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(54) Title: PRIMER-LESS TWO COMPONENT POLYURETHANE ADHESIVE

(57) Abstract: A process of applying an adhesive to an elastomer includes the application to the elastomer of a two part adhesive formulation. The adhesive having a Part A including at least a polyol, an adhesion promoter, a chain extender, a catalyst, a water scavenger; and a Part B comprising: polyurethane prepolymer, adhesion promoter and a plasticizer. The two part adhesive formulation is cured to form the adhesive. In contrast to the prior art, no priming or surface activation is required to obtain a high strength bond to the elastomer. The resulting article of an elastomer with the resultant adhesive is sufficiently strong to result in surface peel off of the elastomer. A kit is provided for the repair of an elastomer without resort to priming the elastomer.

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PRIMER-LESS TWO COMPONENT POLYURETHANE ADHESIVE

RELATED APPLICATIONS

[0001] This application is a non-provisional application that claims priority benefit of the US Provisional Application Serial Number 62/152,031 filed 24 April 2015 and US Non-provisional Application Serial Number 15/053,333 filed 25 February 2016; the content of which is hereby incorporated by reference.

FIELD OF THE INVENTION

[0002] The present inventions in general relates to polyurethane adhesive, and in particular to adhesives that are primer-less, solvent-free and well suited for rubber bonding, especially in the context of conveyors and belts.

BACKGROUND OF THE INVENTION

[0003] Thermoplastic rubbers are relatively inexpensive and widely employed in industries where abrasion resistance is highly needed. Black styrene butadiene rubber (SBR) sheets are used as conveyor belt, belt wipers also for sealing strips, general construction mounting pads, in gasket applications and also in a large number of applications such as (e.g. footwear, adhesives manufacturing, molded or extruded goods). However, due to the non-polar nature of this rubber and indeed elastomers as a class of materials, it is difficult to achieve bonding between elastomers. Vulcanized rubbers are especially difficult to bond due to low molecular weight ingredients therein that tend to migrate to the rubber surface limiting interaction with the adhesive.

[0004] Polyurethane (PU) adhesives and sealants have for years played a significant role in numerous industrial applications due to their advantageous properties such as high hardness, modulus and excellent mechanical properties. However, passage of the Clean Air Act Amendments in 1990 in the United States and similar legislation to restricted exposure to many chemicals including components associated with PU. However, the bonding of elastomeric substrates remains challenging with PU adhesives owing to the difficulty in bonding and the elongation requirements on any such bond. As a result, it is conventional to the art to use a surface treatment to effectively bond adhesives to elastomers. The treatment is typically accomplished by sulfuric acid etching or by the application of a primer such as those described in U.S. Patent Nos. 4,485,135 or 4,485,136. A well accepted primer for use on SBR (styrene-butadiene rubber) and the like is a 2% solution of 1,3-dichloro-5,5-dimethyl hydantoin in methyl chloride.

[0005] Surface treatments have proven to be suitable for the improvement of adhesion and wettability properties of non-polar synthetic rubbers. The adhesion of rubber has improved by changing the rubber composition or by modifying surfaces of the rubber surface by the use of a chemical agent (halogenation, cyclization, etc.) or using high energy irradiation such as bombarding the surface by electron beam or gamma irradiation to otherwise increase the number of surface bonding sites per unit area on the rubber surface. While these costly surface modifications are readily integrated into the production of new products, field repairs relying on such solutions or radiation are difficult to perform reliably and extend the duration of repairs. Additionally, many solvents are toxic to handle and may be prohibited from certain areas such as food or pharmaceutical production facilities. Another limitation of surface activation is the limited duration of such activity before the surface energy reverts to pre-treatment levels.

[0006] Commercially available adhesives for bonding rubber surfaces have met with limited acceptance owing to the need for a primer or a pre-wetting step in order to achieve adhesion, inclusion of organic solvents, low strength bonding compared to rubber to rubber vulcanization and as a result rapid adhesive failure. The reliance of existing adhesives on a primer to ensure a good adhesion poses significant problems with substrates that have distinctly uneven surfaces as the adhesive fails to fill spaces uniformly. Similarly, rigid substrates tend to have adhesive voids that weaken the strength of the adhesive bond.

