Title: BONDING OF THERMOPLASTIC VULCANIZATES TO SURFACES

Abstract: The invention relates to a method for bonding a thermoplastic vulcanizate (TPV) to glass and metal surfaces. The method of the invention allows to bond TPV to the surface of glass substrates in the manufacture of automotive windshields, rear windows or quarter-lights that comprise a glass substrate and a TPV.
Bonding of Thermoplastic Vulcanizates to Surfaces

Field of the Invention

The present invention relates to a method for bonding a thermoplastic vulcanizate (TPV) to glass, metal or painted metal surfaces. The method of the invention allows to bond TPV to the surface of glass substrates in the manufacture of automotive windshields, rear windows or quarter-lights that comprise a glass substrate and a TPV.

Background of the Invention

In the near future the requirements for modular systems automotive field will increase considerably in that the mounting of rubber-gaskets or PVC-frames on the glass near the automobile assembly line will be replaced totally by a "ready-to-install"-module consisting of the glass and a polymer frame. These modules will be supplied by the glass manufacturer or by other special automotive suppliers. The encapsulation of automotive glass is one possibility in this field combining several advantages:

- simplifying glass mounting on an assembly line;
- styling capabilities by the design departments;
- preventing of manual work and labor costs;
- assuring quality in fabrication by controlling an automatic process.

Generally, encapsulation means that the glass is placed in a steel or aluminum mould, the mold is closed and then the polymer is injected into the cavity of the mold. Actually the encapsulation of glass is performed by injection molding or robotic extrusion, as described in United States Patent No. 5,336,349, using thermoplastic vulcanizates (TPV) such as Santoprene® rubbers and suitable adhesion promoting compositions.
One alternative of improving the adhesion of vinyl polymers to glass surfaces is disclosed in United States Patent No. 3,998,985 which relates to the incorporation of certain polyaminosilane compounds into the vinyl polymer to be bonded. Specifically, the vinyl polymer is mixed with a combination of a polyaminosilane and a primer that contains an epichlorohydrin-bisphenol A resin, N-aminoethyl-gamma-aminopropyltrimethoxysilane, ethyleneglycolmono-methylether, and ethyleneglycolmonoethyl ether acetate.

Further examples of vinyl polymer-glass adhesives are disclosed in United States Patent No. 3,666,539 that discloses epoxy reactive silanes which act as coupling agents for adhering various polymers to glass; United States Patent No. 3,362,843 that discloses a mixture of an aminoalkylalkoxysilane and an epoxy resin-methyl methacrylate primer; and United States Patent No. 3,734,763 that discloses the use of N-[beta-(N'-para-vinylbenzyl)aminoethyl]-gamma-amino-propyltrimethoxysilane hydrochloride as a vinyl polymer-glass coupling agent.

Polyurethane adhesive systems are commonly used to promote adhesion between glass surfaces of automotive windscreen, side windows, etc. and the surrounding TPV seals are known from United States Patent No. 5,336,349.

United States Patent Nos. 5,102,937 and 5,051,474 disclose formulations useful as coating, primer or adhesive including a linear polyester polyurethane, a halogenated polyolefin, an alkoxy silane compound, and a cross-linker. The formulations are preferably utilized as two-component adhesive for bonding vinyl polymers such as polyvinyl chloride or thermoplastic elastomers to various substrates such as glass or metal.

United States Patent No. 5,102,937 discloses an adhesive composition for bonding vinyl compounds to glass substrates. The adhesive composition comprises a crosslinkable polyester polyurethane, a halogenated polyolefin, an alkoxy silane primer and an isocyanate crosslinker.


In order to protect the TPVs from degradation by ultra-violet (UV) radiation UV-stabilizers are commonly added to the TPV compositions. Sterically hindered amines that are known in the prior art by the abbreviation HALS (hindered amine light stabilizer) have been established as suitable light stabilizers for TPV gaskets that are applied, for example, to an automobile glazing as a frame along its border.

In particular, polyurethane based adhesive systems suffer from the substantial drawback to react with moisture (penetrating, for instance, the TPV matrix under humid conditions) and/or with the amine-groups of the above-mentioned HALS stabilizers. This interaction often results in complete bonding failures. Additionally, HALS stabilizers that are extracted from the TPV result in alkaline solutions that may cause further adhesion problems, i.e., by cleavage of the urethane bond.

Summary of the Invention

It has been an object of the present invention to provide a method of adhering a thermoplastic vulcanizate to a glass surface that obviates the above disadvantages and drawbacks, i.e., a method involving an adhesion promoting composition that is less sensitive to moisture and that shows a high compatibility with HALS.

