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(54) **COMPOSITION D'AMORCAGE ET COLLAGE DE SUBSTRATS
POLYMERES ORGANIQUES**

(54) **PRIMER COMPOSITION AND BONDING OF ORGANIC
POLYMERIC SUBSTRATES**

(57) Cette invention concerne une composition d'amorçage, laquelle comprend un composé donneur halogène, un composé contenant un isocyanate aliphatique, et un solvant organique.

(57) The present invention provides a primer composition comprising a halogen donor compound, an aliphatic isocyanate-containing compound, and an organic solvent.



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(54) Title: PRIMER COMPOSITION AND BONDING OF ORGANIC POLYMERIC SUBSTRATES		
(57) Abstract		
<p>The present invention provides a primer composition comprising a halogen donor compound, an aliphatic isocyanate-containing compound, and an organic solvent.</p>		

Primer Composition and Bonding of Organic Polymeric Substrates

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Field of the Invention

The present invention relates to a surface treatment or primer composition that improves the adherence of materials such as adhesives, inks, and coatings to organic polymeric substrates, particularly substrates made of organic high polymers.

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Background of the Invention

Many organic high polymers (i.e., large molecules, typically greater than about 10,000 number average molecular weight, composed of repeat units of low molecular weight species, for example, ethylene or propylene), such as ethylene-propylene-diene terpolymer (EPDM) and ethylene-propylene rubber (EPR), have surface energy characteristics that render them difficult to bond to adhesives, inks, and coatings, for example, using conventional bonding agents and methods. Various proposals have been made to overcome these disadvantages.

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For example, compositions of styrene-ethylene/butylene-styrene block copolymers and acrylic polymers in a solvent mixture for priming polymers of low surface energy are known. These compositions improve the bonding of pressure sensitive and structural adhesives to polymers of low surface energy.

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Also, it is known that the receptiveness of rubbers, e.g., copolymer of styrene and butadiene (SBR) used for shoe soling, and other solid high polymers is improved toward bonding with adhesives (e.g., solvent-based polyurethane and polychloroprenes) by the chlorination of the surface with solutions of halogen donors, such as trichloroisocyanuric acid and N,N-dichlorobenzene sulfonamide. This can be done, for example, by incorporating the halogen donor into a primer or the adhesive itself. Typically, however, solutions containing only halogen donors are effective only on substrates containing a high level of ethylenic unsaturation. Also, adhesive compositions,

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such as polyurethane adhesives, containing a halogen donor, have limited stability.

Primer compositions and adhesive compositions (e.g., hydroxy-terminated polyurethane adhesives) that display improved adhesion to organic high polymers having low levels of ethylenic unsaturation are known. Such primer compositions typically contain halogen donors (e.g., dibromodimethylhydantion and trichoroisocyanuric acid) and aromatic isocyanates (i.e., compounds in which isocyanate groups are directly attached to an aromatic carbon, such as in 4,4'-diphenylmethane diisocyanate). See, for example, British Patent Application Nos. 1,458,007 (published December 8, 1976) and 1,460,043 (published December 31, 1976). However, such compositions typically have shelf-lives of less than about 7 days. Thus, they cannot be readily shipped as a one-part system because they must be mixed shortly before use. In addition, the primed substrate, if exposed to UV radiation, will yellow and discolor due to the presence of the aromatic group in the isocyanate compound, which is undesirable on white or clear rubber stock, for example.

Many of these compositions, whether primer compositions or adhesive compositions, require mechanical roughening or abrasion of the surface of the substrate prior to or during application of the composition. However, abrasion of the substrates, especially elastomers in the presence of the primer, is not always easy or convenient for all applications and is sometimes wasteful of primer.

Thus, there is a need for primer compositions and application procedures which will effectively prime a variety of different substrates, especially elastomers, for bonding. In addition, such primer compositions should possess a long shelf-life, and after application, be stable to UV radiation and high temperature and humidity.

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Summary of the Invention

The present invention provides a primer composition comprising a halogen donor compound, an aliphatic isocyanate-containing compound, and an organic solvent. In a preferred embodiment, the primer composition comprises a solution of: a halogen donor compound selected from the group consisting of
5 1,3-dichloro-5,5-dimethylhydantoin, tetrachloroglycoluril, trichloroisocyanuric acid, and combinations thereof; an aliphatic isocyanate-containing compound selected from the group consisting of 1,6-hexamethylene diisocyanate, methylene bis(4-cyclohexyl isocyanate), trimethyl hexamethylene diisocyanate, isophorone diisocyanate, γ -isocyanatopropyl trimethoxysilane, and oligomers and
10 combinations thereof; and an organic solvent.

The present invention also provides a method for adhering two substrates together and the article prepared according to this method. The method involves: applying a primer composition to a surface of a first organic polymeric substrate to provide a primed surface; wherein the primer composition
15 is preparable by combining components comprising a halogen donor compound, an aliphatic isocyanate-containing compound, and an organic solvent; applying an adhesive to the primed surface or to a surface of a second substrate; and positioning the surfaces of the first and second substrates together to form a
bond.

20 Another method of the present invention is a method of forming a traction coating on an article comprising an organic polymeric substrate. The method involves: applying a primer composition to a surface of the organic polymeric substrate to provide a primed surface; wherein the primer composition is preparable by combining components comprising a halogen donor compound,
25 an aliphatic isocyanate-containing compound, and an organic solvent; and applying a traction coating comprising a plurality of hard, inorganic particles to the primed surface. Preferably, the step of applying a traction coating comprises: applying an adhesive to the primed surface to form an adhesive-coated primed surface; and applying a plurality of hard, inorganic particles to the adhesive-
30 coated primed surface. Alternatively, the step of applying a traction coating comprises applying a sheet material having a plurality of hard, inorganic particles

adhered thereto.

Also provided is an article comprising an organic polymeric substrate having at least one surface on which is coated a traction coating. The traction coating is preparable by: applying a primer composition to a surface of
5 the organic polymeric substrate to provide a primed surface; wherein the primer composition is preparable by combining components comprising a halogen donor compound, an aliphatic isocyanate-containing compound, and an organic solvent; and applying a traction coating comprising a plurality of hard, inorganic particles to the primed surface. The article is preferably an article of footwear, such as a
10 shoe having an elastomeric sole, particularly an athletic shoe, or a boot.

As used herein, elastomer or elastomeric material is used in its conventional manner to refer to a material with rubber-like characteristics, as defined by Hawley's Condensed Chemical Dictionary, Eleventh Edition, 1987, New York, NY. This includes materials that are capable of retracting quickly to
15 approximately their original length after being stretched to at least twice their original length, such as thermosetting polymers-like natural and synthetic rubbers. This also includes materials such as uncrosslinked polyolefins that are thermoplastic, which may yield upon stretching.

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Brief Description of the Drawings

FIGS. 1 and 2 are a side view and bottom view, respectively, of a shoe in accordance with the present invention.

