

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization

International Bureau



(10) International Publication Number

WO 2015/017531 A1

(43) International Publication Date

5 February 2015 (05.02.2015)

(51) International Patent Classification:

C08G 18/70 (2006.01) C08G 18/42 (2006.01)

C08G 18/80 (2006.01) C08K 9/04 (2006.01)

C08G 18/02 (2006.01) C09J 175/06 (2006.01)

(21) International Application Number:

PCT/US2014/048876

(22) International Filing Date:

30 July 2014 (30.07.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/860,006 30 July 2013 (30.07.2013) US

(71) Applicant: **H.B. FULLER COMPANY** [US/US]; 1200 Willow Lake Blvd., P.O. Box 64683, St. Paul, MN 55164-0683 (US).

(72) Inventors: **MAI, Felix, D.**; Marie-juchacz-allee 91, 67067 Ludwigshafen, De (DE). **CARLSON, Brian, W.**; 1747 Bowsens Lane, Woodbury, MN 55125 (US).

(74) Agent: **HALLORAN, Kristi**; H.B. Fuller Company, 1200 Willow Lake Blvd., P.O. Box 64683, St. Paul, MN 55164-0683 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))



WO 2015/017531 A1

(54) Title: POLYURETHANE ADHESIVE FILM

(57) Abstract: A thin self-supporting adhesive film is claimed that includes a first polyurethane and a solid surface-deactivated iso-cyanate.

POLYURETHANE ADHESIVE FILM

5 CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application No. 61/860,006, filed July 30, 2013, and incorporated herein.

BACKGROUND

10 Adhesives are often used to bond substrates together so as to maintain the two substrates in a fixed relation to each other.

15 Adhesives based on polyurethane dispersions (PUDs) can be formulated with solid surface-deactivated isocyanates. Such compositions can be preapplied to a substrate and dried such that the isocyanate is not yet activated (i.e. the heat is kept at less than that needed for activation and curing). This gives the user the option of activating the isocyanate with heat at a later date to form a bond and initiate the curing reaction between the polyurethane and isocyanate.

20 In a production environment, it would be convenient if the adhesive could be supplied as a thin self supporting adhesive film to the end user. The end user would then not have to contend with the equipment and the process of applying and drying the adhesive.

SUMMARY

25 In one aspect, the invention features a self-supporting adhesive film including a solid surface-deactivated isocyanate and greater than 70 % by weight of a first polyurethane, said first polyurethane having a weight average Molecular Weight (Mw) of no greater than about 90,000 and an enthalpy of fusion of at least about 25 J/g.

30 In one embodiment, the self-supporting adhesive film is obtained from an aqueous composition. In another embodiment, the solid surface-deactivated isocyanate is derived from toluene diisocyanate. In still another embodiment, the film of said first polyurethane has an enthalpy of fusion of at least about 35 J/g.

In one embodiment, the first polyurethane is derived from a polyester derived from a polyol selected from the group consisting of 1, 4-butane diol and 1, 6-hexane diol. In a second embodiment, the first polyurethane is derived from a polyester derived from adipic acid and a mixture of 1, 6-hexane diol and neopentyl glycol; and an aliphatic isocyanate.

5

In a different embodiment, the film exhibits a bond strength of at least about 20 N/2.5 cm when tested according to the Bond Test Method at a Bond Line Temperature of about 64 °C. In another embodiment, the film exhibits a bond strength of at least about 30 N/2.5 cm when tested according to the Bond Test Method at a Bond Line Temperature 10 of about 82 °C.

In some embodiments, the self-supporting adhesive film has a thickness of from about 1 mil to about 8 mils. In other embodiments, the self-supporting adhesive film further includes a release liner.

In other embodiments, the self-supporting adhesive film additionally includes a 15 second polymer. In one embodiment, the sum of the solid surface-deactivated isocyanate, the first polyurethane and the second polymer amounts to at least about 95 % by weight of the self-supporting adhesive film.

In another aspect, the invention includes a composite structure including a first 20 layer and a second layer, at least one of the first layer and said second layer including the self-supporting adhesive film, where the self-supporting adhesive film includes a solid surface-deactivated isocyanate and greater than 70 % by weight of a first polyurethane, said first polyurethane having a weight average Molecular Weight (Mw) of no greater than about 90,000 and an enthalpy of fusion of at least about 25 J/g.