It has been a still further object of the present invention to provide articles of manufacture comprising glass and a TPV adhered to the glass surface with improved adhesion of the TPV to the glass.
The object of improving adhesion between TPV and glass surfaces has been solved by a method of bonding a TPV to the surface a glass substrate said method comprising the steps of:

(I) applying a silane primer to the glass surface,

(II) applying an adhesive composition comprising

(A) a halogenated polyolefin;

(B) a crosslinkable resin; and

(C) an isocyanate crosslinker,

on top of the primer; and

(III) applying the TPV to the treated surface.

In an alternative embodiment the invention relates to a method of bonding a TPV to the surface a glass substrate said method comprising the steps of:

(I) applying an adhesive composition comprising:

(A) a halogenated polyolefin;

(B) a crosslinkable resin; and

(C) an isocyanate crosslinker; and

(D) a silane primer;

to the glass surface;

(II) applying said TPV to the treated surface.

According to these methods the silane primer can be applied to the glass surface or, alternatively, it can be contained in the adhesive composition. In a still further alternative embodiment the silane primer can be present on the glass surface and in the adhesive composition.

The composite structure obtainable by said method comprises a glass substrate, a thermoplastic vulcanizate, and an adhesive arranged between the glass substrate and the thermoplastic vulcanizate, wherein the adhesive comprises is as defined above. Typical articles of manufacture are those in which a thermoplastic vulcanizate is to be reliably adhered to a glass
surface such as in the field of making automotive or aerospace parts, for instance, automotive windshields, side windows, rear windows, quarter lights, aircraft windows, and the like.

Throughout the present disclosure the terms adhesive composition and adhesion promoting composition are used interchangeably.

Further embodiments of the invention become apparent from the description which follows and the claims.

The composition used in the method of the invention comprising the halogenated and optionally maleated polyolefin, the crosslinkable resin and the isocyanate crosslinker represents an excellent adhesive for bonding a thermoplastic vulcanize to a glass surface.

Due to the absence of polyurethanes the adhesion promoting composition according to the present invention leads to improved bond strength combined with excellent retention of properties over a long period of time, even if TPVs that are stabilized by carbon black and/or organic stabilizers, such as HALS, are used.

Detailed Description of the Invention

Thermoplastic Vulcanizates (i)

The thermoplastic vulcanize to be adhered to a glass surface using the adhesive composition of the present invention has a combination of both thermoplastic and elastic properties (thermoplastic elastomers; TPE). Thermoplastic vulcanizates are generally obtained by blending a thermoplastic polyolefin with an elastomeric composition (rubber) in a way such that the elastomer is intimately and uniformly dispersed as a discrete particulate phase within a continuous phase of the thermoplastic polyolefin. Early work relating to vulcanized compositions is found in U.S. Patent No. 3,037,954 to Gessler. The Reference discloses static vulcanization as well as dynamic vulcanization techniques wherein a vulcanizable elastomer is dispersed into a resinous thermoplastic polymer and the elastomer is cured while continuously mixing and shearing the polymer blend. The resulting composition (thermoplastic elastomer vulcanizate; TPV) is a microgel
dispersion of cured elastomer, such as butyl rubber, chlorinated butyl rubber, polybutadiene, polyisobutene etc. in an uncured matrix of thermoplastic polymer, such as polypropylene.

Accordingly, the thermoplastic rubber component (A) may generally be prepared by mixing

(a) an uncured rubber, and

(b) a thermoplastic polyolefin homopolymer or copolymer and;

optionally

(c) conventional additives and fillers;

melting the mixture under high shear such as kneading until a homogeneous blend is obtained. The addition of curing agents (also referred to as curatives, crosslinking- or vulcanizing agents) to the blend during the mixing under conditions of heat and shear results in a composition of a fully cured (also referred to as fully Vulcanized or fully crosslinked) rubber dispersed in a thermoplastic matrix.

The term "rubber" as used herein means any natural or synthetic polymer which can be cured so as to exhibit elastomeric properties. For the purpose of this invention, the term "elastomer" is used interchangeably with the term "rubber". The terms "thermoplastic vulcanizate (TPV)", "thermoplastic elastomer" or "thermoplastic rubber" are used interchangeably.

Typically, UV stabilized TPVs comprise stabilizers selected from heat stabilizers, acid scavengers and/or sterically hindered amine stabilizers (HALS). Generally a combination of low molecular HALS that can migrate easier to the surface, such as Tinuvin®770, supplied by Ciba Special Chemicals and high molecular HALS, which are more strongly bond to the TPV, such as Chimasorb®, supplied by Ciba Special Chemicals are used.