[0007] Thus, there remains a need for an adhesive for bonding non-polar elastomeric surfaces that exhibits excellent adhesion without the necessity of resorting to primers or other surface treatments that change the surface energy. There further exists a need for such an adhesive to be amenable to application without resort to solvents, as solvents tend to pose health concerns and degrade bond properties.

SUMMARY OF THE INVENTION

[0008] A process of applying an adhesive to an elastomer includes the application to the elastomer of a two part adhesive formulation. The adhesive having a Part A including at least a polyol, an adhesion promoter, a chain extender, a catalyst and a water scavenger; and a Part B includes at least polyurethane prepolymer and a plasticizer. The two part adhesive formulation is cured to form the adhesive. In contrast to the prior art, no priming or surface activation is required to obtain a high strength bond to the elastomer. The resulting article of an elastomer with the resultant adhesive is sufficiently strong to result in surface peel off of the elastomer. A kit is provided for the repair of an elastomer without resort to priming the elastomer.

DETAILED DESCRIPTION OF THE INVENTION

[0009] The present invention has utility as a primer-less and in some embodiments, solvent-free, two-component polyurethane adhesive for bonding of elastomeric substrates. An exemplary elastomeric substrate is a conveyor belt. The resulting elastomer bonded to an elastomer with an inventive adhesive also represents a novel article. As the present invention does not require a primer and lacks solvents, field application to repair conveyor belts and other elastomeric materials are greatly facilitated. A method of forming such an adhesive and the use thereof to form a bond are also detailed herein. A patch kit is also provided that is particularly well suited by repairing elastomeric articles without resort to priming, or surface activation.

[0010] The present invention has many applications that illustratively include field repair of tears or worn spots in rubber-based articles. By way of example, repairing conveyor belt tears or worn spots greatly extends the longevity of such articles while limiting down time of the article and the need to inventory spare articles.

[0011] Elastomers joined by an inventive adhesive include natural and synthetic rubbers, as well as fiber or particle reinforced rubber articles, such as tires, hoses, conveyor belts, transmission belts, tensioning straps, snowmobile treads, and other vehicle treads. Elastomers that are bonded by an inventive adhesive illustratively including butyl rubber (copolymer of isoprene and isobutylene, IIR), chlorinated butyl rubber (CIIR), brominated butyl rubber (BIIR), chloroprene rubber (CR), isoprenes of both natural (NR) and synthetic (IR) origins, butadiene rubber (BR), Nitrile rubber (copolymer of butadiene and acrylonitrile, NBR), SBR (styrene-butadiene rubber), epichlorohydrin rubber (ECO), polyacrylic rubber (ACM), silicone rubber (SI), fluorosilicone rubber (FVMQ), chlorosulfonated polyethylene (CSM), and ethylene vinyl acetate (EVA). While the present invention is further illustrated in terms of bonding worn

out SBR conveyor belt parts, similar performance is observed in several of the aforementioned other elastomers including Styrene-butadiene-styrene thermoplastic rubbers (SBS) are commonly used in the footwear industry as sole materials, ultra high molecular weight rubbers, high heat resistant rubbers and the like.

[0012] As used herein, the terms "elastomer" and "rubber" are used interchangeably.

[0013] As used herein, the molecular weight is the weight-average molecular weight of the polymer which is determined by gel permeation chromatography (GPC, also called SEC). This method is known to one skilled in the art.

[0014] The present invention includes a two part adhesive formulation for use in bonding thermoplastic elastomeric articles. The inventive formulation is readily produced with a functional cure time of from 60 minutes to 6 hours, with still other inventive formulations have functional cure time of from 80 to 180 minutes. The inventive formulation has thermal stability over a wide temperature range of -20 degrees Celsius to 50 degrees Celsius.

[0015] As used herein, the functional cure time is defined as the time the adhesive takes to reach sufficient strength to be put into light operation.