In an embodiment, the first layer comprises the self-supporting adhesive film and 25 the second layer is flexible and is selected from the group consisting of fabric, foil, and paper.

In another aspect, the invention features a composite structure including the self-supporting adhesive film, a rigid layer, and a flexible layer, the rigid layer being bonded to the flexible layer through the self-supporting adhesive film. In some embodiments, the 30 rigid layer comprises at least one of metal, metal composite, plastic, plastic composite, wood, and wood-composite. In other embodiments, the flexible layer comprises at least

one of fabric, foil and paper. In still other embodiments, the rigid layer is nylon and the soft fabric layer is microfiber.

In another aspect, the invention features a method of making a composite including contacting a flexible layer with a first major surface of the self-supporting adhesive film, 5 applying heat to the film before or after the film is applied to the flexible substrate; contacting a rigid layer with a second major surface of the self-supporting adhesive film such that the second major surface is in direct contact with the rigid layer to form a composite; and applying heat and pressure to the composite.

In a different aspect, the self-supporting adhesive film is obtained from an aqueous 10 composition, said aqueous composition including a solid surface-deactivated isocyanate and a first polyurethane dispersion, the dried film of which has an enthalpy of fusion of at least about 25 J/g, the self-supporting adhesive film having a thickness of from about 1 mil to about 8 mils. In one embodiment, the isocyanate is derived from an aromatic isocyanate. In a different embodiment, the self-supporting adhesive film has a thickness 15 of from about 2 mils to about 6 mils. In another embodiment, a composite structure is obtained including the self-supporting adhesive film, a first rigid layer and a second rigid layer, the rigid layers being bonded to each other through the self-supporting adhesive film. In still another embodiment, the composite structure includes the self-supporting adhesive film, a rigid layer, and a flexible layer, the rigid layer being bonded to the 20 flexible layer through the self-supporting adhesive film. The self-supporting adhesive film alternately includes a second polymer.

GLOSSARY

A self supporting adhesive film is an adhesive film absent any substrate.

25 A substrate is the end material the adhesive is used to bond or coat. A release liner is not considered a substrate.

DETAILED DESCRIPTION

The inventors have discovered an adhesive composition that can be supplied to the 30 user as a self-supporting adhesive film with or without a release liner.

The film includes an isocyanate reactive polymer and a solid surface-deactivated isocyanate. The isocyanate reactive polymer is a polyurethane. For purposes of this application, the word polyurethane includes polyurethanes, polyureas and polyurethane ureas.

5 Applicants have discovered that a thin layer of the self-supporting adhesive film is able to form a strong initial bond with a low bond line temperature. This minimizes the time needed to make an individual part and increases the speed of manufacture on a production line.

10 The self-supporting adhesive film exhibits a bond strength of at least about 20 N/2.5 cm, at least about 30 N/2.5 cms, at least about 50 N/2.5 cms, or even from about 15 N/2.5 cm to about 90 N/2.5cm, when tested according to the Bond Test Method.

AQUEOUS COMPOSITION

15 The self-supporting adhesive film can be derived from an aqueous composition that includes a first polymer comprising a first polyurethane dispersion and a solid surface-deactivated isocyanate crosslinking agent. The first polyurethane dispersion and the solid surface-deactivated isocyanate crosslinking agent can be supplied separately as a two part system, and then blended prior to formation of the film or alternately can be supplied as a one part system where the two are already blended.

20

First Polyurethane Dispersion

Useful first polyurethane dispersions include anionic polyurethane dispersions. The first polyurethane has a degree of crystallinity and a melting peak sufficiently low to enable easy activation. One useful indication of crystallinity is enthalpy of fusion -- the 25 higher the enthalpy of fusion of a compound, the higher its crystallinity. One useful method of determining the enthalpy of fusion (ΔH) and melting peak of polyurethane utilizes Differential Scanning Calorimetry (DSC) conducted at a heating rate of 10°C/minute using a PYRIS 1 DSC.

The dried first polyurethane preferably has an enthalpy of fusion of at least about 30 15 Joules per gram (J/g), at least about 25 J/g, at least about 35 J/g, or even from about 15

J/g to about 70 J/g. The dried first polyurethane preferably has a melting peak of no greater than about 65 °C, no greater than about 60 °C, or even no greater than about 55 °C.