The term "glass" used in conjunction with the present invention is meant to relate to any substrate or surface of glass, ceramics, enamel, silicate (coated on plastics or metals) and other silicate containing products such as clay or concrete.
Halogenated Polyolefin (A)

The adhesive composition used according to the present invention comprises a halogenated polyolefin, preferably chlorinated polyolefin.

Halogenated polyolefinic materials which are suitable in accordance with the present invention may be generally described as halogenated alpha-mono-olefin polymers having optionally maleic acid groups grafted thereon. Additionally, the halogenated and/or maleated polyolefinic compounds may also be substituted by halosulfonyl groups. The halo-substituent may be any of the halogens selected from the group consisting of fluorine, chlorine, bromine and iodine with chlorine being especially preferred.

Preferably, specific olefin polymeric materials that fall within the above group of halogenated/maleated polyolefins and that may be employed in the compositions of the present invention may also include chlorosulfonated polymers of ethylene, propylene, isobutylene and the like, chlorinated natural rubber, chlorine- and bromine-containing synthetic rubbers and halogenated polymers derived from dienes having from 4 to 8 carbon atoms, preferably 5 to 7 and most preferred 6 carbon atoms.

Typically, halogenated polyolefins are selected from the group consisting of polychloroprene, chlorinated polychloroprene, chlorinated polypropylene, chlorinated polybutadiene, chlorinated polyisoprene, halogenated polybutylene, halogenated polyhexadiene, chlorinated butadiene styrene copolymers, chlorinated ethylene propylene copolymers and chlorinated ethylene/propylene/non-conjugated diene terpolymers, chlorinated polyethylene, chlorosulfonated polyethylene, halogenated copolymers of alpha-olefins of containing 2 to 8 carbon atoms, preferably 3 to 7 carbon atoms, chlorinated poly(vinyl chloride), and mixtures thereof, and the like, including mixtures of such halogen-containing polymers. The halogenated polyolefin of the first component can also be a halogenated vinyl halide polymer including halogenated homopolymers or copolymers of vinyl halide.

Thus, substantially any of the known halogen-containing derivatives of natural and synthetic elastomers can be employed as the halogenated polyolefin in the practice of this invention, including mixtures of such polymers. In a preferred embodiment of this invention the halogen content
of the halogenated polyolefin is from about 5 wt.-% to about 50 wt.-%, preferably from about 20 wt.-% to about 30 wt.-% and most preferably about 25 wt.-%.

Chlorinated and maleated polyolefins, i.e. polyolefins that are both chlorinated and grafted with maleic acid (MA) and/or maleic acid anhydride (MAH) are especially preferred. Chlorinated and maleated polypropylenes (Cl-MAH-g-PP) are especially preferred as the constituent of the adhesive compositions used according to the present invention. In an alternative and preferred embodiment there is used chlorinated/maleated polypropylene based on isotactic low molecular weight polypropylenes as described by formula I

wherein x is an integer from about 20 to about 500, preferably from about 30 to about 400, most preferably from about 40 to about 300. These polymers have an average molecular weight ($M_w$) of from about 20,000 to about 120,000, preferably from about 30,000 to about 110,000, more preferably from about 40,000 to about 100,000. In general, the chlorine content of the chlorinated/maleated polypropylene is from about 15 to about 35 wt.-%, preferably from about 18 to about 32 wt.-% and more preferably from about 20 to about 30 wt.-%, the content of maleic acid anhydride is from about 0.5 to about 5.0 wt.-%, preferably from about 1 to about 3.0 wt.-% and more preferably from about 1.5 to about 2.0 wt.-%.

Suitable chlorinated and/or maleated polypropylenes are commercially available from Tramaco under the trade designation Trapylene® 803 LS,
196S, 130X, 135X and 822X or from Siber Hegner under the trade
designations Hardlen® 13MLJ, 15 LP and CY-9122P.

Typically, the adhesive composition used according to the present invention
comprises from about 5 wt.-% to about 95 wt.-%, preferably from about
25 wt.-% to about 75 wt.-%, most preferably from about 35 wt.-% to about
55 wt.-% of the halogenated polyolefin, based upon the total weight of the
adhesive composition comprising the halogenated polyolefin (A), the
crosslinkable resin (B), and the isocyanate crosslinker (C).

