The document is a patent application published under the Patent Cooperation Treaty (PCT). It details a composition comprising [-Si-(OR)s], where R comprises an unsaturated hydrocarbon, preferably a methyl or ethyl group. The abstract is not fully visible in the provided image.
ADHESIVE FOR BONDING LIQUID SILICONE RUBBER

CROSS REFERENCE TO RELATED APPLICATIONS


FIELD OF THE INVENTION

[0002] The invention relates to an adhesive suitable for injection and compression molding operations preferably those bonding liquid silicone rubber to polycarbonate, other plastics, and metals.

BACKGROUND OF THE INVENTION

[0003] Liquid silicone rubber (LSR) is used to produce a wide range of parts for many different markets. Some notable segments include medical devices, cookware, electronics, and personal electronic devices. Silicone polymers exhibit many unique properties that other materials cannot achieve, combining rubbery flexibility with excellent thermal stability, durability, low surface energy, biocompatibility, soft feel, etc... Because of its unique performance and relative ease of part manufacturing, the global LSR (silicone) market has seen rapid growth. As the market need for LSR expands, product designs are becoming more sophisticated and require bonding of silicone to other substrates, which can be challenging due to its ultra-low surface energy and chemical resistance.

[0004] Many different adhesives and primers for bonding silicones exist on the market today. Most of the commercial offerings are based on alkoxy silanes that contain functional groups that are appropriate for the curing mechanism used in the silicone. In this embodiment, solvated silane must be applied to the substrate followed by solvent evaporation and subsequent hydrolysis with atmospheric moisture to create silanols that bond to the substrate's surface. In order for bonding to occur, the substrate must contain hydroxyl groups. The reaction kinetics of hydrolysis and bond formation are highly dependent on atmospheric moisture and temperature. This environment, especially in a manufacturing setting, can be very difficult to control. Furthermore, silanes must be applied as very thin coating (<1 micron) that is difficult to control and measure in a production environment. Most plastics require plasma treatment to create hydroxyl groups to promote silane bonding.
Because of all of the shortcomings with silane adhesive technology, there is a market need for silicone adhesives that are easier to use and more effective on various substrates. Thus there is a need for adhesives that will bond a wide range of platinum-cured silicones to many substrates, eliminating the need for complicated surface pretreatment, precise environments, and difficult-to-control reaction kinetics.

SUMMARY OF THE INVENTION

The advantageous properties of silicone elastomers, compared to conventional elastomers, include the following properties: UV resistance, thermal stability, high use temperature, and solvent and ozone resistance. One method of producing silicone parts utilizes a chemical process referred to as addition curing, which is typically catalyzed using platinum complexes. One form of silicone is referred to as LSR (liquid silicone rubber) and is handled in two different containers, one containing vinylated silicon polymer and Pt catalyst, and vinylated silicon polymer and Si-H oligomer in the other. Both are mixed just before use, followed by heating for vulcanization at high temperature. Another form of silicone is referred to as HCR (high consistency rubber). In this form, a platinum catalyst, via a two-roll mill, is added to a high viscosity silicone matrix containing hydrosilane and vinyl groups.

Molding addition-cured silicone onto thermoplastic substrate, particularly polycarbonate, polyester, and polyamide, results in multi material design and performance that combines the best attributes of both substrates. However, it is not an easy task to get a robust adhesion of cured silicone to plastics because of low surface energy and lack of functional groups. Therefore, it is necessary to change or improve the surface properties of the plastic without altering the bulk properties. Several techniques are used to modify the surface for improved adhesion, including plasma treatment, mechanical or chemical treatment, and exposure to flames, photons or ion beams. Among these techniques, plasma treatment is a commonly used method to improve the wettability and adhesion. Such treatment leads to surface oxidization, increasing its surface energy and creating roughness. However, there are performance reproducibility issues associated with the use of plasma treatment. Additionally, even the aforementioned surface treatment techniques do not yield a surface that will covalently bond to silicone.

Therefore, an adhesive system that bonds silicone to plastics, while eliminating the need for addition surface treatments and precise control of the application environment,
would have a significant impact on manufacturing efficiency along with more consistency in bonding.

[0009] In a first embodiment of the present invention, an adhesive is provided that is capable of bonding a wide assortment of rigid substrates to liquid silicone rubber (LSR) compounds during the curing step of the rubber. In a preferred embodiment of the present invention, this curing step is initiated in a mold to acquire the desired geometry and can optionally be later finished in a post curing step.

[0010] In a first aspect of the present invention, the adhesive solves several problems encountered today when using traditional LSR adhesives. Parts can be coated with the single coat adhesive by spray or brush techniques and can sit for several days under normal plant conditions and maintain the capability of bonding the dissimilar materials.

[0011] The inventive adhesive also provides robust adhesion to the various substrates and optionally doesn’t require a plasma treating step to improve the surface for bonding. Removing this step is labor saving and saves the end user both time and money.

[0012] In a first embodiment of the present invention, an adhesive is provided comprising an allyl (urethane) silane, wherein the allyl (urethane) silane comprises at least one allyl-functional group and one silane-functional group connected through a urethane linkage. In a preferred embodiment of the present invention, the allyl(urethane) silane comprises [Ri]-CO-NH-R2-Si(OR3)3, wherein Ri comprises at least one alkenoxy group, and R2 comprises a hydrocarbon chain, preferably where R2 comprises at least three carbon atoms, the alkenoxy group comprises [CH2-CH-CH2-O-], and the silane-functional group comprises an alkoxy silane. The alkoxy silane most preferably comprises [-Si-(OR)3], wherein R comprises an unsaturated hydrocarbon, preferably a methyl or ethyl group. In a further embodiment of the present invention, the allyl (urethane) silane comprises at least two allyl-functional groups. In a most preferred embodiment of the present invention, the allyl (urethane) silane comprises the reaction product of gamma-isocyanate propyl triethoxy silane with trimethylol propane diallyl ether.