[0016] The resulting adhesive exhibits superior mechanical and bonding properties as compared with commercially available and commonly used adhesive for bonding thermoplastic rubbers with adhesive strengths in some embodiments that induce elastomer surface failure instead of adhesive delamination. Additionally, an inventive adhesive formulation cures at a different levels of humidity from extremely dry to almost 90% humid climatic condition and including ambient temperatures with 50% relative humidity thereby facilitating field repairs of elastomers. Attributes of an inventive two part polyurethane adhesive include: a shelf life of a

nine to ten months at 25^0C, embodiments that are solvent-free, and adhesion to substrates besides elastomers that illustratively including fabric and wood.

[0017] As used herein, thermal stability is defined as the ability of the inventive adhesive to exhibit constancy in performance properties when stored at specified temperature for considerable period of time. Typically, this test is used to determine shelf life of formulated material. It has been found that the inventive adhesive separate parts are stable at 60 degrees Celsius for 5 days, which predicts an inventive adhesive formulation will remain stable for minimum 9-10 months under standard temperature and pressure (STP) conditions. This test is important in view of long term performance of sealant.

[0018] It is to be understood that in instances where a range of values are provided that the range is intended to encompass not only the end point values of the range but also intermediate values of the range as explicitly being included within the range and varying by the last significant figure of the range. By way of example, a recited range of from 1 to 4 is intended to include 1-2, 1-3, 2-4, 3-4, and 1-4.

[0019] An inventive formulation provided as a two-part formulation. The following inventive formulation are detailed as weight percentages in Table 1.

Table 1. Components for an inventive adhesive, where amounts are provided in weight percentage per part.

Part-A: Adhesive/Resin

Component:	**Percentage of Part A:**
Polyol	20-97.7%
Water scavenger	0.1-20%
Adhesion promoter	0.01-10%
Chain extender	0.001-10%
Catalyst	0.001-8%
Co-catalyst	0.001-2%
Antioxidants	0.2-3%
UV stabilizers	0.5-5%

Plasticizer	0.5-40%
Filler	1-40%
Thixotropic agent	0-20%
Cross-linker/toughening agents	0-20%
Processing additive/compatibilizer	0-5%
Dispersing agent	0-5%

Part B: Hardener/Activator

Component:	**Percentage of Part B:**
Polyurethane prepolymer	5-99%
Plasticizer	1 – 50%
Adhesion promoter	0.01-10%
Filler	0-40%
Thixotropic agent	0-20%
Blocking agent	0 – 10%
Fungicides/biocides	0-2%
Diluents/other additives	0-2%
Antioxidants	0-2%
Dispersing agent	0-3%

[0020] The Parts A and B are readily admixed to form curable adhesive. While the relative amounts of Parts A and B are varied to form an adhesive, generally the weight ratio of Parts is 1: 1: 1:1 to 1:1.75±10% to weight ratio of Parts being particularly easy to use for field repairs. The term "polyols" is intended to include polyols having 2 or more hydroxyl moieties per molecule; with 2 to 4 hydroxyl moieties per molecule being most common.

[0021] The polyols used in the present invention are those such as are normally used in polyurethane chemistry. Besides hydroxyl-containing polyacrylates, polyethers, polyesters, polycarbonates, oleochemical polyols and polybutadienes; in certain embodiments, the polyol is a polyoxyalkylene polyols, such as polyoxyethylene polyols, polyoxypropylene polyols and polyoxybutylene polyols, and combinations thereof.

[0022] The polyether types of polyols operative in forming a polyurethane according to the present invention also include polyether polyols of higher functionality than three {e.g.,

poly(oxypropylene adducts of pentaerythritols) and poly(oxypropylene adducts of sorbitol)}. The polyester types of polyols operative in forming a polyurethane according to the present invention include chain extended polyesters made from a glycol (e.g., ethylene and/or propylene glycol) and a saturated dicarboxylic acid (e.g., adipic acid). By way of non-limiting example, these include poly(ethylene adipate) glycol, poly(propylene adipate) glycol, poly(butylene adipate) glycol, poly(caprolactone) glycol, poly(ethylene adipate-phthalate) glycol, poly(neopentyl sebacate) glycol, and combinations thereof. Small amounts of trialcohols such as trimethylolproprane or trimethylolethane are included in some embodiments of the polyester preparation.