The first polyurethane has a relatively low weight average molecular weight (Mw). Preferably, the first polyurethane has a molecular weight of no greater than about 90,000, 5 no greater than about 85,000, or even no greater than about 80,000.

The first polyurethane is derived from at least one diol, a polyol, or a combination thereof, and at least one di- and or polyisocyanate.

Examples of useful polyols include polyester polyols derived in part from an aliphatic diol, useful examples of which include ethylene glycol, 1, 3-propanediol, 1, 4-10 butanediol, 1, 5-pentanediol, 1, 6-hexanediol and neopentyl glycol. In an embodiment, the first polyurethane is derived in part from a polyester polyol derived in part from 1, 4-butanediol or 1, 6-hexanediol.

Other useful polyester polyols are derived from linear dicarboxylic acids and/or derivatives thereof (e.g., anhydrides, esters and acid chlorides), and aliphatic, cyclo 15 aliphatic, linear, and branched polyols, and combinations thereof. In an embodiment, the first polyurethane is derived from a polyester polyol derived from a dicarboxylic acid selected from the group comprising adipic acid, succinic acid, sebacic acid, and dodecanedioic diacid.

In another embodiment, the first polyurethane is derived from a polyester polyol 20 based on adipic acid and 1, 4-butanediol or a polyester polyol based on adipic acid and 1, 6-hexanediol or a polyester polyol based on adipic acid and a mixture of 1, 6-hexanediol and neopentyl glycol.

Useful di- and poly- isocyanates include, e.g., any organic compound that has at 25 least two free isocyanate groups in each molecule. Preferred diisocyanates include, e.g., aliphatic diisocyanates (e.g. hexamethylene diisocyanate (HDI), 1-isocyano-3, 3, 5-trimethyl-5-isocyanatomethyl-cyclohexane (IPDI)), and combinations thereof.

The first polyurethane can be present as one polyurethane or as a blend of two or more different polyurethanes.

The dried self-supporting adhesive film includes at least about 30 % by weight, at 30 least about 50 % by weight, at least about 70 % by weight, at least about 80 % by weight,

from about 30 % by weight to about 97 % by weight first polyurethane, or even from about 50 % by weight to about 95% by weight first polyurethane.

Useful commercially available first polyurethane dispersions include, e.g., DISPERCOLL U XP 2682, DISPERCOLL U 56 and DISPERCOLL U 2815 XP all of which are available from Bayer Material Science AG in Germany, and WD4047, which is available from HB Fuller Company (St. Paul, MN).

Solid surface-deactivated isocyanate crosslinking agent

The aqueous composition includes a solid surface-deactivated isocyanate crosslinking agent. Useful solid surface-deactivated isocyanate crosslinking agents are derived from a polyisocyanate and a deactivating agent. A variety of polyisocyanates are suitable including, e.g., aliphatic, cycloaliphatic, heterocyclic, and aromatic polyisocyanates (e.g. methylene diphenyl diisocyanate (MDI), toluene diisocyanate (TDI), and isophorone diisocyanate (IPDI)), and those polyisocyanates disclosed in, e.g., US 6,348,548 B1, which is incorporated herein by reference. Surface deactivated isocyanates derived from aromatic isocyanates are preferred as they react faster than aliphatic isocyanates enabling the formation of a strong initial bond at a low bond line temperature.

A variety of deactivating agents are suitable including, e.g., primary and secondary aliphatic amines, diamines, polyamines, hydrazine derivatives, amidines, guanidines and combinations thereof. Useful examples of deactivating agents include ethylene diamine, 1,3-propylene-diamine, diethylene triamine, triethylene tetramine, 2,5-dimethyl-piperazine, 3,3'-dimethyl-4,4'-diamino -dicylohexyl methane, methyl nonane-diamine, isophorone diamine, 4,4'-diaminodicyclohexyl methane, diamino and triamino polypropylene ether, polyamido amine, and combinations thereof, as well as those deactivating agents disclosed in US 6,348,548 B1.

Useful solid surface-deactivated isocyanate crosslinking agents can be prepared in a variety of ways including those processes described in US 6,348,548 B1.

The solid surface-deactivated isocyanate crosslinking agent can be in a variety of forms including, e.g., aqueous suspensions and micronized particles.