Crosslinkable Resin (B)

A further constituent of the adhesive composition used according to the
present invention is a crosslinkable resin. Crosslinkable resins are polymeric
compounds having functional groups that are able to react with the
isocyanate group of the isocyanate crosslinking agent (C).

The crosslinkable resin may be represented by compounds obtainable by
the reaction of melamines, urea, benzoguanamine, glycoluril or mixtures
thereof with formaldehyde. Moreover, epoxy- and/or acrylic resins can be
used as crosslinkable resins (B) according to the present invention. In a
preferred embodiment due to the crosslinkable amino groups, melamine
resins are used as crosslinkable resins (B). Preferred melamine resins are
selected from the group consisting of hexamethoxymethylmelamine resins,
high solids methylated melamine resins, high solids mixed ether melamine
resins and butylated melamine resins, wherein
hexamethoxymethylmelamine (HMM) resins are highly preferred. "High
solids" means that the solid content is generally above 70 to 98 wt.-%,
based on organic volatile measurements. Said crosslinkable resins (B) are
commercially available, for instance, from SOLUTIA under the trade
designation Resimene® or from CYTEC under the trade designation Cymel®.
In a preferred embodiment the hexamethoxymethylmelamine resins
Resimene® 745 and Resimene® 3521 are used.

In an alternative embodiment of the present invention acrylic resins having
crosslinkable hydroxyl groups may be used as the crosslinkable resin (B).
Acrylic resins that can be used according to the present invention are
available by polymerizing monomers which contain a vinyl group and which may be described as resinous polymers of esters of alpha,beta-ethylenically unsaturated monocarboxylic acids and saturated aliphatic alcohols containing from 1 to about 10 carbon atoms, preferably from 1 to 8 carbon atoms, more preferably from 2 to 6 carbon atoms. Thus, the monomers from which these esters are obtained may be described by the following general formula II

![Chemical structure](image)

wherein \( R \) and \( R^1 \) independently represent hydrogen or alkyl groups, preferably methyl, or straight or branched chain alkyl groups having up to 10 carbon atoms, preferably from 1 to 8 carbon atoms, more preferred from 2 to 6 carbon atoms, and \( R^2 \) is a straight or branched alkyl group having up to 10 carbon atoms, preferably from 1 to 8 carbon atoms, more preferred from 2 to 6 carbon atoms. Under polymerization conditions these acrylate monomers form resinous polyacrylates. Suitable acrylic resins are disclosed in United States Patent No. 3,919,153, the disclosure of which is fully incorporated herein by reference.

In conjunction with the present invention acrylic resins having a crosslinkable hydroxyl group are especially preferred. Such acrylates are commercially available from SOLUTIA under the trade designation Macrynal® SM540/60X. Compared to the melamine resins the use of acrylic resins leads to adhesion promoting compositions which are more sensitive to moisture.

In a further alternative embodiment of the present invention epoxy resins having crosslinkable groups may be used as crosslinkable resins (B). Epoxy resins are prepolymerms that contain on the average two or more epoxide groups per molecule. Their reaction with a variety of curing agents, for
instance, with diols, such as bisphenol A leads to cross-linked or thermoset
plastics with excellent strength, toughness and chemical resistance. Suitable epoxy resins are known from the prior art and are commercially
available. For instance there can be used D.E.R., D.E.N., Tactix, Quartex supplied by Dow Chemical; Epon, Epikote, Eponof, Eponex supplied by
Shell; Araldite, Aracast supplied by Ciba Geigy; Epi-Rz supplied by Celanese, Epotuf supplied by Reichold or Unox supplied by Union Carbide,
Neukadur, Biresin and Belta LM. In a preferred embodiment of the present invention Araldite GT6097Ch supplied by Ciba Geigy is used.

Typically, the adhesive composition according to the present invention
comprises about 10 wt.-% to about 60 wt.-%, preferably about 15 wt.-% to
about 50 wt.-%, most preferably about 20 wt.-% to about 30 wt.-% of the
crosslinkable resin (B), based upon the total weight of the chlorinated
polyolefin (A), crosslinkable resin (B) and the isocyanate crosslinker (C).

Isocyanate Crosslinker (C)

The adhesive composition used according to the present invention further
comprises an isocyanate crosslinking agent that is capable of reacting with
both the functional groups of cross-linkable resin (B) and with the silane
primer (iii) comprised in the adhesion system used according to the present
invention.