[0023] Polyester polyols with functionalities of three or more (e.g., glycerides of 12-hydroxystearic acid) are also useful to induce a degree of branching. Suitable polyester polyols include those obtainable by reacting such polyols as 1,4-butanediol, hydroquinone bis(2-hydroxyethyl) ether, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, 2-methyl-2-ethyl-1,3-propanediol, 2-ethyl-1,3-hexanediol, 1,5-pentanediol, thiodiglycol, 1,3-propanediol, 1,3-butanediol, 2,3-butanediol, neopentyl glycol, 1,2-dimethyl-1,2-cyclopentanediol, 1,2-cyclohexanediol, 1,2-dimethyl-1,2-cyclohexanediol, glycerol, trimethylol propane, trimethylol ethane, 1,2,4-butanetriol, 1,2,6-hexanetriol, pentaerythritol, dipentaerythritol, tripentaerythritol, anhydroaneaheptitol, mannitol, sorbitol, methylglucoside, and the like, with such dicarboxylic acids as adipic acid, succinic acid, glutaric acid, azelaic acid, sebacic acid, malonic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid, terephthalic acid, tetrachlorophthalic acid, and chlorendic acid; the acid anhydrides and acid halides of these acids may also be used. Also biodegradable polyesters such as polycaprolactone diols with low acid value may also be suitable for the said application

[0024] Oleochemical polyols are based on natural oils and fats, e.g. the reaction products of epoxidized fats with mono-, di- or poly-hydric alcohols or glycerine esters of long chain fatty acids that are at least partially substituted with hydroxyl groups, e.g. beef tallow, palm oil, peanut oil, rapeseed oil, cotton seed oil, soya oil, sunflower oil and linseed oil. Epoxidized triglycerides such as epoxidized soya oil and epoxidized linseed oil are commercially available and particularly well-suited to form adhesives according to the present invention.

~~[0025]~~ The molecular weight of the polyols used in the present invention is typically in the range of 250-30,000 atomic mass units.

[0026] The polyurethane prepolymer is prepared from at least one polyol and at least one polyisocyanate, where a polyisocyanate, as used herein is defined as molecule having at least two isocyanate moieties. It is appreciated that the level of functionality in a polyisocyanate comprise ranges from an average of 2 to 6 moieties per molecule, with an average of between 3-4, and between 2 -3 moieties per molecules being used in specific inventive embodiments. Exemplary polyurethane pre-polymer components are known to be based on the reaction products of isocyanates and polyhydric alcohols. Suitable polyisocyanates are aliphatic, cycloaliphatic or aromatic. Diisocyanates are well suited as polyisocyanates in the present invention to limit branching in the resultant polyurethane prepolymer. Polyols used to form the polyurethane prepolymers include any of the aforementioned polyols, or a combination thereof.

[0027] Polyisocyanates operative in the present invention illustratively include 4,4′-diphenylmethane diisocyanate (MDI), hydrogenated MDI (Hi2MDI), xylene diisocyanate (XDI), tetramethylxylene diisocyanate (TMXDI), 4,4′-diphenyidimethylmethane diisocyanate, di- and tetraalkylene diphenylmethane diisocyanate, phenyl isocyanate, 1,5-naphthylene diisocyanate, 4,4′-dibenzyl diisocyanate, 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, the isomers

of toluene diisocyanate (TDI), optionally in a mixture, 1-methyl-2,4-diisocyanato cyclohexane, 1,6-diisocyanato-2,2,4-trimethylhexane, 1,6-diisocyanato-2,4,4-trimethylhexane, 1-isocyanatomethyl-3-isocyanato-1,5,5-trimethylcyclohexane (IPDI), phosphorous-containing diisocyanates, tetramethoxybutane-1,4-diisocyanate, butane-1,4-diisocyanate, hexane-1,6-diisocyanate (HDI), dicyclohexylmethane diisocyanate, cyclohexane-1,4-diisocyanate, ethylene diisocyanate, phthalic acid bis-isocyanatoethyl ester, 1,12-diisocyanato dodecane, dimerized fatty acid diisocyanates, and combinations thereof.