Useful commercially available solid surface-deactivated isocyanates include, e.g., DISPERCOLL BL XP 2514 aqueous suspension of latent-reactive isocyanate containing

approximately 40% TDI dimer. Useful solid particle isocyanates that are capable of being deactivated include DISPERCOLL LP BUEJ 471, a 100% solids micronized IPDI-isocyanurate available from Bayer Material Science AG in Germany and ADDOLINK TT and ADDOLINK ST available from Rhein Chemie Rheinau GmbH in Mannheim,

5 Germany.

The solid surface-deactivated isocyanate can be blended with the first polyurethane dispersion to form a stable aqueous composition.

Additional Components

10 The aqueous composition optionally includes a second polymer. Some examples of possible second polymers include e.g. a second polyurethane (e.g. DISPERCOLL U 53 commercially available from Bayer Material Science AG in Germany), VAE (vinyl acetate ethylene), PVA (poly vinyl alcohol), acrylics, butadiene acrylonitrile and styrene butadiene rubber (SBR).

15 The aqueous composition optionally includes a variety of other additives including, e.g., catalysts (e.g. amine based), preservatives, pH modifiers (e.g. aqueous ammonia), adhesion promoters (e.g. tackifiers, silane containing compounds), color agents, surfactants, defoaming agents, fungicides, bactericides, thickening agents, blocking agents and stabilizers (e.g. amines), fillers (e.g. carbonates, talc, starch), materials to help the

20 adhesive film form a barrier (e.g. nano clay), insulative materials (e.g. mineral fillers, glass microbubbles), conductive materials (e.g. various metals (e.g. silver)) and combinations thereof.

A useful stabilizer is JEFFAMINE T-403 POLYETHERAMINE commercially available from Huntsman Corporation (The Woodlands, Texas). Useful thickeners for the

25 aqueous dispersion include BORCHI®GEL A LA available from OMG Borchers GmbH (Langenfeld, Germany) and STEROCOLL HT commercially available from BASF Chemical Company (Ludwigshafen, Germany). A useful preservative is ACTICIDE MBS commercially available from Thor GmbH (Speyer, Germany).

SELF-SUPPORTING ADHESIVE FILM

The aqueous composition is dried into a self-supporting adhesive film. The film can be formed from the aqueous composition using a variety of methods including, e.g., spraying (e.g. spiral, splatter, etc.) and by various coating techniques (e.g. roll, slot, gravure, 5 pattern, etc.)

In one method, the aqueous composition is roll coated at the desired coat weight onto a release liner. The aqueous composition is then passed through a drying tunnel. The drying temperature in the tunnel can be varied, but preferably is maintained at a temperature that is low enough to prevent the solid surface-deactivated isocyanate from activating. The 10 temperature of the adhesive film during drying preferably is maintained at a temperature of less than about 70 °C, less than about 60 °C, or even less than about 55 °C. After the drying tunnel, the adhesive coated on the release liner optionally can be chilled e.g. passed over a chilled roller. It can then be wound upon itself as in, e.g., a roll, and stored for a later date.

The self-supporting adhesive film can include a solid surface-deactivated 15 isocyanate and greater than 70 % by weight of a first polyurethane, said first polyurethane having a weight average Molecular Weight (Mw) of no greater than about 90,000 and an enthalpy of fusion of at least about 25 J/g. Alternately, the self-supporting adhesive film can include a solid surface-deactivated isocyanate and greater than 70 % by weight of a first polyurethane, said first polyurethane having a weight average Molecular Weight 20 (Mw) of no greater than about 90,000 and an enthalpy of fusion of at least about 25 J/g and a second polymer. The sum of the solid surface-deactivated isocyanate, the first polyurethane and the second polymer can amount to at least about 90% by weight, at least about 95 % by weight, or even at least about 98% of the self-supporting adhesive film.

The dried film has a thickness of less than about 20 mils, less than about 15 mils, 25 less than about 10 mils, less than about 8 mils, less than about 6 mils, from about 1 mil to about 8 mils, or even from about 2 mils to about 6 mils. The thickness of the film can be obtained in any number of ways e.g. by direct coating, by multiple passes through a coater, or by laminating two different thickness films together.