Generally, any diisocyanate having two reactive isocyanate groups can be
used in order to react with the hydroxyl groups of the acrylic or epoxy resin
or the amino group of the melamine resin. Exemplary representative
diisocyanates are typically selected from diisocyanates such as 1,6-
hexamethylene diisocyanate, 1,8-octomethylene diisocyanate, 1,12-
dodecamethylene diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate
and similar isocyanates, 3,3'-diisocyanatodipropyl ether, 3-
isocyanatomethyl-3,5,5'-trimethylcyclohexyl isocyanate, cyclopentalene-
1,3-diisocyanate, cyclohexylene-1,4-diisocyanate, methyl-2,6-
diisocyanatocaprolate, bis-(2-isocyanatoethyl)-fumarate, 4-methyl-1,3-
diisocyanatocyclohexane, trans-vinylene diisocyanate and similar
unsaturated polyisocyanates, 4,4'-methylene-bis-(cyclohexylisocyanate)
and related polyisocyanates, methane diisocyanates, carbonate polyisocyanates such as bis-(2-isocyanatoethyl) carbonate, N,N,N'-tris-(6-isocyanatohexamethylene) biuret and related polyisocyanates as well as other known polyisocyanates derived from aliphatic polyamines, toluene diisocyanates, xylene diisocyanates, dianisidine diisocyanate, 4,4'-diphenylmethane diisocyanate, 1-ethoxy-2,4-diisocyanatobenzene, 1-chloro-2,4-diisocyanatobenzene, tris(4-isocyanatophenyl) methane, naphthalene diisocyanates, 4,4'-biphenyl diisocyanate, phenylene diisocyanates, 3,3'-dimethyl-4,4'-biphenyl diisocyanate, p-isocyanatobenzoyl isocyanate and tetrachloro-1,3-phenylene diisocyanate, and mixtures thereof. In a preferred embodiment blocked isocyanates having reduced reactivity compared to unblocked diisocyanate are used as crosslinking agents (C). Due to the low reactivity of the blocked isocyanates the adhesion promoting compositions of the present invention have significantly increased open times and improved storability. Blocked isocyanates, which are preferably used in conjunction with the present invention are based on isophorone diisocyanate (3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate; IPDI) and supplied by Degussa under the trade designations Vestanat® IPDI and Vestanat® T 1890/100.

According to the invention the adhesive composition typically comprises the isocyanate crosslinker in an amount of about 10 wt.-% to about 60 wt.-%, preferably about 15 wt.-% to about 50 wt.-%, most preferably about 25 wt.-% to about 30 wt.-%, based upon the total weight of the adhesive composition comprising the chlorinated polyolefin (A), the crosslinkable resin (B) and the isocyanate crosslinker (C).

Silane Primer

The adhesion system used according to the invention can further comprise a silane primer that is applied to the glass surface to which the TPV is to be adhered. Therefore, primers that can be used in conjunction with the adhesion promoting composition of the present invention have to be capable of interacting with both the glass surface and the functional groups of the isocyanate crosslinker (C) and/or with the crosslinkable resin (B).
In a preferred embodiment of the present invention the silane primer is selected from the group consisting of epoxy-silanes of formula (III), mercapto-silanes of formula (IV) and amino-silanes of formula (V) as shown herein below:

\[ \text{(III)} \]

\[ \text{(IV)} \]

\[ \text{(V)} \]

wherein n, m and p are integers from 1 to 12, preferably 2 to 8, more preferably 3 to 5 and the substituents \( R^3 \) to \( R^{11} \) are each individually selected from linear and branched alkyl groups having from 1 to 12, preferably from 2 to 8, most preferably 3 to 4 carbon atoms and substituents \( R^{12} \) and \( R^{13} \) are independently selected from hydrogen and linear and branched alkyl groups having from 1 to 12, preferably from 2 to 8, most preferably 3 to 4 carbon atoms, preferably \( R^2 \) and \( R^3 \) are both hydrogen.

In a more preferred embodiment of the invention the silane primer is a compound selected from the group consisting of 3-aminopropyltriethoxysilane and 3-mercaptopropyltriethoxysilane which are supplied by Siventco under the trade names Dynasylan\textsuperscript{\textregistered} 3201, Dynasylan\textsuperscript{\textregistered} AMEO.
further silane primer is 3-glycidyloxypropyl-trimethoxysilane commercially available from Sivento under the trade designation Dynasylan® GLYMO. Additionally, suitable silane primers are commercially available from DOW Chemical under the trade designation Betawipe VP® 046404, from SIKA under the trade designation Sika®-Activator and from Teroson under the designation Terostat®-8540. Typically, the silane primers may be dissolved in suitable solvents such as alcohols, preferably ethanol, methanol, n- or isopropanol.