[0028] Plasticizers operative herein illustratively include tris (2-ethylhexyl) trimellitate (TOTM), trimethyl pentanyl diisobutyrate, phthalate free C_1-C_{20} alkylsulphonic acid ester with phenol, benzoate ester, mesamoll, biobased plasticizers such as bio succinic acid or soy based plasticizers and combinations thereof.

[0029] A moisture scavenger operative herein illustratively includes methyldiphenylethoxysilane; vinyl trimethoxy silane (VTMO), vinyl triethoxy silane; molecular sieves, p-toulenesulfonyl isocyanate (PTSI), p-toluenesulfonyl isocyanate (TI), acid anhydride esters, such as diethyl malonate and dimethyl succinate; and combinations thereof.

[0030] A chain extender operative in the present invention illustratively includes a mixture of 2,4 and 2,6 isomers of diethyltoluenediamine (DETDA), piperazine, diethylenediamine (DEDA), monoethanolamine (MEA), methylenebis(N,N-dibutyldianiline), isophoronediamine (IPDA), a mixture of 3,5-dimethylthio-2,4-toluenediamine and -2,6-toluenediamine isomers, dodecyl mercaptan, tertiary dodecyl mercaptan, 1,3 butanediol, 1,4 butane diol, propane 1 2 diol 1,6 hexane diol or a combination thereof.

[0031] An adhesion promoter is also present in certain inventive formulations to achieve improved surface bonding of inventive adhesive compared to formulations lacking the same by

modifying the hydrophobicity of the substrate surface. An adhesion promoter operative in the present invention illustratively includes 3-aminopropyl triethoxy silane (AMEO), 3-aminopropyl trimethoxy silane, 3-glycidoxypropyltrimethoxysilane, N-(beta-aminoethyl) gamma aminopropyltrimethoxysilane, Bis(3-triethoxysilylpropyl)tetrasulfide, gamma mercapro propyl trimethoxy silane, N-beta-(aminoethyl)-gamma-aminopropyl-methyldimethoxysilane, Bis(pentane-2,4-dionato-O,O')bis(alkanolato)titanium, Tetrabutyl Titanate , diamino-functional silane (e.g. DAMO), a bifunctional oroganosilane having a primary amine and a hydrolyzable methoxysilyl groups(e.g. AMMO) and combinations thereof.

[0032] Antioxidant operative herein illustratively include ditri-decyl-thiodipropionate (DTDTDP), dilauryl thiodipropionate (DLTDP), distearyl thiodipropionate (DSTDP) and 3,5-Bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoic acid octadecyl ester (1076), Tris(2,4-di-*tert*-butylphenyl) phosphite, and combinations thereof.

A filler operative herein illustratively includes carbon black, talc, calcium carbonate, fumed silica, colloidal silica, calcite, limestone, mica, talc, asbestos fibers or powder, diatomaceous earth, metal particulate, barium sulfate, alumina, slate flour, calcium silicate, magnesium carbonate, magnesium silicate, TiO_2 (rutile), materials like corundum (Al_2O_3) or zirconia (ZrO_2) and combinations thereof.

[0033] UV stabilizers operative herein illustratively includes benzotriazoles, benzophenones, triazines, hindered amine light stabilizers, 2-(benzotriazol-2-yl)-4-(2,4,4-trimethylpentan-2-yl)phenol, 3,5-di-t-butyl-4-hydroxybenzoic acid, hexadecyl ester and combinations thereof.

[0034] A catalyst operative herein illustratively includes bismuth carboxylates such as acetate, oleate, octoate or neodecanoate; bismuth nitrate; bismuth halides such as bromide,

chloride or iodide; bismuth sulfide; basic bismuth carboxylates such as bismuthyl neodecanoate, bismuth subgallate, or bismuth subsalicylate; and combinations thereof.

[0035] An inventive polyurethane adhesive formulation includes in specific embodiments an organometallic catalyst that is customary in polyurethane chemistry, as a co-catalyst. A co-catalyst illustratively includes organo-tin compounds, such as tin(II) octoate, dibutyltin dilaurate or dibutyltin diacetate; tertiary amines such as DABCO (=1,4-diazabicyclo[2.2.2]octane) or 2,2′-dimorpholinodiethyl ether; or combinations thereof.