The film can form a strong bond between two different substrates. The substrates 30 can be in layers. The strong bond can be obtained with a bond line temperature (i.e. the

temperature of the bond as it is formed) of no greater than about 90 °C, no greater than about 80 °C, no greater than about 70 °C or even from about 50 °C to about 90 °C.

COMPOSITE STRUCTURE

5 The self-supporting adhesive film can be used to form a composite structure. The composite structure includes the adhesive film and at least one additional layer (e.g., substrate). The layer can be rigid or flexible. The adhesive film can be placed over the top of, so as to cover at least one surface of the layer.

10 Examples of useful rigid layers include tiles, ceramics, metals (e.g. aluminum, stainless steel), plastics (e.g. polyethylene, polypropylene, polyamides (e.g. nylon), polyurethanes, polycarbonate, acrylonitrile-butadiene-styrene (ABS), ABS/polycarbonate blends, polyether ether ketone (PEEK), etc.), plastic composites (e.g. fiber reinforced plastics), glass, cardboard, wood and wood-containing products. The rigid layer can include one layer or it can be multilayered (i.e. including at least two layers).

15 The rigid layer can be pre-treated to improve adhesion of the self-supporting adhesive film. It can be pre-treated in any number of ways, including (e.g. corona, plasma, flame, by various chemical primers, and combinations thereof).

20 Examples of useful flexible layers include various textiles (e.g. fabrics (e.g. microfiber based polyethylene, cotton, canvas and nonwovens), artificial leathers and furs, foils (e.g. decorated foils), papers, films (e.g. plastic films (e.g. polyester, polyimide (i.e. Kapton), polypropylene and polyethylene)) and combinations thereof.

25 The self-supporting adhesive film can alternately be used to form a composite structure including a rigid layer and a flexible layer, where the self-supporting adhesive film layer is positioned between the rigid layer and the soft layer so as to adhere the two layers together.

30 The self-supporting adhesive film can further be used to form a composite structure selected from a group consisting of two rigid layers and two flexible layers. The self-supporting adhesive film layer is positioned between the two layers so as to adhere the two layers together. The two rigid layers/two flexible layers composite can include the same material or they may include different materials.

The composite structure can be formed by a number of different methods.

In one method, a flexible layer is contacted with a first major surface of the self-supporting film and heat is applied to the film before or after the film is applied to the flexible substrate, or a combination thereof. A rigid layer is then contacted with a second major surface of the self-supporting film such that the second major surface is in direct contact with the rigid layer to form a composite. The composite can be heated to a temperature of at least about 70 °C to activate the isocyanate and begin the curing process. Alternately, the composite can be heated to a temperature just hot enough to form a bond. Pressure can be used to help form the bond (e.g. membrane or bladder press). A limited amount of time is needed to form the bond.

10

USES

The self-supporting adhesive film is useful in the manufacture of a variety of items including but not limited to, e.g., shoes, automobile parts, truck bed covers, textile laminations (e.g. outdoor apparel, lingerie), various assembled goods (e.g panels, laminations, filters, flooring, etc.).

EXAMPLES

Test Procedures

Test procedures used in the examples and throughout the specification, unless stated otherwise, include the following.

Molecular Weight

The GPC molecular weight distribution curve of each dried polyurethane sample was obtained using a Waters 2695 Separations Module connected to a Waters 2414 RI detector, running 0.05M LiBr/DMF mobile phase through two Agilent Resipore GPC columns. The molecular weight data was calculated versus polymethyl methacrylate standards.

Melting Peak and Enthalpy of Fusion Test Method

The melting peak and enthalpy of fusion (ΔH) of the dried polyurethane dispersions was determined using Differential Scanning Calorimetry (DSC) at a heating rate of 10°C/minute using a PYRIS 1 DSC.

5 Bond Test Method

Dry films are prepared from waterborne compositions in Table 2. The films are drawn down using a 10 cm wide draw down bar with a 250 μm gap. The films are dried for 20 minutes at a temperature of 40 °C to form 100 μm (3.94 mils) thick dry films.

10 Bonds are then made between polycarbonate and polyurethane based fabric. The bonds were made using the specified bond line temperature with a bonding pressure of 5 N/cm² and a bonding time of 60 seconds.

Bonds are then aged for 5 minutes at room temperature and pulled apart using a ZWICK peel tester at a speed of 300 mm/minute. An average of two bonds is reported.