FIG. 3 is a partially exploded view of a boot having a traction coating on the exposed surface of the sole.

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FIG. 3A is a traction coating on the exposed surface of the sole of the boot of FIG. 3.

Detailed Description

The present invention provides primer compositions of a halogen
30 donor compound and an aliphatic isocyanate-containing compound in an organic solvent. Preferably, these components are substantially unreactive (i.e.,

nonreactive) with each other. That is, although there may be weak interactions between the components, such as hydrogen bonding interactions, for example, there are no covalent or ionic bonds broken or formed to produce new species in preferred compositions. Thus, preferably, the primer compositions are stable at
5 elevated temperatures up to about 60°C for at least about 14 days, when stored in a moisture-free environment. More preferably, they are stable at room temperature (25-30°C) for at least about 1 month, and most preferably at room temperature for at least about 6 months, when stored in a moisture-free environment. As used herein, "stable" refers to a composition that does not
10 decompose, react, precipitate, or significantly discolor during the specified time when stored in a moisture-free environment. That is, the composition is substantially unchanged after a period of time when stored in a moisture-free environment. Herein, a "moisture-free environment" is an environment from which substantially all atmospheric moisture has been removed. Typically, there
15 is less than about 0.01% water in a "moisture-free environment," such as a moisture-free solvent and/or a moisture-free atmosphere, as used herein.

Primer compositions according to the present invention typically effectively modify the surface of an organic polymeric substrate (e.g., substrates made of organic high polymers, which can be synthetic or natural) for improved
20 adhesion of an adhesive, an ink, or other coating. They also preferably have relatively long shelf-lives and preferably do not significantly discolor upon exposure to UV light. Such primers are typically effective on a wide variety of organic polymeric substrates having low surface energies, thereby rendering them adherent to an adhesive, an ink, or other coating. This allows for improved
25 adhesion to other organic polymeric substrates or other nonpolymeric substrates, such as glass, metal, ceramic, and the like, using a variety of adhesives.

Further, such primers are generally particularly effective on organic polymeric substrates containing some degree of ethylenic unsaturation. For example, adhesion of adhesives, inks, coatings, and the like, to substrates,
30 particularly elastomers containing ethylenic unsaturation such as polybutadiene, polychloroprene, polyisoprene, natural rubber, isobutene-isoprene copolymer,

styrene-butadiene copolymer, styrene-butadiene-styrene block copolymers, and the like, can be improved using primers according to the present invention. Also, adhesion of such materials to substrates that contain low levels of, or no ethylenic unsaturation, such as ethylene-propylene-diene terpolymer, ethylene-propylene
5 rubber, butyl and bromobutyl rubber, can also be improved by the primer compositions of the present invention. Significantly, other substrates, such as polyethylene vinyl acetate foams and polyurethane rubber or foams, as well as other organic high polymer substrates such as synthetic and natural leather, polyester, polyamide, and plasticized polyvinyl chloride, are also effectively
10 primed for adhesive bonding using the primers according to the present invention. The surface of the organic polymeric substrates can be mechanically roughened, prior to priming, to enhance adhesion, although this is not a requirement.

Suitable halogen donor compounds for making primers according to the present invention are well known in the art (see, e.g., U.S. Pat. No.
15 3,991,255 (Blaskiewicz et al.). Such materials are referred to in the art as "halogen donor compounds" typically because it is believed that such materials "donate" a halogen atom to an unsaturated moiety in the substrate, although this is not a necessary requirement for the present invention. Classes of such compounds include, but are not limited to, N-monohalogenated aromatic
20 sulfonamides, N,N-dihalogenated aromatic sulfonamides, wherein sulfonamide nitrogen is bonded to two atoms of chlorine, bromine, or iodine and the sulfonyl sulfur is bonded directly to the aromatic nucleus; and saturated N-halogenated heterocyclic amides, wherein the carbonyl carbon is situated in the ring with the carbonyl carbon being bonded to two N-halogenated nitrogen atoms both of
25 which also reside on the heterocyclic ring. Examples of such compounds include 1,3-dichloro-5,5 dimethylhydantoin, tetrachloroglycoluril, and trichloroisocyanuric acid. Various combinations of such materials can be used. They may be prepared by methods well known in the art or obtained from commercial sources. Chlorine donors such as trichloroisocyanuric acid (which is
30 available, for example, under the trade designation "ACL 90 PLUS" from

Occidental Chemical Corporation of Dallas, TX) are preferred since they are more economical and available than are bromine or iodine donors.

Aliphatic isocyanate-containing compounds useful in making primers according to the present invention are those in which the isocyanate (-NCO) groups are directly attached to aliphatic carbons. Thus, although not typically preferred, the aliphatic isocyanate-containing compounds may include aromatic moieties. Preferably, the aliphatic isocyanate-containing compounds do not contain any aromatic moieties. Thus, the aliphatic isocyanate-containing compounds may include unsaturation, although saturated materials are typically preferred. Furthermore, preferred aliphatic isocyanate-containing compounds are substantially nonreactive with the halogen donor compounds.

The isocyanate-containing compound can be in the form of monomers, oligomers, or polymers, as long as there are available (i.e., unreacted) isocyanate groups. Examples of such aliphatic isocyanate-containing compounds include monomers such as 1,6-hexamethylene diisocyanate, methylene bis(4-cyclohexyl isocyanate), trimethylhexamethylene diisocyanate, isophorone diisocyanate, γ -isocyanatopropyl trimethoxysilane, dimer acid diisocyanate, xylene diisocyanate, benzene-1,3-bis(1-isocyanato-1-methylethyl), and benzene-1,4-bis(1-isocyanato-1-methylethyl), oligomers of aliphatic isocyanate monomers, and polymers or prepolymers (i.e., reaction products) of aliphatic isocyanates with active hydrogen containing compounds. Of these, isophorone diisocyanate, γ -isocyanatopropyl trimethoxysilane, and oligomers and combinations thereof are preferred. Oligomers of aliphatic isocyanates, such as the trimer of isophorone diisocyanate (which is available, for example, under the trade designation "VESTANAT T1890E" from Hülls America, Inc. of Piscataway, NJ), are particularly preferred because they are less volatile and therefore less toxic than monomeric isocyanates.

The reaction products of aliphatic isocyanates with active hydrogen-containing compounds are suitable if they contain unreacted isocyanate groups. Preferred such materials are substantially unreactive with the halogen donor compound and the organic solvent. Any of the above-listed aliphatic

isocyanates can be used to make such materials. Examples of active hydrogen-containing compounds include ethylene glycol, 1,4-butanediol, 1,6-hexanediol, trimethylol propane, pentaerythritol, and 1,4-cyclohexane dimethanol. Polyester and polycarbonate polyols are also useful. The reaction products of aliphatic isocyanates with active hydrogen-containing compounds that contain ethylenic unsaturation or other functional groups that react with the halogen donor compounds may be useful, but are not preferred. For example, prepolymers of polytetramethylene oxide polyether, polypropylene oxide polyether, or polyethylene oxide polyether polyols with an aliphatic isocyanate, such as isophorone diisocyanate, are typically not preferred as they may react with the halogen donor compound, particularly trichloroisocyanuric acid. Mixtures of the aliphatic isocyanate monomers, oligomers, and/or prepolymers have also been found to be useful.