[0036] A thixotropic agent operative herein illustratively includes hydrophobic silica, carbon black, calcium carbonate, or combinations thereof. It is appreciated that different types of thixotropic agent can be employed as reinforcing agent/rheology modifiers.

[0037] A cross-linkers/toughening agent operative herein illustratively includes copolymers of styrene, copolymers of styrene and butadiene, carboxylated polychloroprenes, carboxylated polyacrylonitrile-butadiene copolymers, copolymers of ethylene and vinyl acetate, copolymers of styrene and olefinically unsaturated hydrocarbons, polybutylene, acrylate-based elastomers, acrylate/methacrylate based oligomers and mixtures thereof.

[0038] Silane includes mercapto silane, tetrasulfide silanes, silquest A-15, A-35, epoxy silane, isocyanate silane, vinyl silane, thiocyanato silane, phenyl silane and the like.

[0039] Additions of various other constituents known in the art may be made to the basic composition. For example, blocking agent, Inhibitors, resin, chelating agent, corrosion inhibitor, pigments, spacers, fragrance, fire retardants, accelerator, fungicides/biocides and the like.

[0040] Diluents operative herein illustratively include dimethylcarbonate, propylene carbonate, tert butyl acetate, ethyl acetate, propyl acetate, methyl ethyl ketone, dichloromethane, trochloro ethylene and the like.

[0041] A block agent operative herein illustratively includes phenols, oximes, alcohols, caprolactam, and diethyl malonate. The choice of the blocking agent depends in part on its volatility and processing temperature. Some of the advantages of the blocked isocyanate in coated abrasive belt repair applications are long pot life and insensitivity to moisture levels of the ambient air.

[0042] The inventive compositions optionally include other additives conventional to the sealant art including but not limited to non-reactive resins, chelating agents, colorants (e.g. pigments, dyes), flame retardants, spacers, cure inhibitors, accelerators and mixtures thereof.

[0043] Based on the above description, it would be appreciated that an inventive adhesive formulation is readily formed free of VOCs and solvents. Additionally, the rheological properties of the formulation are readily adjusted for a range of viscosities to serve a desired application. Further, with inclusion of adhesion promoters, an inventive adhesive is readily applied without resort to prior application of a primer to the substrate, sanding, or otherwise roughening the substrate surface.

[0044] Regardless of the form of an inventive formulation, upon induction of pot life for the formulation, the formulation is present in simultaneous contact with two or more substrates for an amount of time sufficient to achieve a bond between the substrates. Two such substrates can be brought together to form various jointed structures such as a lap joint, butt joint, corner joint, edge joint, and T-joint. In still other embodiments, an inventive formulation is applied to a single substrate and allowed to cure to form a coating that affords substrate protection or is operative as a primer for subsequent material applications. Substrates are fixtured or otherwise held in relative desired alignment for a time period of from 5 minutes to 120 minutes. The joined substrates are then amenable to being removed from the fixture while an inventive formulation

continues to cure to achieve terminal strength. Typical thicknesses of an inventive adhesive formulation are between substrates ranges from 0.001-4 mm. Alternatively, the inventive adhesive is applied to form a bulk plug.

[0045] A kit is provided including a Part A and a Part B of an inventive adhesive formulation along with instructions for the mixing the Parts together and applying to a first substrate. Conditions for forming a plug, patch, or joinder to a second substrate are also provided. Instructions also include in some embodiments the removal of debris and particulate from the substrate prior to application of the mixed Parts A and B thereto. Instructions in some instances detail application thickness and fixturing specific to elastomeric substrates.

[0046] The present invention is further described with respect to the following non-limiting examples. These examples are intended to illustrate specific formulations according to the present invention and should not be construed as a limitation as to the scope of the present invention.

Example 1. Process for preparing Polyurethane Adhesive Part A.

[0047] **Step 1** Polyether polyols, processing additive/compatibilzer, moisture scavenger, antioxidants, UV stabilizers, dispersing agent and plasticizer are added together to the mixing kettle equipped with mechanical stirrer and nitrogen gas blanketing. All the ingredients were blended by swirling the mixture for approx. 10 - 15 minutes at room temperature of 20° Celsius.

