap, a 45 psig air atomization pressure, and a 10-inch gun-to-part distance. Each coat was applied by 8 gun passes (left-right-left) per coat at 80 kilovolts and
25 56 microamps current. The paint had an unreduced viscosity (Fischer Number 2 Viscosity Cup) of 88 seconds; a spray viscosity (Fischer Number 2 Viscosity Cup) of 21 seconds; and contained 30 percent by volume isobutyl acetate. Prior to the application of the second coat, the first coat was permitted to flash for 30 seconds. After the application of the second coat, the painted panels were allowed to flash for 5 minutes. The painted panels were subsequently cured in a
30 Despatch Model PWC3-14-1 electric air circulation oven for 40 minutes at a temperature of 127°C.

The standard metal panel support rods on the SPRAYMATION™ were replaced with fiberglass rods of the same dimensions to reduce the attraction of paint to the support rod. The rack cross-members were replaced with oak wood, which was glued on with epoxy
35 resin. Two aluminum plates 4 inch by 6 inch by 1/4 inch were mounted 1 inch apart on the top oak cross-bar with wood screws. A metal bolt was flush mounted to the face of the metal plates. The bolt was centered on the plate and it protruded on the back where it served as a

grounding point. A grounding wire was attached with a nut and a washer. The ground had a resistivity of 0.15 ohms.

Test samples were mounted in such a way that half of the sample was backed by the grounded aluminum plate and half was unbacked. The test samples were held in place by clamping on the outside edge, onto the aluminum plate with conductive metal clips having a resistivity of no greater than 0.15 ohms. This ensured that the plastic parts were grounded. Masking tape was used to cover any exposed aluminum.

The film thickness on the plastic panels was measured by first cutting a small piece of the painted substrate out of the test samples. The chip was placed painted side down on a flat cutting surface. A cross-section was cut through the plastic and paint layers. The cross-sectional piece was placed on a microscope slide and paint thickness was measured at a magnification of 200 times with a graduated ocular. Film thickness measurements were made on both the aluminum-backed half and the unbacked half of the panels. The results were given in the following table, which showed the paint thicknesses obtained on two separate samples. As used in Table I, "% NPani" refers to the weight percent solids of polyaniline, on an undoped basis, present in the sample.

Table I

20	<u>Sample</u>	With Aluminum Plate (mil)	Without Aluminum Plate (mil)	% NPani
	Control* - Sample 1	1.5	0.6	0
	Control* - Sample 2	1.5	0.5	0
25	Conductive Blend - Sample 1	1.8	1.7	8
	Conductive Blend - Sample 2	1.8	1.7	8

*Not an example of the invention.

Example 2

Zn(DBSA)₂ was prepared by the following method: DBSA (320 g) was placed in a large evaporating dish and heated gently while stirring. While warm, 40.7 g of ZnO were slowly added to the DBSA. The mixture was kept under N₂ flow. The temperature was slowly raised to the point where the mixture began to froth and H₂O steam was evolved, formed by the reaction between the acid and the base. The mixture was maintained at this temperature for about 5 hours. (After about 3 hours the steam evolution ceased). The product, Zn(DBSA)₂, was allowed to cool to room temperature (about 25°C), and then was further cooled to about

-10°C. The sample was further cooled with dry ice and pulverized into a powder for easier blending.

Pani(DBSA)_{0.5} was prepared by combining neutral polyaniline ("NPani") (obtained from Allied Signal) (93 g) with 161 g of DBSA in about 1.5 liters of toluene. The toluene was sparged with N₂ for 15 minutes, and 0.6 g PEPQ (PEPQ powder from Sandoz Chemical Corporation) was added as an antioxidant. The mixture was sonicated at 40°C for 2 days.

The Pani(DBSA)_{0.5} and Zn(DBSA)₂ were then combined in a 1:1 mole ratio, which was a 1:2.9 weight ratio. The Zn(DBSA)₂ was first dissolved in warm toluene, and then solutions of the two are combined. The resulting mixture was blended with polyethylene (ENGAGE™ 8100) which has been dissolved in warm toluene, in a 64:36 weight ratio (ratio of Pani(DBSA)_{0.5} and Zn(DBSA)₂ to ENGAGE™). The solution of these components was poured into a large glass evaporating dish, and the solvent evaporated off in a fume hood. After 2 days, this mixture was cooled with dry ice, vacuum dried at 40°C and ground to a consistency which fed smoothly into a twin-screw extruder, and then dried under vacuum again.

The ground mixture and a blend of polypropylene and ethylene/octene elastomer prepared and compounded as described in Example 1 (in a 1-inch counter-rotating intermeshing twin-screw extruder running at 100 rpm (Brabender extruder/Haake drive)) were combined in amounts sufficient to give the weight percent polyaniline shown in Table II. Zone temperatures were profiled from 190°C to 210°C from the feed throat to the die, respectively. The melt temperature during extrusion varied from 205°C to 215°C. The molten polymer blend strand was cooled in a water bath and pelletized. Plaques for paint transfer testing were prepared on a Tetrahedron compression molding press at 200°C and 50,000 psi clamp force. Injection molding of tensile and impact test specimens was carried out on a BOY™ 30 ton injection molding machine. The following conditions were used: Injection temperature - 200°C to 210°C; Injection pressure - 17 to 22 bar (250 to 325 psi); Mold temperature - 50°C; Injection time - 2 seconds; Cooling time - 20 seconds.