[0013] In another embodiment of the present invention, the adhesive further comprises a phenoxy resin, a carrier fluid, and optionally a catalyst, and in further embodiments a vinyl-functional PDMS, an alkoxylated PDMS, and a blocked isocyanate.

[0014] In one embodiment of the present invention, the adhesive is provided in a two-part composition comprising:
in an A-side:
   a) an allyl (urethane) silane,
   b) an optional vinyl-functional PDMS,
   c) an optional alkoxylated PDMS,
   d) an optional isocyanate-functional silane,
   e) a phenoxy resin,
   f) and a carrier fluid,

and, in a B-side:
   a) a primary catalyst,
   b) an optional metal acetylacetone,
   c) and a carrier fluid.

[0015] In this two-part embodiment, the vinyl-functional PDMS comprises about 3.0% vinyl, the alkoxylated PDMS comprises an ethoxylated PMDS, and the isocyanate-functional silane comprises at least 2 carbon atoms between the urethane and silane functional groups. In a further embodiment, phenoxy resin comprises a PKHH grade phenoxy resin, the primary catalyst comprises at least one of a platinum methylvinylcyclotetrasiloxane complex or platinum chloride (PtCl₂), and the metal acetylacetone comprises zinc acetylacetonate. Further, the carrier fluid comprises at least one of water, methyl ethyl ketone and xylene.

[0016] In a further embodiment of the present invention, a process for bonding an article is provided comprising, a) providing in a molding cavity a rigid substrate having an adhesive comprising the adhesive described above applied thereto, b) contacting within the molding cavity an elastomeric or thermoplastic material at a temperature and pressure to allow the elastomeric or thermoplastic material to flow and contact a portion of the adhesive-applied section of the rigid substrate, and c) maintaining the temperature and pressure sufficient to solidify the elastomeric or thermoplastic material and form an adhesive bond between the material and the rigid substrate.

[0017] In a further embodiment of the present invention, the elastomeric or thermoplastic material comprises a silicone material, and the adhesive is capable of forming rubber tearing bonds between the silicone material and the rigid substrate. In another embodiment of the present invention, the rigid substrate comprises at least one of polycarbonate, polyester thermoplastic elastomer, and polyamide. In a further embodiment of the present invention, the process comprises at least one of a compression molding operation or an injection molding operation.
Thus, there has been outlined, rather broadly, the more important features of the invention in order that the detailed description that follows may be better understood and in order that the present contribution to the art may be better appreciated. There are, obviously, additional features of the invention that will be described hereinafter and which will form the subject matter of the claims appended hereto. In this respect, before explaining several embodiments of the invention in detail, it is to be understood that the invention is not limited in its application to the details and construction and to the arrangement of the components set forth in the following description or illustrated in the drawings. The invention is capable of other embodiments and of being practiced and carried out in various ways.

It is also to be understood that the phraseology and terminology herein are for the purposes of description and should not be regarded as limiting in any respect. Those skilled in the art will appreciate the concepts upon which this disclosure is based and that it may readily be utilized as the basis for designating other structures, methods and systems for carrying out the several purposes of this development. It is important that the claims be regarded as including such equivalent constructions insofar as they do not depart from the spirit and scope of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In a first embodiment of the present invention, an adhesive is provided for bonding a variety of rigid substrates to elastomers, plastics, and TPVs. In a preferred embodiment of the present invention, the adhesive is particularly useful for injection and compression molding operations where the adhesive is applied to a substrate and a liquid silicone rubber (LSR) is applied through an injection or compression molding operation. The adhesive provides excellent adhesion to a variety of substrates including polycarbonate, polyester, stainless steel, aluminum, glass, and steel. Further, the range of adhesion to liquid silicone rubbers includes a variety of filled and unfilled, colored or transparent liquid silicone rubber compounds.

In an embodiment of the invention, the adhesive comprises an allyl (urethane) silane. The allyl (urethane) silanes employed in the present provide both silane functionality and terminal unsaturation. In one embodiment of the present invention, mono- di- or tri- allyl (urethane) silanes may be employed, with di-allyl silanes being preferred. In another embodiment of the present invention, the allyl (urethane) silane comprises a mono- or di-silane, with tri-silanes being particularly preferred. In another preferred embodiment of the
present invention, the silane and allyl functional groups are separated by at least 4 and most preferably at least 6 carbon atoms.

[0022] In one embodiment of the present invention, the allyl (urethane) silane comprises at least one allyl-functional group and one silane-functional group connected through a urethane linkage. The preferred allyl-functional groups comprise alkenoxy groups having one carbon atom between the double bond and the oxygen. In a preferred embodiment of the present invention, the allyl (urethane) silane comprises at least two allyl-functional groups.

[0023] The preferred silane-functional group comprises an alkoxy silane, preferably methoxy or ethoxy. In a most preferred embodiment of the present invention, the silane functionality comprises a tri-methoxy or tri-ethoxy silane, and although less preferred, longer chain alkenoxy groups may be used with the present invention.