[0048] **Step 2**-Fillers, short chain diol as a chain extender , and cross-linkers are added in the above mix and were stirred for 30 minutes at 500 -1500 rpm.

[0049] **Step 3**-After 15 minutes, desired amount of thixotropic is added slowly to the mixture and stirred for another 180 minutes to form a homogeneous mass. Further agitator speed is raised to 800 rpm to ensure uniform mixing of all the ingredients.

[0050] **Steps 4-**Stirred the mass for 15 minutes at 1000 rpm till mass becomes smooth paste. Reduce the speed to 200 rpm and adhesion promoters (silane) and catalyst & co-catalyst were added very slowly to the reaction mass. Evacuate the reactor for 20 minutes under vacuum 600 mm Hg to remove entrapped bubbles and packed in nitrogen atmosphere.

[0051] Recorded lab batch cycle time for Adhesive is approximately 4 - 4.5 hours.

Example 2. Process for preparing Hardener/Activator-Part B.

[0052] **Step 1**–Mid Functional, mid-NCO polyurethane prepolymer, plasticizer, fillers and thixotropic agent are added together to the reaction kettle equipped with mechanical stirrer and nitrogen gas blanketing. All the ingredients are blended by swirling the mixture for approx. 10 - 15 minutes at room temp.

[0053] **Step 2-**Adhesion promoter, blocking agent and fungicide/biocides, dispersing agent if need be are added in the above mix and were stirred for 15 minutes at 200 rpm.

[0054] **Step 3-**After 15 minutes, desired amount of diluent if need be is added slowly to the reaction mixture and is stirred for another 15 minutes until a homogeneous mass forms.

[0055] **Steps 5-** Stopped the agitator. Evacuate the reactor for 20 minutes under vacuum 600 mm Hg to remove entrapped bubbles and packed in nitrogen atmosphere.

[0056] Recorded lab batch cycle time for Adhesive is approximately 1-1.5 hours.

Example 3. Experimental data -Development of peel adhesion strength

[0057] Peel strength is tested on reinforced high strength styrene butadiene rubber substrates. A rapid strength development for an inventive adhesive formulation by combining Examples 1 and 2 Parts A and B is noted in Table 2.

Table 2. Peel strength as a function of time for adhesive formulation

Time	**Peel strength in pounds per linear inch (pli)/(N/mm)**
2 Hr.	30/5.25
3 Hrs.	52/9.1
5 Hrs.	83/14.5
24 Hrs.	190/33.3
7 Days	266/46.6

Example 4. Inventive Adhesive properties relative to reference materials

[0058] Properties of an inventive adhesive are provided in Table 3 and compared to 3 reference comparative compositions on the same substrates and applied at a like thickness of 1 mm.

Table 3. Properties of inventive adhesive compared to conventional prior art adhesives.

Description	Ref 1	Ref 2	Ref 3	Inventive formulation
Components	4	4	4	2
	Resin (Part A) Hardener (Part B) Primer Cleaning agent	Resin(Part A) Hardener (Part B) Primer Cleaning agent	Resin (Part A) Hardener (Part B) Primer Cleaning agent	Resin (Part A) Hardener (Part B)
Pot life in min / Working time – Quantitatively	4.30 mins	10 mins	30 mins	10-15 mins
Functional cure time	2 hrs	5-6 hrs	6-8 hrs	1.5 hrs
Hardness shore A	90	78	60	90

Peel strength (pli) 2 hrs	8	Not cured	Not cured	30
Peel strength (pli) 3 hrs	9.7	Not cured	Not cured	52
Peel strength (pli) 5 hrs	12 AF*	16 CF**	Not cured	83
Peel strength (pli) 24 hrs	70 AF	45 AF	8	190 surface pull off rubber
Peel strength (pli) 7 days	137 Surface pull off	85 Surface pull off	21	266 surface pull off rubber

* AF – adhesive failure
**CF – component failure

[0059] Patent documents and publications mentioned in the specification are indicative of the levels of those skilled in the art to which the invention pertains. These documents and publications are incorporated herein by reference to the same extent as if each individual document or publication was specifically and individually incorporated herein by reference.