Any of a wide range of organic solvents may also be used, including, for example, aliphatic esters, aliphatic hydrocarbons, and halogenated aromatic or aliphatic hydrocarbons. Preferably, the organic solvent is an aliphatic solvent (e.g., aliphatic hydrocarbons, aliphatic esters, and halogenated aliphatic hydrocarbons). Examples include, but are not limited to, ethyl acetate, butyl acetate, trichloroethylene, cyclohexane, heptane, and benzotrifluoride. Mixtures of such solvents can be used. Preferably, the solvent is substantially nonreactive with the halogen donor compounds and the aliphatic isocyanate-containing compounds. Solvents such as ketones are not preferred since they react with the halogen donor to form chlorinated by-products, thereby decreasing the shelf stability and efficacy of the primer solutions. A preferred solvent is a mixture of ethyl acetate and cyclohexane in weight ratios of about 95:5 to about 5:95, and more preferably about 80:20 to about 20:80 (ethyl acetate to cyclohexane).

Primer compositions according to the present invention include the aforementioned components in amounts sufficient for providing improved adhesion of an ink, an adhesive, and/or other coating to high organic polymeric substrates. Preferably, the halogen donor compound is present in an amount of about 0.5% to 10% by weight, and more preferably about 1.5% to about 5% by

weight, based on the total weight of the primer composition. Preferably, the aliphatic isocyanate-containing compound is present in an amount of about 1% to about 15% by weight, and more preferably about 1% to about 10% by weight, based on the total weight of the primer composition. The organic solvent is preferably present in the primer composition in an amount of at least about 75% by weight, based on the total weight of the composition.

Primer compositions according to the present invention may further include additives. These include, for example, coupling agents such as silane coupling agents, adhesion promoting agents such as chlorinated polyolefins (e.g., chlorinated polypropylene), and acid scavengers such as aliphatic epoxy resins. Typically, the additives are present in the primer compositions in an amount to provide the desired effect. Preferably, they do not exceed about 10% by weight, based on the total weight of the primer composition.

Primer compositions according to the present invention are typically homogeneous solutions, although this is not a necessary requirement. They may be applied to a substrate using a variety of techniques including dipping, spraying, brushing, rotogravure coating, as well as Meir rod and knife coating. The primer is typically dried before the adhesive, ink, or other coating material is applied. A particularly preferred method involves mechanically abrading the surface of the substrate, brushing on the primer, and allowing it to dry, prior to adhesive bonding.

The adhesives, inks, and other coating materials that demonstrate improved adhesion to primed organic high polymers (i.e., substrates coated with the primer compositions according to the present invention) can be thermosetting, thermoplastic, and hybrid materials. The term hybrid as used herein refers to combinations of two or more different types of materials (e.g., adhesives) as well as two or more polymers suitable for forming adhesives, inks, and other coating materials. Typically, the material coated on the primed organic high polymers are adhesives.

Thermosetting adhesives are generally formed by addition polymerization. Examples of thermosetting adhesives include polysulfides,

silicones, polyesters, polyurethanes, epoxies, anaerobic and aerobic acrylics, radiation curable polymers and vulcanizing rubbers. Thermosetting adhesives typically cure by heat, catalysts or light or moisture activation. After curing, thermosetting adhesives are generally insoluble (i.e., the adhesive will not dissolve
5 in an organic solvent or water) and infusible (i.e., the adhesive will not flow when heated).

Thermoplastic adhesives are soluble and fusible materials.

Examples of thermoplastic adhesives include vinyl adhesives (e.g., polyvinyl chloride, polyvinyl butyral, polyvinyl alkyl esters and ethers and vinyl-acetate-
10 ethylene copolymer adhesives, acrylic adhesives, and polyurethane adhesives), hot melt adhesives, cellulosic adhesives, and asphalt-based adhesives. Thermoplastic adhesives may be in the form of emulsions, solutions, or solids.

When the primer composition is applied to a substrate, it is typically allowed to dry prior to application of the coating, typically an adhesive.
15 The adhesive may include components that react with the aliphatic isocyanate-containing compound. For example, polyurethane-based adhesives and epoxy-based adhesives may react with the aliphatic isocyanate-containing compounds. In order to increase the rate of reaction between the aliphatic isocyanate and the polyurethane adhesive, a catalyst may be added to the adhesive, although this is
20 not required. Examples of such catalysts include dialkyltin dicarboxylates, mixtures of dialkyltin dicarboxylates and trialkyltin oxides, metal acetyl acetonates, metal carboxylates, mixtures of metal acetyl acetonates and tertiary amines, and the like.

Primer compositions according to the present invention may be
25 used in the manufacture of any of a wide variety of articles, such as footwear, particularly footwear with elastomeric components such as athletic shoes, as well as tennis rackets, and roofing membranes. They are also suitable for bonding two organic polymeric substrates together, or one such substrate to a variety of other substrates such as those containing metal, glass, ceramic, wood, and the like.

30 Primer compositions according to the present invention are particularly useful in the manufacture of footwear with elastomeric soles, such as

athletic shoes. Referring to Figures 1 and 2, an athletic shoe 20 is shown, which has upper 22, optional midsoles 24 and 25, and sole (or outsole) 26. In the manufacture of athletic shoes 20, for example, the primer composition is applied by spraying, brushing, or wiping to the attachment side of a rubber sole 26.

5 Typically, the solvent is removed by evaporation (e.g., air drying) to form a primed surface. The primed surface of the sole 26 is then treated in the conventional manner by applying adhesive, preferably a polyurethane adhesive. If the adhesive is solvent based, the solvent is allowed to evaporate. The upper portion 22, and optionally the midsoles 24 and 25, of the shoe 20 may be coated

10 with the same or a different adhesive and any solvent allowed to evaporate. When the adhesives have dried, the sole 26, and optional midsoles 24 and 25, and upper 22 are bonded in a conventional manner, typically with heat reactivation of the adhesive coatings. For example, the adhesive on the sole may be reactivated at about 80°C and the sole applied to the upper, which may or may not have been

15 heat reactivated. The assembly is then treated in a manner known in the art, such as using a press at an elevated pressure.