[0024] In one preferred embodiment of the present invention, the allyl (urethane) silanes are prepared by reacting an isocyanato-silane in the presence of a catalyst with an allyl-containing alcohol to produce the desired allyl (urethane) silane. For example, reacting 3-(triethoxysilyl)propyl isocyanate, in the presence of a dibutylin dilaurate catalyst with; a) 2-propen-l-ol to make a mono-allyl 1(urethane) tri-alkoxy silane; b) with trimethylolpropane allyl ether to make a mono-allyl (urethane) di(tri-alkoxysilane); c) with trimethylolpropane diallyl ether to make a di-allyl (urethane) mono(tri-alkoxysilane); and d) pentaerythritol allyl ether to make a tri-allyl (urethane) mono(tri-alkoxysilane).

[0025] In one embodiment of the present invention, the allyl (urethane) silane is present in the adhesive from about 5 to about 95, more preferably about 10 to about 50, and most preferably about 15 to about 30 weight percent based on the dry weight of the adhesive.

[0026] In another embodiment of the present invention, a vinyl functional siloxane is optionally included in the adhesive. The vinyl functional siloxane of the present invention comprises any siloxane with vinyl functionality, such as trimethyl terminated poly(methylnvinyl) siloxane, vinyl terminated polydimethyl siloxane, monovinyl terminated polydimethyl siloxane, trimethyl terminated vinylmethyl-dimethyl polysiloxane copolymer, monovinyldimethyl terminated vinylmethyl-dimethyl polysiloxane copolymer, vinyldimethyl terminated cinylmethyl-dimethyl polysiloxane copolymer, and the like. In a preferred embodiment of the present invention, the vinyl-functional siloxane comprises vinyl-terminated polydimethyl siloxane. In a preferred embodiment of the present invention, the vinyl-functional silane comprises at least 2.0 and preferably about 3.0 % vinyl.
In one embodiment of the present invention, the vinyl functional siloxane is present in the adhesive up to about 40, more preferably up to about 30, and most preferably up to about 25 weight percent based on the dry weight of the adhesive.

In another embodiment of the present invention an optional material comprises an alkoxylated PDMS corresponding to the general formula (1)

\[
(CH_3)_3SiO-((CH_3)_2SiO)_{y}-((CH_3-SiO)-Si(CH_3)_3)^{x}
\]

wherein,

PE is the monovalent radical \(-CH_2-CH_2-CH_2-0(eo/poO_w)_mZ\),

eo represents ethylene oxide,

po represents propylene oxide and

Z is either hydrogen or a \(-C_6-\text{alkyl}\) radical,

v and w are integers greater than or equal to 0, wherein v and w are not simultaneously 0,

x is an integer greater than or equal to 0, and y and m are integers greater than or equal to 1, which are preferably so selected that the molecular weight (number average) of formula (1) does not exceed 30,000 g/mol. and the viscosity of component C) is from 10 to 5000 cSt (25°C).

In another embodiment of the present invention an optional isocyanate-functional silane is provided comprising at least 2 carbon atoms between the urethane and silane functional groups. In a preferred embodiment of the present invention, the isocyanate functional silane comprises a trimethoxy or triethoxy isocyanatopropyl silane.

In a preferred embodiment of the present invention, the adhesive further comprises a phenoxy resin. Phenoxy reins are commercially important thermoplastic polymers derived from bisphenols and epichlorohydrin. Their molecular weights are higher, i.e., at least about 45,000, than those of conventional epoxy resins, i.e., 8,000 maximum. They lack terminal epoxide functionality and are therefore thermally stable and can be fabricated by conventional thermoforming techniques. The phenoxies have the same repeat unit as advanced epoxy resins and are classified as polyols or polyhydroxy ethers.
Phenoxy resins are prepared by reaction of high purity bisphenol A with epichlorohydrin in a 1:1 mole ratio. Solution polymerization may be employed to achieve the molecular weight and processibility needed.

[0031] In another embodiment of the present invention, a solvent-soluble phenoxy resin is employed for use in a solvent-based adhesive. Solvent-soluble phenoxy resins are known in the art from a number of producers, however particularly suitable examples of phenoxy resins for solvent-based adhesives include the solid PKHH grade sold by Phenoxy Associates or PKHS-40, which is a PKHH grade pre-dissolved in methylethyl ketone (MEK).

[0032] Further examples of suitable amine neutralized, carboxylated phenoxy resins are those phenoxy resins which have been carboxylated with lower alkanoic acids having 1 to 6 carbon atoms such as formic acid, acetic acid, propionic acid, butyric acid, pentanoic acid and hexanoic acid, which have been amine neutralized, by reaction with ammonia or ammonium hydroxide.

[0033] In an embodiment of the present invention comprising an adhesive in an aqueous carrier, the phenoxy resin comprises A suitable example of a phenoxy resin that may be used in the present invention is a polymer of bisphenol "A", specifically, diglycidyl ethers of bisphenol "A". Suitable for use in the present invention as the phenoxy resin is that sold as Phenoxy Resin PKHW-35, and manufactured by Gabriel Performance Products in Ohio, USA. PKHW-35 is an amine-neutralized, carboxylated phenoxy resin in water, and is a waterborne product that is surfactant-free, colloidal in natured with excellent emulsion stability from 0°C. to 55°C, exhibiting a high degree of consistency in viscosity and solids, and having up to 40 percent solids by weight.

[0034] In one embodiment of the present invention, the phenoxy resin is present in the adhesive from about 10 to about 80, more preferably about 35 to about 68, and most preferably about 50 weight percent based on the dry weight of the adhesive.