15 Commerically available polyurethane dispersions were tested according to the Melting Peak and Enthalpy of Fusion test method and according to the Molecular Weight Test Method. The results are set forth in Table 1 below.

Table 1 – Polyurethane Dispersion Comparison

	% Solids*	Delta H (J/g)	Melting peak (°C)	Molecular Weight (Mw)
DISPERCOLL U 53	40	39.7	47.9	96700
DISPERCOLL U 56	50	46.5	47.9	73600
DISPERCOLL U XP 2682	50	41.3	47.8	73800

20

*As reported by supplier

Examples 1-4

Aqueous compositions were prepared by combining the components and in the amounts set forth in Table 2 below. The resulting compositions were then tested according to the Bond Test Method and the results are reported in Table 2.

5 Table 2 – Examples

	Ex. 1	Ex. 2	Ex. 3	Ex. 4
DISPERCOLL U 53	23.68	27.82		
DISPERCOLL U 56	52.52	61.71		
DISPERCOLL U XP 2682			80	94
ACTICIDE MBS	.16	.19		
STEROCOLL HT	.546	.643		
AMMONIA (25% solution in water as pH modifier)	.074	.087		
DISPERCOLL BL XP 2514 (TDI)		6		6
Water	3.02	3.55		
DESMODUR LP BUEJ 471 - (37 wt % in Water)	20		20	
Wt % of first polyurethane in dried film	60	68	84	95
Bond Test at a bond line temperature of about 64°C (N/2.5 cm)	11.1	5.8	36.2	36.4
Bond Test at a tool temperature of about 82°C (N/2.5 cm)	47.1	12.8	48.1	79.6

Other embodiments are within the claims.

What is claimed is

1. A self-supporting adhesive film comprising:
 - a.) a solid surface-deactivated isocyanate; and
 - b.) greater than 70 % by weight of a first polyurethane having a weight average Molecular Weight (Mw) of no greater than about 90,000 and an enthalpy of fusion of at least about 25 J/g.
2. A self-supporting adhesive film obtained from an aqueous composition, said aqueous composition comprising:
 - a.) a solid surface-deactivated isocyanate; and
 - b.) a first polyurethane dispersion, the dried film of which has an enthalpy of fusion of at least about 25 J/g,
the self-supporting adhesive film having a thickness of from about 1 mil to about 8 mils.
3. The self-supporting adhesive film of claim 1, wherein the self-supporting adhesive film is obtained from an aqueous composition.
4. The self-supporting adhesive film of claim 1, wherein said solid surface-deactivated isocyanate is derived from toluene diisocyanate.
5. The self-supporting adhesive film of claim 1, wherein a film of said first polyurethane has an enthalpy of fusion of at least about 35 J/g.
6. The self-supporting adhesive film of claim 1, wherein the first polyurethane is derived from a polyester derived from a polyol selected from the group consisting of 1, 4-butane diol and 1, 6-hexane diol.

7. The self-supporting adhesive film of claim 1, wherein the first polyurethane is derived from:

a.) a polyester derived from adipic acid and a mixture of 1, 6-hexane diol and neopentyl glycol; and

5 b.) an aliphatic isocyanate.

8. The self-supporting adhesive film of claim 1, wherein said film exhibits a bond strength of at least about 20 N/2.5 cm when tested according to the Bond Test Method at a Bond Line Temperature of about 64 °C.

10

9. A composite structure comprising:

a first layer; and

a second layer,

15 at least one of said first layer and said second layer comprising the self-supporting adhesive film of claim 1.

10. A composite structure comprising:

the self-supporting adhesive film of claim 1,

a rigid layer, and

20 a flexible layer,

the rigid layer being bonded to the flexible layer through the self-supporting adhesive film.

25 11. The composite structure of claim 10, wherein the rigid layer comprises at least one of metal, metal composite, plastic, plastic composite, wood, and wood-composite.

12. The composite structure of claim 10, wherein the flexible layer comprises at least one of fabric, foil, film and paper.

30 13. The composite structure of claim 10, wherein the rigid layer is nylon and the soft fabric layer is microfiber.