Additionally, for enhanced traction, the exposed surface of the sole 26 of the shoe 20 may be coated with a primer composition according to the present invention. A layer of adhesive may be coated thereon and a plurality of

20 hard, inorganic particles 28 coated on the layer of adhesive to form a traction coating. Alternatively, an adhesive-coated sheet (e.g., paper or polymeric sheet material) having hard, inorganic particles adhered thereto can be adhered to the primed surface of the sole forming a traction coating. The adhesive used in the preparation of a traction coating can be any of the adhesives described above or

25 other binders typically used in the abrasives industry.

The exposed surfaces of the soles of many types of footwear can be coated with a primer composition according to the present invention and a traction coating. Traction coatings are particularly suitable on shoes, such as athletic shoes, and boots, such as overshoes, hip-waders, etc. Referring to

30 Figures 3 and 3A, a boot 30 is shown having a boot body 32 secured to a sole 34. The exposed surface 36 of the sole 34 is coated with a primer composition, a

layer of adhesive, and a plurality of hard, inorganic particles to form a traction coating 36A and 36B (Figure 3A). This traction coating can be on the entire exposed surface of the sole 34 or it can be on selected portions of the exposed surface of the sole for a particular application, such as on the front and rear portions only, as shown in Figure 3A.

Hard, inorganic particles, typically have irregular surfaces and sufficient hardness to provide improved gripping characteristics as described in U.S. Patent No. 5,038,500 (Nicholson), the disclosure of which is incorporated herein by reference. Preferably, the particles are made of an inorganic compound having a Mohs hardness of at least about 7, and more preferably, having a Mohs hardness of at least about 9. Examples of some typical hard, inorganic particles for use in the traction coating include fused aluminum oxide, heat treated aluminum oxide, white fused aluminum oxide, black silicon carbide, green silicon carbide, titanium diboride, silica, silicates, boron carbide, tungsten carbide, titanium carbide, silicon nitride, ceria, zirconia, titania, diamond, cubic boron nitride, garnet, fused alumina zirconia, sol gel derived alumina particles and the like. Examples of sol gel derived alumina particles can be found in U.S. Pat. Nos. 4,314,827 (Leitheiser et al.), 4,623,364 (Cottringer et al.); 4,744,802 (Schwabel), 4,770,671 (Monroe et al.); 4,881,951 (Wood et al) and 5,366,523 (Rowenhorst et al.). The diamond and cubic boron nitride hard, inorganic particles may be monocrystalline or polycrystalline. The preferred inorganic particles are metal oxides (e.g. alumina), metal carbides (including silicon carbide), metal borides and metal nitrides. In one preferred mode, silicon carbide is preferred due to the spectral appearance of the silicon carbide particles.

The traction coating will typically comprise a distribution of particle sizes of the hard, inorganic particles. These distributions may be a narrow distribution or a broad distribution, depending upon the end application. The mean particle size of the hard, inorganic particles can range from about 0.2 mm to about 5 mm, preferably from about 0.3 mm to about 2.5 mm, and more preferably from about 0.5 mm to about 1.5 mm. The particle size of the hard, inorganic particle is typically measured by the longest dimension of the hard,

inorganic particle. It is generally preferred that the traction coating contain at least 50% by weight of the hard, inorganic particles that have a particle size greater than about 50 micrometers and more preferably greater than about 100 micrometers. In some instances it is preferred that the traction coated hard,
5 inorganic particles having a particle size less than about 7500 micrometers, and more preferably less than about 6000 micrometers. Thus, the traction coating should preferably not contain particles greater than about 7.5 mm, and more preferably, not greater than about 6 mm.

The hard, inorganic particle may be randomly shaped. In many
10 instances, very large hard, inorganic particles are crushed or broken into smaller pieces to form smaller size particles. Subsequently, these smaller hard, inorganic particles are screened to the desired particle size distribution. In some instances, it is preferred that the randomly shaped hard, inorganic particles have a more elongate shape, rather than a blocky shape. Alternatively, the hard, inorganic
15 particle may have a shape associated with it. Examples of such shapes include rods, triangles, pyramids, cones, solid spheres, hollow spheres and the like. For example, methods to make shaped sol gel derived alumina particles are further described in U.S. Pat. Nos. 5,009,676 (Rue et al.), 5,090,968 (Pellow), 5,201,916 (Berg et al.), and 5,366,523 (Rowenhorst et al.).

20 It is also within the scope of this invention to use diluent particles, coated along side of the hard, inorganic particles. In some instances, these diluent particles may accomplish one of the following goals: (1) reduce the cost of the traction coating; (2) reduce the weight of the traction coating; (3) improve traction; or (4) increase cushion. Examples of diluent particles include metal
25 carbonates (such as calcium carbonate (chalk, calcite, marl, travertine, marble and limestone), calcium magnesium carbonate, sodium carbonate, magnesium carbonate), metal sulfates (such as calcium sulfate, barium sulfate, sodium sulfate, aluminum sodium sulfate, aluminum sulfate), gypsum, aluminum trihydrate, graphite, metal oxides (such as calcium oxide (lime)) and metal sulfites (such as
30 calcium sulfite), metal particles (tin, lead, copper and the like) and the like. The

diluent particles may have essentially the same particle size as the hard, inorganic particles or the two particle size distributions may be different.

The traction coating may also contain a mixture of two or more different hard, inorganic particles. Conversely, the traction coating may comprise
5 a uniform mixture of hard, inorganic particles and diluent particles. Alternatively, the traction coating may contain a layer of diluent particles and a layer of hard, inorganic particles present over the diluent particles.

The hard, inorganic particles may also be present in the form of an agglomerate; this agglomerate is a particulate of a plurality of individual hard,
10 inorganic particles bonded together by an agglomerate binder. The abrasive agglomerates may be irregularly shaped or have a predetermined shaped. The abrasive agglomerate may utilize an organic binder or an inorganic binder to bond the hard, inorganic particles together. Examples of organic binders include phenolic binders, epoxy binders, acrylate binders, urea formaldehyde binders and
15 the like. Examples of inorganic binders include vitreous binders, silicate binders, frit binders, metal binders and the like. Examples of how to make such agglomerates containing hard, inorganic particles can be found in the following U.S. Pat. Nos. 4,652,275 (Bloecher et al.), 4,799,939 (Bloecher et al.) and 5,500,273 (Holmes et al.). These agglomerates of containing hard, inorganic
20 agglomerates should have a particle size less than about 5 mm, typically less than about 2.5 mm and preferably less than about 1.5 mm.

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed
25 to unduly limit this invention. All parts and percentages are by weight unless otherwise indicated.