[0035] In one embodiment of the present invention, the adhesive further comprises a catalyst. The catalyst comprises a typical metal hydrosilylation catalyst and used in an amount specified below which is sufficient to effect the cure of the adhesive composition. In a preferred embodiment of the present invention, the catalyst comprises a platinum cyclovinylmethysiloxane complex. An additional suitable platinum catalyst is available from Gelest, Inc. under the SIP 6830 designation, also known as Karstedt Catalyst, or a COD
catalyst such as dichloro(1,5-cyclooctadiene)platinum(II), available from Sigma-Aldrich, Missouri, USA.

[0036] In another embodiment of the present invention, suitable catalysts include but are not limited to chloroplatinic acid, Karstedt's catalyst (Pt2\{[(CH2=CH)Me2Si]20}\3), Ashby's catalyst \{[(CH2=CH)MeSiO]4\}3Pt, Wilkinson's catalyst [tris(triphenylphosphine)rhodium (I) chloride], polymer bound Wilkinson's catalyst, tris(triphenylphosphine)iridium (I) chloride, chloroplatinic acid/octanol complex, platinum cyclovinylmethyilsiloxane complex (Ashby-Karstedt catalyst), platinum carbonyl cyclovinylmethyilsiloxane complex, bis(benzonitrile)dichloropalladium (II), tetrakis(triphenylphosphine)palladium (0), palladium 2,4-pentanedionate, iridium 2,4-pentanedionate, iridium cyclooctadiene chloride, Pt metal, Pd metal, Ir metal, and Rh metal.

[0037] In a preferred embodiment of the present invention, the catalyst comprises a platinum methylvinylcycloctetrasiloxane complex. An additional suitable platinum catalyst comprises dichloro(1,5-cyclooctadiene)platinumII.

[0038] In one embodiment of the present invention, the catalyst is present in the adhesive up to about 3.0, more preferably about 0.05 to about 2.0, and most preferably about 0.10 to about 1.5 weight percent based on the dry weight of the adhesive.

[0039] In another aspect of the present invention, it has been found that improved performance can be obtained by employing one or more co-catalysts. While typically employed in embodiments where a catalyst is present in the adhesive formulation, co-catalysts may also be employed in adhesive formulations without a primary catalyst. These co-catalysts are preferable based on the elements from Groups VII, VIII, IB, IIB, IVA or VA of the Periodic Table of the Elements such as manganese, cobalt, nickel, copper, zinc, zirconium germanium, antimony, or bismuth, especially compounds based on an element from the foregoing groups metals, such as bivalent metals, and particularly chelates of metals, or oxides or salts of these metals and especially carbonate salts are preferred. Zinc, bismuth, and antimony are especially preferred metallic elements, with zinc being most preferred. Representative salts of these co-catalyst metals are based on inorganic acids, carboxylic acids, hydroxy carboxylic acids, alcohols, glycols and phenols.

[0040] Representative carboxylic acids include both mono and dicarboxylic acids containing from 1 to about 20 carbon atoms and include aliphatic and cycloaliphatic saturated or unsaturated acids, and aromatic acids, and include formic, acetic, acrylic, methacrylic.
propionic, butyric, hexanoic, octanoic, decanoic, stearic, oleic, eiconsanoic and benzoic acids. Examples of dicarboxylic acids include oxalic, malic, maleic, succinic, sebacic and the various isomeric phthalic acids. Typical hydroxy carboxylic acids preferably contain from 2 to about 20 carbon atoms and include hydroxy acetic, lactic, citric, tartaric, salicylic, and gluconic acids.

[0041] Inorganic acids or the mineral acids include carbonic acid, halogen acids such as hydrochloric, hydrobromic, and hydriodic acids, nitrogen acids, sulfur acids and phosphorus acids, all of which are known in the art.

[0042] The alcohols comprise straight chain or branched chain mono- or polyhydroxy alcohols, alkyl substituted or unsubstituted mononuclear or polynuclear mono or polyhydroxy cycloaliphatic alcohols and the like containing from 1 to about 20 carbon atoms. The phenols comprise alkyl substituted or unsubstituted mononuclear or polynuclear mono or polyhydroxy phenols.

[0043] The carbonates of the aforesaid metals may exist as pure carbonates or as basic carbonates which are believed to be mixtures of the carbonate and the oxide or hydroxide of the metal in a single molecule and include metal carbonates such as basic zinc carbonate, basic copper carbonate and the like.

[0044] The chelates of the aforesaid metals that may be employed may be based on any metal chelating compounds known in the art but typically comprise beta-diketones such as acetyl acetone to provide the acetylacetonates of the metals.

[0045] Metal catalysts that are generally most suitable as cocatalysts are the ones that are soluble in the formulation especially if soluble in the functional compound, e.g. the polyol resin or soluble in the solvent if the formulation uses a solvent.

[0046] Some specific metal catalysts that may be employed comprise zinc carbonate (basic), zinc acetylacetonate, zinc acetate, copper acetylacetonate, iron acetylacetonate, nickel acetylacetonate, zinc acetate, zinc lactate, and copper acetate. Such suitable metal cocatalysts are generally described by Leiner and Bossert in U.S. Pat. No. 4,395,528.

[0047] In one embodiment of the present invention, the co-catalyst is present in the adhesive up to about 10, preferably up to about 5, and most preferably about 1.0 to about 3.0 weight percent based on the dry weight of the adhesive.
[0048] In another embodiment of the present invention, the adhesive further comprises a self-blocked isocyanate. Self-blocked isocyanates are also referred to as internally-blocked isocyanates and commonly comprise dimerized diisocyanates.