CLAIMS

1. A process of applying an adhesive to an elastomer comprising:

applying to the elastomer a two part adhesive formulation of a Part A comprising: a polyol, an adhesion promoter, a chain extender, a catalyst, water scavenger; and a Part B comprising: polyurethane prepolymer, adhesion promoter and a plasticizer; and

curing the two part adhesive formulation to form the adhesive.

2. The process of claim 1 wherein said polyol is 20-98.8% of said Part A.

3. The process of claim 1 wherein said polyurethane prepolymer is 5-99% of said Part B.

4. The process of claim 3 wherein said polyurethane prepolymer has a weight-average molecular weight 250-30,000 atomic mass units.

5. The process of claim 1 wherein said two part adhesive formulation is premixed prior to the applying.

6. The process of claim 1 wherein the applying is not preceded by priming the elastomer.

7. The process of claim 1 wherein the applying is not preceded by exposing the elastomer to surface activation.

8. The process of claim 1 further comprising bringing a substrate into simultaneous contact with said two part adhesive prior to the curing to form a bond between the elastomer and the substrate via the adhesive.

9. The process of claim 1 wherein the elastomer is styrene butadiene rubber.

10. The process of claim 1 wherein the elastomer and the substrate are each independently one of: ethylene-propylene terpolymer from the butyl rubber (copolymer of isoprene and isobutylene, IIR), chlorinated butyl rubber (CIIR), brominated butyl rubber (BIIR), chloroprene rubber (CR), isoprenes of both natural (NR) and synthetic (IR) origins, butadiene rubber (BR), Nitrile rubber (copolymer of butadiene and acrylonitrile, NBR), SBR (styrene-butadiene rubber) epichlorohydrin rubber (ECO), polyacrylic rubber (ACM), silicone rubber (SI), fluorosilicone rubber (FVMQ), chlorosulfonated polyethylene (CSM), or ethylene vinyl acetate (EVA).

11. The process of claim 1 wherein the elastomer is a conveyor belt.

12. An article comprising:

an elastomer;

a layer of cured polyurethane adhesive in direct contact with the elastomer produced by condensation of a polyol and a polyurethane prepolymer in the presence of an adhesion promoter and a moisture scavenger.

13. The article of claim 12 wherein said polyol is a polyalkylene polyol.

14. The article of claim 12 wherein said polyol is a polyacrylate, a polyether, polyesters, a polycarbonate, an oleochemical polyol or a polybutadiene.

15. The article of claim 12 further comprising a chain extender, a catalyst, a compatibilizer, a dispersing agent, a filler, and a thixotropic agent.

16. The article of claim 12 further comprising a simultaneous contact between said adhesive and a substrate.

17. The article of claim 16 wherein the substrate is a portion of the elastomer to form a belt.

18. The article of claim 16 wherein the substrate is a patch.

19. The article of claim 12 wherein the elastomer is not surface activated or primed.

20. A kit for repairing a defect in an elastomer comprising:

a two part adhesive formulation of a Part A comprising: polyol, an adhesion promoter, a chain extender, a catalyst, a water scavenger; and a Part B comprising: polyurethane prepolymer, adhesion promoter and a plasticizer; and

instructions for applying said two part adhesive to repair the defect in the elastomer without resort to priming the elastomer.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/029071

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/10 C09J175/04
ADD.

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)
C08G 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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/058420 A1 (TECHNOLOGIES MICHELIN SOC D [FR]; MICHELIN RECH TECH [CH]; LAUBRY PHIL) 7 May 2009 (2009-05-07) paragraphs [0001], [0004], [0015], [0021], [0035], [0045], [0050], [0053] - [0054], [0060], [0065] - [0066], [0069] paragraphs [0073] - [0074] examples 1, 5	1-20
A	US 5 175 228 A (WANG CHIA L [US] ET AL) 29 December 1992 (1992-12-29) column 1, lines 40-60 column 10, line 56 - column 11, line 15	1-20

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* 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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 August 2016	16/08/2016

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/029071

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0 449 616 A2 (MINNESOTA MINING & MFG [US]) 2 October 1991 (1991-10-02) page 2, lines 1-5 page 5, lines 45-53 -----	1-20

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INTERNATIONAL SEARCH REPORT

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International application No
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