Examples

Examples 1-6, Comparative Examples A-D, and Control I: Stability of

Compositions

Preparation and Stability of Example 1

A solution comprising 2% trichloroisocyanuric acid, which is a halogen donor compound, and 2% isophorone diisocyanate trimer (i.e., the trimer of 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate), which is available as 70% isophorone diisocyanate trimer in butyl acetate under the trade designation
5 "VESTANAT T1890E" from Hüls America, Incorporated, Piscataway, NJ, was prepared as follows. A 20 ml amber colored glass vial was dried at 120°C for 30 minutes, capped, and cooled. Ethyl acetate was dried over molecular sieves (Type 4A, Grade 514 available from W.R. Grace and Company, Davison
10 Chemical Division, Baltimore, MD) to remove residual water. The cap from the vial was removed, 14.4 grams of the dried ethyl acetate were added to the vial, followed by the additions of 0.3 gram of trichloroisocyanuric acid and 0.3 gram of the 70% isophorone diisocyanate trimer solution. After the addition of the isophorone diisocyanate trimer solution the vial was again capped.

The composition in the vial was placed in a 60°C oven and
15 monitored daily for formation of insoluble cyanuric acid and/or a color change, which was an indication that the trichloroisocyanuric acid had reacted with the isocyanate. Even after 21 days, the solution of Example 1 remained colorless with no apparent precipitate formation.

20 Preparation and Stability of Example 2

The composition of Example 2 was prepared as described in Example 1 except meta-tetramethylxylene diisocyanate, which is available under the trade designation "M-TMXDI" from Cytec Industries Incorporated of West
25 Patterson, NJ, was used in place of the 70% isophorone diisocyanate trimer solution. The composition in the vial was placed in a 60°C oven and monitored daily for formation of insoluble cyanuric acid. Even after 21 days, the solution remained colorless with no apparent precipitate formation.

Preparation and Stability of Example 3

30 The composition of Example 3 was prepared as described in Example 1 except isophorone diisocyanate, which is available under the trade

designation "VESTANAT IPDI" from Hüls America, Incorporated of Piscataway, NJ, was used in place of the 70% isophorone diisocyanate trimer solution. The composition in the vial was placed in a 60°C oven and monitored daily for formation of insoluble cyanuric acid. Even after 21 days, the solution
5 remained colorless with no apparent precipitate formation.

Preparation and Stability of Example 4

The composition of Example 4 was prepared as described in Example 1 methylene bis(4-cyclohexyl isocyanate), which is available under the
10 trade designation "DESMODUR W" from Bayer Corporation of Pittsburgh, PA, was used in place of the 70% isophorone diisocyanate trimer solution. The composition in the vial was placed in a 60°C oven and monitored daily for formation of insoluble cyanuric acid. Even after 21 days, the solution remained colorless with no apparent precipitate formation.

15

Preparation and Stability of Example 5

The composition of Example 5 was prepared as described in Example 1 except an isophorone diisocyanate polyester prepolymer, which is available under the trade designation "ASN-540 M" from Air Products and
20 Chemicals, Incorporated of Allentown, PA, was used in place of the 70% isophorone diisocyanate trimer solution. The composition in the vial was placed in a 60°C oven and monitored daily for formation of insoluble cyanuric acid. Even after 21 days, the solution remained colorless with no apparent precipitate formation.

25

Preparation and Stability of Example 6

The composition of Example 6 was prepared as described in Example 1 except dimer acid diisocyanate, which is available under the trade designation "DDI-1410" from Henkel Corporation of Kankakee, IL, was used in
30 place of the 70% isophorone diisocyanate trimer solution. The composition in the vial was placed in a 60°C oven and monitored daily for formation of insoluble

cyanuric acid. Even after 21 days, the solution remained colorless with no apparent precipitate formation.

Preparation and Stability of Comparative Example A

5 The composition of Comparative Example A was prepared as described in Example 1 except an isophorone diisocyanate poly-tetramethylene ether glycol prepolymer, which is available under the trade designation "APC-504" from Air Products and Chemicals Incorporated of Allentown, PA, was used in place of the 70% isophorone diisocyanate trimer solution. The composition in
10 the vial was placed in a 60°C oven and monitored daily for formation of insoluble cyanuric acid. After 6 days, the solution turned brown with the noticeable formation of a precipitate. This example demonstrates the instability of an active hydrogen-containing compound capable of reacting with the halogen donor compound.

15

Preparation and Stability of Comparative Example B

 The composition of Comparative Example B was prepared as described in Example 1 except 4,4'-diphenylmethane diisocyanate, which is available under the trade designation "MONDUR M" from Bayer Corporation of
20 Pittsburgh, PA, was used in place of the 70% isophorone diisocyanate trimer solution. The composition in the vial was placed in a 60°C oven and monitored daily for formation of insoluble cyanuric acid. After 6 days, the solution turned brown with the noticeable formation of a precipitate. This example demonstrates the instability of a composition prepared from an aromatic isocyanate.

25

Preparation and Stability of Comparative Example C

 The composition of Comparative Example C was prepared as described in Example 1 except tris(para-isocyanatophenyl)thiophosphate, which is available under the trade designation "DESMODUR RFE" from Bayer
30 Corporation of Pittsburgh, PA, was used in place of the 70% isophorone diisocyanate trimer solution. The composition in the vial was placed in a 60°C

oven and monitored daily for formation of insoluble cyanuric acid. After 3 days, the solution turned yellow. This example demonstrates the instability of a composition prepared from an aromatic isocyanate.

5 Preparation and Stability of Comparative Example D

The composition of Comparative Example D was prepared as described in Example 1 except a reaction product of a low molecular weight polyol and toluene diisocyanate, which is available under the trade designation "DESMODUR L-75N" from Bayer Corporation, was used in place of the 70%
10 isophorone diisocyanate trimer solution. The composition in the vial was placed in a 60°C oven and monitored daily for formation of insoluble cyanuric acid. After 3 days, the solution turned yellow. This example demonstrates the instability of a composition prepared from an aromatic isocyanate.

15 Preparation and Stability of Control I

The composition of Control I was a solution containing 2% trichloroisocyanuric acid in ethyl acetate, prepared as described in Example 1 but without the isocyanate. The composition in the vial was placed in a 60°C oven and monitored daily for formation of insoluble cyanuric acid. Even after 21 days,
20 the solution remained clear with no apparent precipitate formation.

Accelerated Aging of Example 1 and Comparative Example B

Compression molded polyethylene vinyl acetate (EVA) foam plaques, 203 mm x 203 mm x 15 mm, density of 193.3 Kg/m³, which is available
25 under the trade designation "ECLIPSE-5000" from Kim Incorporated, Kyeong Nam, Korea, were die-cut into test specimens, 75 mm x 125 mm x 15 mm. The test specimens were cleaned with a lintless tissue, which is available under the trade designation "KIMWIPE" from Kimberly-Clark Corporation, Roswell, GA, saturated in a solvent mixture of heptane:xylene in a weight ratio of 7.0:3.0, and
30 allowed to dry for 15 minutes. The primer compositions of Example 1 and of Comparative Example B were brushed onto the surfaces of individual specimens

and allowed to dry for 24 hours. The samples were mounted into an accelerated weathering tester, which is available from Q-Panel Company of Cleveland, OH, set to alternatively cycle 4 hours for exposure to UV and condensation for a total of 140 hours. The specimens were removed and the chromaticity of each were
 5 measured in L*a*b* coordinates using a portable color analyzer for measuring reflected-light color, which is available under the trade designation "MINOLTA CHROMAMETER CR-221" from Minolta Camera Company of Osaka, Japan. The L*a*b* results for a calibration white standard, the primer composition of Example 1, and the primer composition of Comparative Example B are given in
 10 Table 1.