[0049] Bis (cyclic ureas) are blocked aliphatic diisocyanates and are preferred in some embodiments because no by-products are formed upon thermal release of the reactive isocyanates. These comprise compounds that can be referred to as self-blocked isocyanates. Examples of these bis-cyclic ureas are described by Ulrich, ACS Symp. Ser. 172 519 (1981), Sherwood, J. Coat. Technol. 54 (689), 61 (1982) and Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 23, p. 584 all of which are incorporated herein by reference. As an example of such an internally-blocked isocyanate, uretdione-bound self-blocked isophorone diisocyanate, which is marketed from Huls Co. under a tradename "IPDI-BF 1540", may be cited.

[0050] In a further embodiment of the present invention, the "internally blocked isocyanates" comprise the dimerized diisocyanates discussed above, however there may be some isocyanate functionalities on the ends of the molecule that are partially blocked or unblocked. These functionalities may react slowly with water and decrease shelf life in aqueous formulations, however the primary "internally blocked" isocyanate functionality remains reactive in the as-applied adhesive formulation and is available for bonding.

[0051] In an alternate embodiment of the present invention, the self-blocked isocyanate comprises dimeric isocyanates such as dimeric toluene diisocyanate (TDI-uretdione), dimeric methylene diphenyl diisocyanate (MDI-uretdione) or a mixture thereof. An example of a uretdione of MDI is GRILBOND A2BOND available from EMS-Griitech (Switzerland), and an example of a uretdione of TDI is ADOLINK TT available from Rhein Chemie Rheinau GmbH (Mannheim, Germany).

[0052] In one embodiment of the present invention, the self-blocked isocyanate is present in the adhesive up to about 30, more preferably about 15 to about 25, and most preferably about 20 weight percent based on the dry weight of the adhesive.

[0053] In one embodiment of the present invention, the adhesive is provided in an aqueous carrier with the optional inclusion of small amounts of co-solvent. In another embodiment of the present invention, the adhesive is provided in a solvent carrier system, though small amounts of water may be present in an emulsion or colloidal mixture.
In a further embodiment of the present invention, the adhesive is provided in a hydrocarbon-solvent based system. Non-limiting examples of suitable solvents are solvents which are inert towards isocyanate groups, such as hexane, toluene, xylene, chlorobenzene, ethyl acetate, butyl acetate, diethylene glycol dimethyl ether, dipropylene glycol dimethyl ether, ethylene glycol monomethyl or monoethyl ether acetate, diethylene glycol-ethyl and butyl ether acetate, propylene glycol monomethyl ether acetate, 1-methoxyprop-2-yl acetate, 3-methoxy-n-butyl acetate, propylene glycol diacetate, acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, lactones such as β-propiolactone, γ-butyrolactone, ε-caprolactone and ε-methyl caprolactone, for example, but also solvents such as N-methylpyrrolidone and N-methylcaprolactam, 1,2-propylene carbonate, methylene chloride, dimethyl sulfoxide, triethyl phosphate or any mixtures of such solvents. In a preferred embodiment of the present invention, the solvent-based adhesive formulation comprises xylene, methylethyl ketone, cyclohexanone or mixtures thereof as the primary carrier.

The adhesive compositions of the present invention can optionally contain other well-known additives including plasticizers, fillers, pigments, surfactants, dispersing agents, wetting agents, rheology modifiers, reinforcing agents and the like.

In an embodiment of the present invention, the adhesives are applied to the rigid substrate through common application procedures such as spray application, brush application, or a dip process. The adhesive is preferably applied in a uniform wet film and hot air is employed to assist the drying and removal of the carrier fluid. The dry film thickness is targeted for about 0.20-1.0 mils or 5 to 25 microns.

Bonded assemblies are prepared using a compression or injection molding process. For compression molding, a mold having two separate cavities is employed. The rigid substrate having the dry adhesive film coating is placed in the preheated mold and the plastic/elastomer to be bonded is placed on top in the cavity. The hot mold is closed and placed in a hydraulic press and clamped under a known pressure. Once cured, the bonded assemblies are removed from the mold. Once the bonded assemblies cooled to room temperature they can be manually and visually tested for bond quality. Injection molding is similar, except the plastic/elastomer is injected into the mold cavity as a liquid and an elevated temperature and pressure are maintained until the assembly is cured and bonded.

Although the present invention has been described with reference to particular embodiments, it should be recognized that these embodiments are merely illustrative of the
principles of the present invention. Those of ordinary skill in the art will appreciate that the compositions, apparatus and methods of the present invention may be constructed and implemented in other ways and embodiments. Accordingly, the description herein should not be read as limiting the present invention, as other embodiments also fall within the scope of the present invention as defined by the appended claims.

EXAMPLES

[0059] In one exemplary embodiment of the present invention, a 2-part adhesive as described in the table below was made and tested with the results presented below.

[0060] The adhesive bonds platinum-cured liquid silicone rubber (LSR) to polycarbonate and polyester thermoplastic elastomer without the need for any surface pretreatment process, such as plasma, corona, flame, or solvent treatment. The adhesive is not affected by the addition of colorant to the LSR (4 weight percent pink colorant). The adhesive demonstrates layover performance of at least 3 days, meaning that the plastic parts can be sprayed with this adhesive and stored under ambient conditions for 3 days before LSR molding, and still achieve effective bond strength.