In a first embodiment a thin layer of the silane primer is applied to the glass surface to be adhered to the TPV. In order to facilitate the thin coating of the glass the primer is usually dissolved suitable in a solvent, such as methyl-, ethyl- or isopropyl alcohol to give a 1 to 5 wt.-% solution. That solution is then applied to the glass surface as thinly as possible by spraying, brushing or wiping. In a preferred embodiment of the invention wipe on/wipe off techniques are used, wherein the applied film is wiped off immediately after its application.

The wet coating thickness of the primer is in the range of about 0.3 μm to about 5 μm, preferably about 0.5 μm to about 3 μm, most preferably about 0.8 μm to about 2 μm.

In an alternative embodiment of the invention the silane primer is admixed with the adhesion promoting composition. In this embodiment the application of the primer to the glass surface simultaneously occurs with the adhesive composition and, as a consequence, a separate coating step is redundant.

The adhesive composition according to the invention is prepared by admixing the chlorinated polyolefin (A), the crosslinkable resin (B), the isocyanate crosslinker (C) and, in the alternative embodiment of the invention described above, the silane primer. Preferably, an organic solvent is used in order to facilitate mixing of the compounds and application of the adhesion promoting composition. Typically, solvents suitable for the adhesion promoting composition are selected from polar and aromatic organic solvents such as n-butylacetate, benzene, tetrahydrofurane,
trichloroethane, trichloroethylene, dichloromethane, methylene chloride, xylene and toluene, with toluene being preferred.

The silane primer may be present in said solution in an amount of from about 0.1 wt.-% to about 5 wt.-%, preferably from about 0.5 wt.-% and 2.5 wt.-%, most preferably from about 0.7 wt.-% and 1.2 wt.-%, based on the total weight of the solution.

The solvent is utilized in an amount sufficient to provide a solution of the adhesion promoting composition having a total solids content (TSC) of about 5 wt.-% to about 30 wt.-%, preferably about 8 wt.-% to about 20 wt.-%, most preferably about 10 wt.-% to about 16 wt.-%.

The adhesive formulation used according to the present invention may optionally contain other well-known and common additives including plasticizers, fillers, pigments, reinforcing agents, and the like, in amounts employed by those skilled in the art in order to obtain the desired color and consistency.

To increase the storage stability and the shelf-life of the adhesive composition, the isocyanate crosslinker (C) is preferably stored separately from the precursor comprising the chlorinated and optionally maleated polyolefin (A), the crosslinkable resin (B) and the silane primer. Prior to its application to the substrate the precursor and the crosslinker (C) are thoroughly mixed in the amounts described above.

In a preferred embodiment the formulation is applied to the glass substrate immediately after mixing the components in order to avoid any increase in viscosity that might create problems associated with the corresponding application technique. The formulation may be applied to a desired substrate by techniques commonly known in the art such as by wiping, brushing, spraying, or dipping the substrate with the formulation. Preferably, the formulation is applied to the surface by spraying or brushing.

Typically, the amount of adhesion promoting composition applied to the substrate surface is from about 5 to about 50 μm, preferably about 10 to
about 40 μm, most preferably about 15 to about 30 μm, based upon the total adhesive (wet state) of the adhesion promoting composition.

Generally, after the adhesive composition has been applied to the surface the TPV is applied to the pre-coated glass surface using conventional state of the art injection molding, robotic extrusion or any other suitable method. If the adhesive composition has been dissolved in a solvent the formulation is dried for a time sufficient to evaporate the solvent prior to applying the TPV. After having applied the adhesive composition on top of the silane primer coating, or if the silane primer is comprised in the composition on top of the glass surface, the adhesive composition is dried by an air or a hot air stream. The TPV can be applied to the treated surface at room temperature or, alternatively, at an elevated temperature. For instance, prior to the application of the TPV the glass surface can be pre-heated to a temperature of about 80 to about 100°C, preferably to about 85 to 95°C, most preferably to about 90°C. Thereafter the TPV is applied to the pre-treated surface by injection molding, (robotic) extrusion as disclosed in United states Patent No. 5,336,349 the content which is fully incorporated by reference, laminating welding or any other method known in the art.

In the embodiment of the invention in which the glass surface is pretreated with a silane primer and a silane primer is present in the adhesion promoting composition the silane primer in the adhesion promoting composition can be the same or different from the silane primer used to pre-treat the glass surface.

The method of the invention has proven beneficial when bonding TPV to the surface of glass substrates such as, for instance, in the manufacture of automotive and aerospace/aircraft windows such as windshields, rear windows or quarter-lights that comprise a glass substrate and a TPV.