Table 1

<u>Test Specimen</u>	<u>L*</u>	<u>a*</u>	<u>b*</u>
Calibration Standard White	93.3	0.2	-4.0
Example 1	93.3	-0.6	-0.5
Comparative Example B	87.5	-0.7	18.0

15

This demonstrates that the primer compositions of the prior art (Comparative Example B containing an aromatic isocyanate) severely discolor when exposed to ultraviolet light and accelerated weathering while the compositions of the present invention do not display significant discoloration.

20

Examples 7-14 and Control II: Peel Strengths of Adhesive on EPDM Rubber

Preparation of Examples 7-12

Examples 7-12 were prepared as described for Examples 1-6, respectively, in 30 ml dried amber glass vials except that the solvent used was a
 25 mixture of dried ethyl acetate and trichloroethylene in a ratio of 3.5:6.5 by weight.

Preparation of Control II

Control II was prepared by combining 0.3 gram of trichloroisocyanuric acid and 14.7 grams of the solvent mixture described above in Examples 7-12 in a 30 ml dried amber glass vial.

5

Preparation of Example 13

A 25% by weight solution of the reaction product of 1,6-hexanediol and isophorone diisocyanate was prepared by combining 21.0 grams of the 70% isophorone diisocyanate trimer described in Example 1, 6.0 grams of 1,6-hexanediol, and 81.0 grams of the ethyl acetate/trichloroethylene solvent mixture described above in Examples 7-12 in a dried, 250 ml, narrow-mouthed amber bottle, which was then capped. The mixture was heated at 70°C for 24 hours. A priming solution of 2% by weight of the above reaction product and 2% by weight of trichloroisocyanuric acid was prepared by combining 0.3 gram of trichloroisocyanuric acid, 1.2 grams of the above reaction product, and 13.5 grams of the ethyl acetate/trichloroethylene solvent mixture in a 30 ml dried amber glass vial.

10
15Preparation of Example 14

About 98 grams of the primer solution prepared in Example 7 was modified by the addition of 1.7grams of 3-isocyanopropyl trimethoxysilane coupling agent, which is available under the trade designation "SILQUEST A-1310" from OSI Specialties, Danbury, CT, and 0.5 gram of gamma-glycidyloxypropyl trimethoxysilane coupling agent, which is available under the trade designation "SILQUEST A-187" from OSI Specialties, Danbury, CT, and stored in a dry, amber, narrow-mouthed bottle.

20
25Examples 7-13 and Control II Peel Strengths

Vulcanized EPDM rubber plaques, 127 mm x 127 mm x 2.5 mm, which are available under the trade designation "SHORE A-68" from Shin Ho Incorporated, Pusan, Korea, were die-cut into 25.4 mm x 127 mm x 2.5 mm test

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specimens. The surface of each test specimen was lightly abraded with grade P-220, fabric-backed abrasive material, which is available under the trade designation "3M-ITE P-220" from the 3M Company, St. Paul, MN, and cleaned of debris with compressed air. For each of Examples 7-13 and Control II, the
5 priming solution was brushed onto the abraded surface of two test specimens and allowed to dry for 30 minutes. A 20% by weight solution of polycaprolactone polyurethane adhesive, which is available under the trade designation "DESMOCOLL 530" from Bayer Corporation, Pittsburgh, in methyl ethyl ketone was brushed onto the primed surface of each test specimen, except for a region
10 about 25 mm from one edge of the specimen, and allowed to dry for 30 minutes. The primed and adhesive coated specimens were placed in an 80°C oven for 5 minutes.

For each of Examples 7-13 and Control II, the adhesive-coated surfaces of two specimens having the same primer were bonded together under
15 about 10 Kpa pressure to form a peel sample and allowed to stand for 7 days at room temperature and humidity. Each of the peel samples was mounted in an Instron tensile tester, which is available from Instron Corporation, Canton, MA, to determine the 180° peel of the two specimens adhered together. The 180° peel adhesion was measured at a jaw speed of 12.7 cm per minute. The average of
20 three 180° peel values for Control II and Examples 7-13 reported in N/100 mm were 158, at least 386 (sample elongated to maximum jaw separation), 298, 298, 316, 351, 316, 333, respectively. These results demonstrate that the primer solutions of this invention improves the adhesion of polyurethane adhesives to EPDM rubber over that of just a halogen donor compound.

25

Peel Strengths With Humidity Aging of Examples 7 and 14

The primer solution of Example 14, and for comparison, the primer solution of Example 7 and Control II were brushed onto abraded EPDM rubber test specimens, adhesively bonded together with the polyurethane
30 adhesive, and tested as described above. The average of three 180° peel values

for Control II and Examples 7 and 14 reported in N/100 mm were 175, 368, and 386, respectively.

The primer solution of Example 14, and for comparison, the primer solution of Example 7 and Control II were brushed onto abraded EPDM rubber test specimens and adhesively bonded together with the polyurethane adhesive as described above. The bonded specimens were then allowed to stand for 7 days at room temperature and humidity, and then they were exposed to 70°C and 100% relative humidity for 7 days. Peel values were then determined 7 days after termination of the test. The 180° peel adhesion was measured as described above. The average of three 180° peel values for Control II and Examples 7 and 14 reported in N/100 mm were 123, 351, and 579 (sample elongated to maximum jaw separation), respectively.

These results demonstrate that EPDM rubber primed with compositions of this invention and adhesively bonded result in improved peel values even after humidity aging, when compared to the use of a halogen donor compound alone. In addition, coupling agents that do not compromise solution stability can be utilized to further improve peel values, particularly after humidity aging.

Examples 15-17: Alternative Halogen Donor Compounds, Adhesives, and Substrates

Preparation and Peel Strength of Example 15

A solution comprising 2% 1,3-dichloro-5,5-dimethylhydantoin, a halogen donor which is available from Aldrich Chemical Company Incorporated, Milwaukee, WI, and 2% isophorone diisocyanate trimer (i.e., trimer of 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate), which is available as 70% isophorone diisocyanate trimer in butyl acetate under the trade designation "VESTANAT T1890E" from Hüls America, Incorporated, Piscataway, NJ, was prepared as follows. A 30 ml amber colored glass vial was dried at 120°C for 30 minutes, capped, and cooled. Ethyl acetate was dried over molecular sieves (Type 4A, Grade 514 available from W.R. Grace and Company, Davison

Chemical Division, Baltimore, MD) to remove residual water. A solvent mixture of dried ethyl acetate and trichloroethylene in a ratio of 3.5:6.5 by weight was prepared. The cap from the vial was removed, 14.3 grams of the ethyl acetate/trichloroethylene solvent mixture were added to the vial, followed by the
5 additions of 0.3 gram of 1,3-dichloro-5,5-dimethylhydantoin and 0.4 gram of the 70% isophorone diisocyanate trimer solution.