[0061] The adhesive gives bond strengths that exceed the tear strength of the LSR material. The adhesive has a large processing window in terms of thickness - it is effective at thicknesses ranging from 3 to 20 microns. The adhesive shows favorable spraying characteristics that allow it to be easily applied with an air powered spray gun. These attributes include low viscosity, fast drying time, good wetting of polymer surfaces, and homogeneous consistency.

Adhesive 1

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diallyl (urethane) silane</td>
<td>2</td>
</tr>
<tr>
<td>Vinyl-functional silane</td>
<td>2.7</td>
</tr>
<tr>
<td>Ethoxylated silane</td>
<td>0.5</td>
</tr>
<tr>
<td>Isocyanate-functional silane</td>
<td>1.3</td>
</tr>
<tr>
<td>Phenoxy resin (PKHH)</td>
<td>17.8</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>5.0</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>25.7</td>
</tr>
<tr>
<td>Total A</td>
<td>100</td>
</tr>
<tr>
<td>Zinc Acetylacetonate</td>
<td>4.0</td>
</tr>
<tr>
<td>Platinum Catalyst</td>
<td>0.3</td>
</tr>
<tr>
<td>-------------------</td>
<td>-----</td>
</tr>
<tr>
<td>Xylene</td>
<td>95.7</td>
</tr>
<tr>
<td><strong>Total B</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

Preparation of two pack adhesive for bonding PC to LSR

**Side A (900g scale)**

[0062] In a glass jar, 160 grams of 25% of phenoxy resin (40 grams PKHH and 120 grams of MEK) was diluted with 450 grams of cyclohexanone. The mixture was stirred for 10 minutes to get a clear solution. In another container containing 231 grams of methyl ethyl ketone, diallyl(urethane)silane, vinyl-functional silane, a surfactant, and isocyanate silane were added. The mixture was stirred to get a turbid solution which phase-separates with standing.

**Side B**

[0063] In a 100 grams jar, 0.3 grams of platinum catalyst and 95.7 grams of xylene were added; the catalyst is insoluble in xylene. Then, zinc acetylacetonate catalyst (solid powder insoluble in xylene) was added to the mixture. The mixture was stirred for 30 minutes to a homogenous dispersion of PtCh (COD) and zinc acetylacetonate catalyst in xylene. The solution formed a thick suspension.

**Mixing A and B**

1. The adhesive is prepared by mixing 9 parts of A side and 1 part of B side.
2. Before weighing out the required amounts of each side, both sides should be mixed very well to make sure the mixtures are homogenous.
3. After shaking side A, it should be a homogenous turbid solution.
4. Side B should be stirred well to give a homogenous suspension.
5. Side B should be added to side A, followed by mixing by shaking for a few min to give a slightly turbid pale yellow solution that has no visible particles.

**Materials**

[0064] For this experiment, a representative spread of thermoplastic materials were gathered from various suppliers, and selected as substrates. These materials will be referred to by their generic designations: polycarbonate (PC), flame-retardant polycarbonate (PCFR),
thermoplastic elastomer (TPE), and polyamide (PA). Stainless steel (304) with polished and grit blasted surface finishes was also included in this experiment.

[0065] Three LSR's were chosen, all of them were 70 durometer silicones with very similar mechanical properties and curing profiles, and manufactured by three major silicone producers so that a range of commercial offerings could be evaluated. They are denoted as LSR 1, LSR 2, and LSR 3.

Adhesive Application

[0066] The substrate was masked with Kapton tape such that only half of the test plaque would receive adhesive. In the case of the plastic substrates, adhesive was applied to the section with VDI-26 finish. Adhesives were applied with a Binks Model 95 siphon feed HVLP spray gun to a thickness of 10 to 15 microns. Immediately after spraying, parts were dried in a hot air convection oven at 50°C for 15 minutes. After removing from the oven, parts were stored at 21°C / 50% RH for up to 4 hours before overmolding with LSR.

LSR Molding

[0067] The A and B sides of the silicone were mixed in a mixer at low speed for five minutes. The substrate was overmolded with LSR in a Wabash MPI G30H-18-BX compression press that was heated to 125°C. In each cycle, three pieces of substrate were placed into a 150 mm x 150 mm x 5 mm mold, along with 150 grams of LSR. The parts were then molded at 20 tons of pressure for 5 minutes. After 5 minutes, parts were carefully removed and allowed to cool to room temperature before being separated with a utility knife. Strips 25 mm wide were cut into the LSR for peel testing.

Peel Testing

[0068] After at least 24 hours after molding, parts were peel tested at 180 degrees at 300 mm/min in an Instron Model 3365 tensile tester utilizing a 1 kN load cell. Peak strength and failure modes were recorded.

Failure Modes

[0069] In addition to peel strength, failure mode analysis is key to understanding product performance and bonding mechanism. For the results reported in this paper, the test area is a 25 mm strip that is approximately 45 mm long. Failure mode is reported as a percentage of this area based on its state after testing is carried out. Failure modes were divided into four categories, each one is described below:
• Thick Rubber Retention: the entire thickness of the silicone rubber is intact. This is the most desirable failure mode and means that the strength of the adhesive exceeds the strength of the silicone.

• Thin Rubber Retention: a thin layer of rubber is retained on the substrate. This means that the silicone rubber itself failed, but failed at a layer that is close to the adhesive interphase. This failure mode can be influenced by the performance of the adhesive, and can be caused, for example, if the adhesive retards or interrupts the silicone curing mechanism. A small amount (<20%) of thin rubber failure is normal and unavoidable in this test method.