The methods of the invention and the compositions employed are likewise and without limitation applicable to the bonding of TPV to metal substrates such as steel, zinc, copper, aluminum, chromium, nickel, lead, titan, silver, gold, platinum, metal alloys such as brass or bronze, and the respective painted metal substrates. Therefore the term "glass substrate" can
interchangeably be used with the term "metal substrate" or "painted metal substrate" in this description and the appending claims.

The following examples are intended to further illustrate the invention but not to limit the scope of the invention.

Examples

The adhesion force between glass and TPE has been determined by the Peel test according to ASTM D429B and DIN 53531. Therefore, the glass/ceramic surfaces have been cleaned with pure acetone and coated with a thin layer of Betawipe® VP 04604 using a felt. After having dried the primer coating the adhesion promoting compositions as described in Table 1 were applied to the surface using a soft polyethylene foam sponge. After having completely dried the adhesion promoting composition Santoprene® 121-50E500 rubber was coated to the surface by extrusion. The test samples were stored for 7 days at 23°C. Then the initial peel test (H-0) was performed. For carrying out the Cataplasma Test the bonded specimen was wrapped in a clean cellulose paper so that the edges were covered. The wrapped specimen was then put in a 1 liter polyethylene bag one third thereof being filled with demineralized water (the specimen must not have direct contact with the water). After a 7 days storage at 70°C (H-7) the test specimen were removed from the plastic bags and cooled to room temperature. Thereafter, peel tests as described above were performed. In case of a cohesive rupture the tear occurs within the TPV whereas in case of adhesive rupture the TPV detaches from the glass surface with the TPV staying intact. The following Table summarizes the results obtained:
### TABLE

<table>
<thead>
<tr>
<th>Example</th>
<th>1 [wt.-%]</th>
<th>2 [wt.-%]</th>
<th>3 (Comp.)</th>
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<tr>
<td><strong>Composition</strong></td>
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<tr>
<td>Trapylene® 130 X</td>
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<td>Trapylene® 135 X</td>
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<tr>
<td>Vestanat® IPDI</td>
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<tr>
<td>Toluene</td>
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**Peel test according to ASTM D429B**

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<td>5</td>
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<tr>
<td>H-7 (ceramic)</td>
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</tbody>
</table>

**Note:** 1 = >95 % cohesive rupture; 2 = >75 % cohesive rupture; 3 = >25 % cohesive rupture; 4 = <25 % cohesive rupture; 5 = 0 % cohesive rupture (100 % adhesive rupture)
What is claimed is:

1. A method of adhering a thermoplastic vulcanizate to the surface of a glass substrate the method comprising the steps of:
   (I) applying a silane primer to the glass surface,
   (II) applying an adhesive composition comprising
         (A) a halogenated polyolefin;
         (B) a crosslinkable resin; and
         (C) an isocyanate crosslinker
   on top of the silane primer, and
   (III) applying said thermoplastic vulcanizate to the treated surface.

2. A method of adhering a thermoplastic vulcanizate to the surface of a glass substrate the method comprising the steps of:
   (I) applying an adhesive composition comprising
        (A) a halogenated polyolefin;
        (B) a crosslinkable resin;
        (C) an isocyanate crosslinker and
        (D) a silane primer;
   to the glass surface, and
   (II) applying the thermoplastic vulcanizate to the treated surface.

3. The method according to anyone of claims 1 or 2, wherein the halogenated polyolefin is selected from the group consisting of polychloroprene, chlorinated polychloroprene, chlorinated polypropylene, chlorinated polybutadiene, chlorinated polyisoprene, chlorinated polybutylene, chlorinated polyhexadiene, chlorinated butadiene styrene copolymers, chlorinated ethylene propylene
copolymers, chlorinated ethylene/propylene/non-conjugated diene terpolymers, chlorinated polyethylene, chlorosulfonated polyethylene, chlorinated copolymers alpha-olefins of 2 to 8 carbon atoms, chlorinated poly(vinyl chloride) and chlorinated polypropylene, and mixtures thereof.

4. The method according to anyone of claims 1 to 3, wherein the halogenated polyolefin (A) is grafted with maleic acid anhydride and/or maleic acid.