Test specimens of abraded EPDM rubber were primed with this primer solution and Control II solution, adhesively bonded together, and the 180° peel strengths determined as described above for Examples 7-13. The average of
10 three peel values of Examples 15 and Control II in N/100 mm were 360 and 132, respectively. This example demonstrates that other halogen donor compounds are effective in priming solutions of this invention.

Example 16: Peel Strengths Using Various Substrates

15 Plaques, 127 mm x 127 mm x 3.1 mm of a typical, vulcanized SBR rubber of the following formulation were prepared by Rubber Industries, Incorporated, Shakopee, MN: 65.0 parts SBR 1502, 35.0 parts per hundred rubber (phr) SBR 1904, 25.0 phr silica, 23.0 phr carbon black (N-330), 1.8 phr sulfur, 3.0 phr cumarone-indene resin (85°C), 3.8 phr zinc oxide, 0.8 phr stearic
20 acid, 1.1 phr N-cyclohexyl-2-benzothiazolesulfenamide, and 0.8 phr phenolic antioxidant. Die cut test specimens of 25.4 mm x 127 mm x 3.1 mm were prepared from the plaques.

Compression molded polyethylene vinyl acetate (EVA) foam plaques, 203 mm x 203 mm x 15 mm, density of 193.3 Kg/m³, which is available
25 under the trade designation "Eclipse-5000" from Kim Incorporated, Kyeong Nam, Korea, were die-cut into test specimens, 25.4 mm x 127 mm x 15 mm.

The test specimens were cleaned with a lintless tissue, which is available under the trade designation "KIMWIPE" from Kimberly-Clark Corporation, Roswell, GA, saturated in a solvent mixture of heptane:xylene in a
30 weight ratio of 7.0:3.0, and allowed to dry for 15 minutes. The primer compositions of Examples 7 and Control II were brushed onto the specimens (but

were not abraded) and bonded with polyurethane adhesive to prepare test samples of EVA/EVA, EVA/SBR and SBR/SBR in a manner described in Examples 7-13. The 180° peel strengths were determined as described above for Examples 7-13. The average of three peel values of the primer of Control II in N/100 mm for EVA/EVA, EVA/SBR, and SBR/SBR were 509, 526, and 1754 (sample failure), respectively. The average of three peel values of the primer of Example 7 in N/100 mm for EVA/EVA, EVA/SBR, and SBR/SBR were 710 (sample failure), 1017 (sample failure), and 1754 (sample failure), respectively. This example demonstrates that a primer solution of this invention substantially improves the peel values of a wide variety of adhesively bonded substrates compared to the control solution containing only a halogen donor compound and solvent.

Example 17: Peel Strengths Using Various Adhesives

Test specimens of SBR were prepared and cleaned as described in Example 16. The primer of Example 1 was brushed on each and allowed to dry for 30 minutes. A thin layer of a premixed, two-part polyurethane adhesive, which is available under the trade designation "SCOTCH-WELD 3549 B/A" from the 3M Company, was applied to the primed sides of two specimens as previously described. The adhesive coated sides of the specimens were bonded together using hand pressure from a light rubber-covered roller. In a similar manner, primed test specimens were bonded with a two-part epoxy adhesive, which is available under the trade designation "SCOTCH-WELD 2216 B/A" from the 3M Company.

A solvent-based neoprene contact adhesive, which is available under the trade designation "FASTBOND 5" from the 3M Company was applied to the primed sides of two specimens, allowed to dry until tack-free, then bonded together using hand pressure from a light rubber-covered roller.

A 50% polymer solids polyurethane dispersion in water, which is available under the trade designation "DISPERCOLL U-54" from Bayer Corp., Pittsburgh, PA, was applied to the primed sides of two specimens and allowed to

dry for 40 minutes. The specimens were heated at 80°C for 5 minutes and bonded together under 10 KPa pressure.

All bonded specimens were allowed to condition for 7 days prior to determining 180° peel values. The average of three peel values of the primer of Example 1 in N/100 mm for the 2-part polyurethane, the 2-part epoxy, the neoprene contact adhesive, and the polyurethane dispersion were 1491, 1754 (sample elongated to maximum jaw separation), 351, and 965, respectively. This example illustrates that adhesives other than solvent-based polyurethanes, result in high peel values to substrates primed with a composition of this invention.

10

Example 18: Preparation of Traction Enhanced Shoe Sole

A vulcanized rubber shoe sole made from a blend of natural rubber, styrene-butadiene rubber, and inorganic fillers was obtained from LaCrosse Footwear Inc., LaCrosse, WI (LaCrosse Number 200 black rubber compound). The sole was abraded using a wire brush and rinsed with ethanol to remove debris. The shoe sole was primed with one coat of the primer solution detailed in Example 14 at a coating weight of 5 milligrams/square centimeter. The sole was allowed to dry for 30 minutes. A urethane adhesive made from 86.7 parts of a toluene diisocyanate polyether prepolymer, which is available under the trade designation "ADIPRENE L-167" from Uniroyal Adhesives and Sealants Co., Mishawaka, IN, and 13.3 parts of a catalyst, which is available under the trade designation "ETHACURE 300" from Ethyl Corp., Baton Rouge, LA, was brushed on the primed shoe sole in the areas where traction needed to be enhanced (as shown in Figure 3A) at a coating weight of 40 milligrams/square centimeter. Silicon carbide mineral (ANSI grade 20 abrasive grit, typically about 980 micrometers in particle size) was drop coated on the surface and the excess removed by gravity. The coating weight of the mineral was approximately 200 milligrams/square centimeter. The traction coating was allowed to cure for 24 hours. This process yielded an excellent traction surface suitable for rubber soled shoes or boots on icy, oily, or greasy surfaces with excellent durability. Without the primer, no adhesion between the urethane adhesive and the rubber occurred.