• Substrate to Adhesive Failure: the adhesive does not stick to the substrate, delaminating from it during testing and usually sticking to the silicone.

• Rubber to Adhesive Failure: the adhesive does not stick to the silicone and remains on the substrate. This failure mode indicates that reaction between the adhesive and silicone did not occur.

Adhesive Bonding to Multiple LSR’s

[0070] The first test evaluated the effectiveness of each adhesive on three different representative LSR's of similar durometer from three major silicone producers. Each LSR was mixed, per the manufacturer recommendation, at a 50:50 ratio of A to B and cured via addition reaction catalyzed by platinum. The same process conditions (125°C for 5 minutes) were also used for all three silicones. Bonding data is shown below:

<table>
<thead>
<tr>
<th></th>
<th>Peel Strength (N/cm)</th>
<th>Thick Rubber Retention (%)</th>
<th>Thin Rubber Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSR 1</td>
<td>79</td>
<td>83</td>
<td>17</td>
</tr>
<tr>
<td>LSR 2</td>
<td>74</td>
<td>73</td>
<td>28</td>
</tr>
<tr>
<td>LSR 3</td>
<td>73</td>
<td>90</td>
<td>10</td>
</tr>
</tbody>
</table>

[0071] The results show that the adhesive bonds completely to all three LSRs with high peel strength values of greater than 70 N/cm, at which point the silicone fails. This sample group did not show any evidence of failure to either the substrate or the silicone/adhesive interface, indicating good adhesive performance.

Adhesive Bonding to Multiple Substrates

[0072] To further understand the applicability of these adhesive technologies, they were evaluated on multiple substrates, which included polycarbonate (PC), flame-retardant
polycarbonate (PCFR), thermoplastic elastomer (TPE), and 304 stainless steel (SUS). In this experiment, LSR 1 was used on all of the substrate and adhesive combinations. Adhesive 1 provided robust bonding to all four substrates.

<table>
<thead>
<tr>
<th></th>
<th>Peel Strength (N/cm)</th>
<th>Thick Rubber Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>79</td>
<td>83</td>
</tr>
<tr>
<td>PCFR</td>
<td>80</td>
<td>85</td>
</tr>
<tr>
<td>TPE</td>
<td>83</td>
<td>85</td>
</tr>
<tr>
<td>304 SUS</td>
<td>71</td>
<td>100</td>
</tr>
</tbody>
</table>

[0073] Three new adhesive technology was tested for bonding platinum-cured liquid silicone rubber to multiple substrates. Common, off-the-shelf silicones of 70 durometer were chosen for this study. The inventive adhesive bonded to all LSR's, and to multiple substrates, including PC, PCFR, TPE, and 304 SUS.

[0074] The adhesive system was successful in bonding multiple platinum-cured silicones to multiple substrates that do not require special surface preparation techniques such as plasma or flame treatment, and does not have the same application limitations as typical silane primers.

EXAMPLE 2 - INJECTON MOLDING

[0075] The purpose of this experiment is to demonstrate the effectiveness of an adhesive of the present invention in an injection molding operation. Process parameters such as DFT, cure time, cure temperature, and layover, were evaluated.

[0076] A mold was constructed to accept 1" x 2.5" x 0.060" coupons (25.4mm x 63.5mm x 1.5mm), and overmold it with a strip of liquid silicone. In this experiment, approximately half of the surface area of coupons of polycarbonate were sprayed with adhesive per the conditions in the table listed below. These coupons were overmolded with a LSR and tested 24 hours later in 90 degree peel at 300 mm/min. Peak peel values were recorded.

<table>
<thead>
<tr>
<th>Layover Condition</th>
<th>Layover (Days)</th>
<th>Peel Strength (N/cm)</th>
<th>Rubber Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21C/40RH</td>
<td>0</td>
<td>41</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>43</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>41</td>
<td>100</td>
</tr>
<tr>
<td>27C/80RH</td>
<td>0</td>
<td>41</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>41</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>50</td>
<td>95</td>
</tr>
</tbody>
</table>
In all cases, robust adhesion of greater than 40N/cm was noted, as well as 100% rubber retention. The small and possibly insignificant devcerase in rubber tear after 2 days at 27°C / 80 RH may be experimental error and further study will be done.

EXAMPLE 3 - AQUEOUS ADHESIVE

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dialyl (urethane) silane</td>
<td>2.5</td>
</tr>
<tr>
<td>Self-Blocked Isocyanate</td>
<td>2.0</td>
</tr>
<tr>
<td>Phenoxy resin (PKHW)</td>
<td>5.0</td>
</tr>
<tr>
<td>Zinc Acetylacetonate</td>
<td>0.30</td>
</tr>
<tr>
<td>Platinum Catalyst</td>
<td>0.15</td>
</tr>
<tr>
<td>Dapro W-77 (wetting agent)</td>
<td>0.05</td>
</tr>
<tr>
<td>Water</td>
<td>68.90</td>
</tr>
<tr>
<td>Glycol Ether (cosolvent)</td>
<td>6.7</td>
</tr>
<tr>
<td>Propylene carbonate (cosolvent)</td>
<td>2.15</td>
</tr>
<tr>
<td>Dimethyl Carbonate (cosolvent)</td>
<td>12.25</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

The above-adhesive was mixed, applied, bonded and tested as described in Example 1. The self-blocked isocyanate, A2 Bond, arrives as a dispersion in glycol ether, and the phenoxy resin and zinc acetylacetonate arrive as dispersion in water. All these materials are separated above to illustrate the individual components. The adhesive was employed to bond three different LSR materials to a polycarbonate substrate. The adhesive produced rubber-tearing bonds (100%R) in all three trials, demonstrating a robust bond between the LSRs and the polycarbonate substrate.
What is Claimed is:

1. An adhesive comprising an allyl (urethane) silane, wherein the allyl (urethane) silane comprises at least one allyl-functional group and one silane-functional group connected through a urethane linkage.