Static decay data was obtained using U.S. Military Test No. B-81705B, Method 4046, to measure the time necessary for the 5000 V static charge to decay to 500 V at ambient conditions. The molded article was painted according to the procedure given in Example 1. The paint thickness was measured according to the procedure given in Example 1. The results are shown in Table II. Table II also included the weight percent polyaniline (on an undoped basis) in each of the samples.

Examples 3 to 10

Using the procedure given in Example 2, molded articles were prepared using the doped polyanilines and zinc salts shown in Table II. As additional examples of methods for preparing the mixtures of polyaniline(DBSA) complex and the Zn(DBSA) salts, a 1:1 molar ratio of Pani(DBSA)_{1.3} and ZnO(DBSA)_{0.74} (Example 5) may be prepared by combining solutions of

118 g of DBSA and 40.7 g of ZnO according to the above procedure, to prepare the zinc salt; and combining solutions of 93 g of polyaniline and 418.6 g DBSA to prepare the doped polyaniline. The resulting solutions were then combined and processed as described in Example 2 to obtain a ground solid form of the mixture. Similarly, a 1:1.5 molar ratio of
5 $\text{Pani}(\text{DBSA})_{1.3}$ and $\text{ZnO}(\text{DBSA})_{0.74}$ (Example 6) may be prepared by combining solutions of 177 g of DBSA and 70.1 g of ZnO according to the above procedure, to prepare the zinc salt; and combining solutions of 93 g of polyaniline and 418.6 g DBSA to prepare the doped polyaniline. The resulting solutions were then combined and processed as described in Example 2 to obtain a ground solid form of the mixture. In Example 7, the mixture of $\text{Pani}(\text{DBSA})_{1.3}$ and
10 $\text{ZnO}(\text{DBSA})_{0.74}$ was predispersed in the thermoplastic polyolefin blends instead of the ENGAGE™ 8100.

15

20

25

30

35

Table II

<u>Example</u>	<u>Pani Complex</u>	<u>Wt% Pani (w/o dopant)</u>	<u>Average Static Decay Time at 10% Cutoff</u>	<u>Paint Film Thickness (Unbacked) (mm)</u>	<u>Paint Film Thickness (Backed) (mm)</u>	<u>Conductivity (S/cm)</u>
2	[Pani (DBSA) _{0.5}] _{1.0} [Zn(DBSA) _{2.0}] _{1.0}	1.5	>50 sec.	0.7	--	--
3	[Pani (DBSA) _{0.5}] _{1.0} [Zn(DBSA) _{2.0}] _{1.0}	2.0	0.01 sec.	1.2	--	--
4	VERSICON™	8.0	0.03 sec.	1.7	--	--
5	[Pani (DBSA) _{1.3}] _{1.0} [ZnO(DBSA) _{0.74}] _{1.0}	2.0	>50 sec.	0.5	1.0	10 ⁻¹⁵
6	[Pani (DBSA) _{1.3}] _{1.0} [ZnO(DBSA) _{0.74}] _{1.5}	2.0	0.02 sec.	1.2	1.5	10 ⁻¹⁰
7	[Pani (DBSA) _{1.3}] _{1.0} [ZnO(DBSA) _{0.74}] _{1.5} (predispersed in TPO)	4.2	0.01 sec	1.6	1.5	3 x 10 ⁻⁸
8	[Pani (DBSA) _{1.3}] _{1.0} [ZnO(DBSA) _{0.76}] _{1.5}	1.0	--	0.5	--	--
9	[Pani (DBSA) _{1.3}] _{1.0} [ZnO(DBSA) _{0.76}] _{1.5}	1.0	--	0.6	--	--
10	[Pani (DBSA) _{0.5}] _{1.0} [ZnO(DBSA) _{1.8}] _{1.5}	2.0	0.01 sec.	1.3	--	--

"--" - data not obtained

CLAIMS:

1. A process for preparing a coated article which includes the step of electromotively coating an article molded or extruded from a composition having a conductivity of at least 10^{-14} S/cm, which comprises (a) a thermoplastic polymer, reaction components for the preparation of a thermoset polymer, or a mixture thereof and (b) an electronically-conductive charge transfer complex or inherently semi-conducting polymer different from (a).
2. The process of Claim 1 wherein the composition has a conductivity which is at least 10^4 times greater, in S/cm, than the conductivity of a composition which is the same in all respects except that it does not contain component (b).
3. The process of Claim 1 wherein the composition has a conductivity which is at least 10^8 times greater, in S/cm, than the conductivity of a composition which is the same in all respects except that it does not contain component (b).
4. The process of Claim 1 wherein the component (b) is a doped intrinsically-conductive polymer.
5. The process of Claim 4 wherein the intrinsically-conductive polymer is polyaniline.
6. The process of Claim 1 wherein the composition contains less than 10 percent by weight of the doped intrinsically-conductive polymer.
7. The process of Claim 1 wherein component (a) is a thermoplastic polyolefin.
8. The process of Claim 1 wherein component (a) comprises reaction components for the preparation of a thermoset polyurethane or polyurea.
9. The process of Claim 1 wherein component (a) is an unsaturated polyester resin.
10. A process for preparing a coated article which includes the step of electrostatically coating an article molded or extruded from a composition having a conductivity of at least 10^{-14} S/cm, which comprises (a) a thermoplastic or thermoset polymer, and (b) an electronically-conductive charge transfer complex or inherently semi-conducting polymer different from (a).
11. A process for preparing a coated article which includes the step of electroplating an article molded or extruded from a composition having a conductivity of at least 10^{-5} S/cm, which comprises (a) a thermoplastic or thermoset polymer, and (b) an electronically-conductive charge transfer complex or inherently semi-conducting polymer different from (a).