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Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

What Is Claimed Is:

1. ^{countable} A primer composition comprising a halogen donor compound, an aliphatic isocyanate-containing compound, and an organic solvent. ~~wherein the composition~~ ^{composition <->}
2. ~~The primer composition of claim 1 which~~ (is stable at 60°C for at least about 14 days when stored in a moisture-free environment.)
3. The primer composition according to claim 1 wherein the aliphatic isocyanate-containing compound is substantially nonreactive with the halogen donor compound.
4. The primer composition according to claim 1 wherein the organic solvent is substantially nonreactive with the halogen donor compound and the aliphatic isocyanate-containing compound.
5. The primer composition according to claim 1 which comprise, by weight, at least about 75% of the organic solvent, about 0.5% to about 10% of the halogen donor compound, and about 1% to about 15% of the aliphatic isocyanate-containing compound, based on the total weight of the primer composition.
6. The primer composition according to claim 1 wherein the aliphatic isocyanate-containing compound is a saturated aliphatic isocyanate.
7. The primer composition according to claim 1 wherein the aliphatic isocyanate is selected from the group consisting of 1,6-hexamethylene diisocyanate, methylene bis(4-cyclohexyl isocyanate), trimethyl hexamethylene diisocyanate, isophorone diisocyanate, γ -isocyanatopropyl trimethoxysilane, dimer acid isocyanate, xylene diisocyanate, benzene-1,3-bis(1-isocyanato-1-

methylethyl), benzene-1,4-bis(1-isocyanato-1-methylethyl), and oligomers and combinations thereof.

7 8. The primer composition according to claim 1 wherein the halogen
5 donor compound is selected from the group consisting of a saturated N-
halogenated heterocyclic amide, an N,N-dihalogenated aromatic sulfonamide, an
N-monohalogenated aromatic sulfonamide, and combinations thereof.

8 9. The primer composition according to claim 1 wherein the organic
10 solvent is selected from the group consisting of an aliphatic ester, an aliphatic
hydrocarbon, and an halogenated aromatic or aliphatic hydrocarbon.

9 10. The primer composition according to claim 1 further comprising a
silane coupling agent.

15

10 11. The primer composition according to claim 1 further comprising an
epoxy resin.

11 12. The primer composition of claim 1 comprising a solution of: a
20 halogen donor compound selected from the group consisting of 1,3-dichloro-5,5-
dimethylhydantoin, tetrachloroglycoluril, trichloroisocyanuric acid, and
combinations thereof; an aliphatic isocyanate-containing compound selected from
the group consisting of 1,6-hexamethylene diisocyanate, methylene bis(4-
cyclohexyl isocyanate), trimethyl hexamethylene diisocyanate, isophorone
25 diisocyanate, γ -isocyanatopropyl trimethoxysilane, and oligomers and
combinations thereof; and an organic solvent.

12 13. ^{coatable} A primer composition preparable by combining components
comprising a halogen donor compound, an aliphatic isocyanate-containing
30 compound, and an organic solvent \leftarrow see original claim 2

13 ~~14~~. A method for adhering two substrates together, said method comprising the steps of:

- (a) applying the primer composition of claim ~~13~~¹² to a surface of a first organic polymeric substrate to provide a primed surface;
- 5 (b) applying an adhesive to the primed surface or to a surface of a second substrate; and
- (c) positioning the surfaces of the first and second substrates together to form a bond.

10 14 ~~15~~. The method according to claim ~~14~~¹³ further comprising a step of applying the primer composition of claim 1 to the surface of the second organic polymeric substrate to provide a primed surface.

15 15 ~~16~~. The method according to claim ~~14~~¹³ wherein the first organic polymeric substrate is made of a material selected from the group consisting of ethylene propylene diene monomer, polyethylene, vinyl acetate foam, polyurethane rubber, synthetic leather, natural leather, plasticized polyvinyl chloride, polyamide, polyester, polybutadiene, polychloroprene, polyisoprene, natural rubber, isobutene-isoprene copolymer, styrene-butadiene copolymer, 20 styrene-butadiene styrene block copolymers, butyl and bromobutyl rubber, polyethylene vinyl acetate foams, and polyurethane rubber, and foams.

25 16 ~~17~~. The method according to claim ~~14~~¹³ further comprising the step of roughening the surfaces before applying the primer composition thereto.

17 ~~18~~. An article made according to the method of claim ~~14~~¹³.

18 ~~19~~. The article of claim ~~18~~¹⁷ which is an article of footwear.

- 19 ~~20~~. A method of forming a traction coating on an article comprising an organic polymeric substrate, the method comprising:
- (a) applying the primer composition of claim ~~13~~¹² to a surface of the organic polymeric substrate to provide a primed surface; and
 - 5 (b) applying a traction coating comprising a plurality of hard, inorganic particles to the primed surface.
- 20 ~~21~~. The method according to claim ~~20~~¹⁹ wherein the step of applying a traction coating comprises:
- 10 (a) applying an adhesive to the primed surface to form an adhesive-coated primed surface; and
 - (b) applying a plurality of hard, inorganic particles to the adhesive-coated primed surface.
- 15 ~~21~~ ~~22~~. The method according to claim ~~20~~¹⁹ wherein the step of applying a traction coating comprises applying a sheet material having a plurality of hard, inorganic particles adhered thereto.
- 20 ~~22~~ ~~23~~. The method according to claim ~~20~~¹⁹ wherein the article is an article of footwear.
- ~~23~~ ~~24~~. The method according to claim ~~23~~²² wherein the article of footwear is a shoe.
- 25 ~~24~~ ~~25~~. The method according to claim ~~24~~²³ wherein the organic polymeric substrate is an elastomeric sole on the shoe.
- ~~25~~ ~~26~~. The method according to claim ~~25~~²⁴ wherein the shoe is an athletic shoe.
- 30

26 ~~27~~. The method according to claim ~~27~~²⁰ wherein the article of footwear is a boot.

27 ~~28~~. An article comprising an organic polymeric substrate having at least one surface on which is coated a traction coating; the traction coating preparable by:

- (a) applying the primer composition of claim ~~13~~¹² to a surface of the organic polymeric substrate to provide a primed surface; and
- (b) applying a traction coating comprising a plurality of hard, inorganic particles to the primed surface.

28 ~~29~~. The article according to claim ~~28~~²⁷ wherein the step of applying a traction coating comprises:

- (a) applying an adhesive to the primed surface to form an adhesive-coated primed surface; and
- (b) applying a plurality of hard, inorganic particles to the adhesive-coated primed surface.

29 ~~30~~. The article according to claim ~~28~~²⁷ wherein the step of applying a traction coating comprises applying a sheet material having a plurality of hard, inorganic particles adhered thereto.

30 ~~31~~. The article according to claim ~~28~~²⁷ which is an article of footwear.

31 ~~32~~. The article according to claim ~~31~~³⁰ which is a shoe.

32 ~~33~~. The article according to claim ~~32~~³¹ wherein the organic polymeric substrate is an elastomeric sole on the shoe.

33 ~~34~~. The article according to claim ~~33~~³² which is an athletic shoe.

34 ~~35~~. The article according to claim ~~34~~³⁰ which is a boot.

[] see page 31 A

[35. A coatable primer composition comprising a halogen donor compound, an aliphatic isocyanate-containing compound, and an organic solvent, wherein the halogen donor compound, aliphatic isocyanate-containing compound, and organic solvent are substantially unreactive with each other.]

AMENDED SHEET
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