14. A method of making a composite comprising:

- a.) contacting a flexible layer with a first major surface of the self-supporting adhesive film of claim 1;
- 5 b.) applying heat to the film before or after the film is applied to the flexible substrate;
- c.) contacting a rigid layer with a second major surface of the self-supporting adhesive film such that the second major surface is in direct contact with the rigid layer to form a composite; and
- d.) applying heat and pressure to the composite.

10

15. The self-supporting adhesive film of claim 2, wherein said film has a thickness of from about 2 mils to about 6 mils.

16. The self-supporting adhesive film of claim 1 additionally comprising a second

15 polymer.

17. The self-supporting adhesive film of claim 16 wherein the sum of the solid surface-deactivated isocyanate, the first polyurethane and the second polymer amounts to at least about 95 % by weight of the self-supporting adhesive film.

20

18. The self-supporting adhesive film of claim 2 wherein the solid surface-deactivated isocyanate is derived from an aromatic isocyanate.

19. A composite structure comprising:

25

- the self-supporting adhesive film of claim 2,
- a first rigid layer, and
- a second rigid layer,

the rigid layers being bonded to each other through the self-supporting adhesive film.

30 20. A composite structure comprising:

- the self-supporting adhesive film of claim 2,

a rigid layer, and

a flexible layer,

the rigid layer being bonded to the flexible layer through the self-supporting adhesive film.

5 21. The self-supporting adhesive film of claim 2 additionally comprising a second polymer.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/048876

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G18/70 C08G18/80 C08G18/02 C08G18/42 C08K9/04
C09J175/06

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 C08K 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	EP 2 099 840 A1 (BAYER MATERIALSCIENCE AG [DE]) 16 September 2009 (2009-09-16) paragraph [0051]; claims 1, 16 -----	1-21
X	EP 1 231 232 A1 (JOWAT LOBERS & FRANK GMBH & CO [DE] JOWAT AG [DE]) 14 August 2002 (2002-08-14) claims 1,3,7,10,20,22; example 2 -----	1-21
X	EP 0 922 720 A1 (ABEND THOMAS P [CH] ABEND THOMAS [CH]) 16 June 1999 (1999-06-16) paragraphs [0010], [0021], [0030]; claim 3; examples 13-16,20-24 -----	1-21

Further documents are listed in the continuation of Box C.

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

1 December 2014

Date of mailing of the international search report

09/12/2014

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

Buestrich, Ralf

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/048876

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 2099840	A1 16-09-2009	AT 532807 T BR PI0720278 A2 CN 101652398 A DE 102006058527 A1 EP 2099840 A1 JP 2010512436 A KR 20090088949 A RU 2009126425 A US 2008171208 A1 WO 2008071307 A1 ZA 200904058 A		15-11-2011 28-01-2014 17-02-2010 19-06-2008 16-09-2009 22-04-2010 20-08-2009 20-01-2011 17-07-2008 19-06-2008 25-08-2010
EP 1231232	A1 14-08-2002	AT 299903 T DE 10106630 A1 EP 1231232 A1 ES 2245996 T3 US 2002164486 A1		15-08-2005 22-08-2002 14-08-2002 01-02-2006 07-11-2002
EP 0922720	A1 16-06-1999	AT 203035 T AT 252121 T AT 264351 T AU 748817 B2 AU 1330299 A BR 9813562 A CA 2314320 A1 CN 1284973 A DE 59705314 D1 DE 59809938 D1 DK 0922720 T3 DK 1029879 T3 DK 1037935 T3 EP 0922720 A1 EP 1029879 A1 EP 1037935 A1 ES 2161429 T3 ES 2209221 T3 ES 2218026 T3 GR 3036520 T3 HK 1034985 A1 ID 24970 A JP 4099312 B2 JP 2001525468 A PT 922720 E PT 1037935 E US 6348548 B1 US 2002193534 A1 WO 9929755 A1		15-07-2001 15-11-2003 15-04-2004 13-06-2002 28-06-1999 10-10-2000 17-06-1999 21-02-2001 06-12-2001 20-11-2003 29-10-2001 19-07-2004 16-02-2004 16-06-1999 23-08-2000 27-09-2000 01-12-2001 16-06-2004 16-11-2004 31-12-2001 19-11-2004 31-08-2000 11-06-2008 11-12-2001 30-01-2002 31-03-2004 19-02-2002 19-12-2002 17-06-1999