2. The adhesive of claim 1, wherein the allyl(urethane) silane comprises \([\text{R}_1]-\text{CO-NH-R}_2-\text{Si(OR}_3)_3\), wherein \(\text{R}_1\) comprises at least one alkeneoxy group, and \(\text{R}_2\) comprises a hydrocarbon chain.

3. The adhesive of claim 2, wherein \(\text{R}_2\) comprises at least three carbon atoms.

4. The adhesive of claim 2, wherein the alkeneoxy group comprises \([\text{CH}_2-\text{CH-CH}_2-\text{O-}]\).

5. The adhesive of claim 1, wherein the silane-functional group comprises an alkoxy silane.

6. The adhesive of claim 5, wherein the alkoxy silane comprises \([-\text{Si-(OR}_3]\), wherein \(\text{R}\) comprises an unsaturated hydrocarbon.

7. The adhesive of claim 6, wherein \(\text{R}\) comprises a methyl or ethyl group.

8. The adhesive of claim 1, comprising at least two allyl-functional groups.

9. The adhesive of claim 1, wherein the allyl(urethane) silane comprises the reaction product of gamma-isocyanate propyl triethoxy silane with trimethylol propane diallyl ether.
10. The adhesive of claim 1, further comprising a phenoxy resin, a carrier fluid, and optionally a catalyst.

11. The adhesive of claim 10, further comprising a vinyl-functional PDMS and an alkoxylated PDMS.

12. The adhesive of claim 10, further comprising a blocked isocyanate.

13. The adhesive of claim 1, comprising a two-part composition comprising:
   in an A-side:
   a) an allyl (urethane) silane,
   b) an optional vinyl-functional PDMS,
   c) an optional alkoxylated PDMS,
   d) an optional isocyanate-functional silane,
   e) a phenoxy resin,
   f) and a carrier fluid,
   and, in a B-side:
   a) a primary catalyst,
   b) an optional metal acetylacetone,
   d) and a carrier fluid.

14. The adhesive of claim 13, wherein the vinyl-functional PDMS comprises about 3.0% vinyl.

15. The adhesive of claim 13, wherein the alkoxylated PDMS comprises an ethoxylated PMDS.
16. The adhesive of claim 13, wherein the isocyanate-functional silane comprises at least 2 carbon atoms between the urethane and silane functional groups.

17. The adhesive of claim 13, wherein the phenoxy resin comprises a PKHH grade phenoxy resin.

18. The adhesive of claim 13, wherein the primary catalyst comprises at least one of a platinum methylvinylcyclotetrasiloxane complex or platinum chloride (PtCl₂).

19. The adhesive of claim 13, wherein the metal acetylacetone comprises zinc acetylacetonate.

20. The adhesive of claim 13, wherein the carrier fluid comprises water.

21. The adhesive of claim 13, wherein the carrier fluid comprises at least one of methyl ethyl ketone and xylene.

22. A process for bonding an article comprising:
   a) providing in a molding cavity a rigid substrate having an adhesive comprising the adhesive of claim 1 applied thereto;
   b) contacting within the molding cavity an elastomeric or thermoplastic material at a temperature and pressure to allow the elastomeric or thermoplastic material to flow and contact a portion of the adhesive-applied section of the rigid substrate; and,
   c) maintaining the temperature and pressure sufficient to solidify the elastomeric or thermoplastic material and form an adhesive bond between the material and the rigid substrate.
23. The process of claim 22, wherein the elastomeric or thermoplastic material comprises a silicone material.

24. The process of claim 23, wherein the adhesive is capable of forming rubber tearing bonds between the silicone material and the rigid substrate.

25. The process of claim 22, wherein the rigid substrate comprises at least one of polycarbonate, polyester thermoplastic elastomer, and polyamide.

26. The process of claim 22, wherein the process comprises a compression molding operation.

27. The process of claim 22, wherein the process comprises an injection molding operation.
A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G18/71 C07C269/02 C08G18/80 C09J163/04

ADD.

According to International Patent Classification (IPC) or both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G C07C C09J

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 practicable, search terms used)

EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
</table>

Further documents are listed in the continuation of Box C.

* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
  "E" earlier application or patent but published on or after the international filing date
  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  "O" document referring to an oral disclosure, use, exhibition or other means
  "P" document published prior to the international filing date but later than the priority date claimed
  "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  "A" document member of the same patent family

Date of the actual completion of the international search

22 February 2017

Date of mailing of the international search report

02/03/2017

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040;
Fax: (+31-70) 340-3016

Authorized officer

Bergmeier, Martin

Form PCT/ISA/210 (second sheet) (April 2005)
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td>US 2008108767 A1</td>
<td>08-05-2008</td>
<td>CN 101014633 A</td>
<td>08-08-2007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN 102516459 A</td>
<td>27-06-2012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 5012025 B2</td>
<td>29-08-2012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>KR 20070088595 A</td>
<td>29-08-2007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US RE44096 E</td>
<td>19-03-2013</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2008108767 A1</td>
<td>08-05-2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 2006027958 A1</td>
<td>16-03-2006</td>
</tr>
</tbody>
</table>