5. The method according to anyone of claims 1 to 4, wherein the isocyanate crosslinker (C) is a blocked or unblocked disiocyanate selected from the group consisting of 1,6-hexamethylene disiocyanate, 1,8-octomethylene disiocyanate, 1,12-dodecamethylene disiocyanate, 2,2,4-trimethylhexamethylene diisocyanate, 3,3'-diisocyanatodipropyl ether, 3-isocyanatomethyl-3,5,5'-trimethylcyclohexyl isocyanate, cyclopentane-1,3-diisocyanate, cyclohexylene-1,4-diisocyanate, methyl-2,6-disiocyanatocaprolate, bis-(2-isocyanatoethyl)-fumarate, 4-methyl-1,3-disiocyanatocyclohexane, trans-vinylene diisocyanate, 4,4'-methylene-bis-(cyclohexylisocyanate), methane disiocyanates, bis-(2-isocyanatoethyl) carbonate and similar carbonate polyisocyanates, N,N,N'-tris-(6-isocyanatohexamethylene) biuret, toluene disiocyanates, xylene disiocyanates; dianisidine diisocyanate, 4,4'-diphenylmethane diisocyanate, 1-ethoxy-2,4-diisocyanatobenzene, 1-chloro-2,4-diisocyanatobenzene, tris(4-isocyanatophenyl) methane, naphthalene diisocyanates, 4,4'-biphenyl diisocyanate, phenylene disiocyanates, 3,3'-dimethyl-4,4'-biphenyl diisocyanate, p-isocyanatobenzoyl isocyanate, tetrachloro-1,3-phenylene disiocyanate and isophorone diisocyanate (3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate), and mixtures thereof.
6. The method of claims 1 or 2, wherein the silane primer is selected from

- epoxy-silanes having the formula

\[
\begin{align*}
\text{O} & \quad \text{OR}^3 \quad \text{OR}^4 \\
\text{OR}^5 \\
\text{Si} & \quad \text{n} \\
\text{OR}^7 \\
\end{align*}
\]

wherein \(n\) is an integer from 1 to 12 and the residues \(R^1\) to \(R^6\) are each individually selected from the group consisting of linear and branched alkyl residues having from 1 to 12 carbon atoms;

- mercapto-silanes having the formula

\[
\begin{align*}
\text{HS} & \quad \text{OR}^7 \\
\text{OR}^8 \\
\text{OR}^9 \\
\text{Si} & \quad \text{m} \\
\end{align*}
\]

wherein \(m\) is an integer from 1 to 12 and the substituents \(R^6\) to \(R^9\) can be the same or independently selected from the group consisting of linear and branched alkyl groups having from 1 to 12 carbon atoms; and

- amino-silanes having the formula

\[
\begin{align*}
\text{R}^{12} & \quad \text{R}^{13} \\
\text{R}^9 & \quad \text{OR}^{10} \\
\text{OR}^{11} \\
\text{Si} & \quad \text{p} \\
\end{align*}
\]
wherein \( p \) is an integer from 1 to 12 and the substituents \( R^p \) to \( R^q \) can be the same or independently selected from the group consisting of linear and branched alkyl groups having from 1 to 12 carbon atoms and substituents \( R^{12} \) and \( R^{13} \) are independently selected from the group consisting of hydrogen and linear and branched alkyl groups having from 1 to 12 carbon atoms, preferably \( R^{12} \) and \( R^{13} \) are both hydrogen.

7. The method according to any of claims 1 to 6 wherein the TPV is applied to the treated surface by robotic extrusion using an extruder apparatus comprising an extruder barrel and an extrusion die said extruder barrel discharging through a extrusion die connected to a robotic handling unit, wherein the extruder barrel is connected to the extrusion die by means of a flexible pressure hose.

8. The method of any of claims 1 to 7, wherein the thermoplastic vulcanizate is bonded to the surface of a metal substrate or painted metal substrate instead of a glass substrate.

9. The method of claim 8, wherein the metal is selected from the group consisting of steel, zinc, copper, brass, bronze, aluminum, chromium, nickel, lead, titan, silver, gold, platinum, metal alloys, and the respective painted metal substrates.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBSTANCE MATTER

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<th>C09J5/02</th>
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According to International Patent Classification (IPC) or to both national classification and IPC.

B. FIELDS SEARCHED

- Minimum documentation searched (classification system followed by classification symbols)
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- Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched.

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

- EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>US 5 102 937 A (PFISTER WILLIAM S ET AL) 7 April 1992 (1992-04-07) cited in the application claims 1,3-5,10,15,17 column 4, line 22 - line 44 column 6, line 12 - line 49</td>
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Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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Date of the actual completion of the International search: 18 November 2004

Date of mailing of the International search report: 29/11/2004

Name and mailing address of the ISA

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