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(54) **Title:** RUBBER-BASED PRESSURE-SENSITIVE ADHESIVE

(57) **Abstract:** The present disclosure relates to a pressure sensitive adhesive comprising: a) a multi-arm block copolymer of the formula Q_n-Y , wherein: (i) Q represents an arm of the multi-arm block copolymer and each arm independently has the formula G-R, (ii) n represents the number of arms and is a whole number of at least 3, and (iii) Y is the residue of a multifunctional coupling agent, wherein each R is a rubbery block comprising a polymerized conjugated diene, a hydrogenated derivative of a polymerized conjugated diene, or any combinations thereof; and each G is a glassy block comprising a polymerized monovinyl aromatic monomer; b) a polymeric plasticizer having a weight average molecular weight M_w of at least 10.000 g/mol; c) at least one hydrocarbon tackifier, wherein the hydrocarbon tackifier(s) have a Volatile Organic Compound (VOC) value of less than 1000 ppm, when measured by thermogravimetric analysis according to the weight loss test methods described in the experimental section; and d) optionally, a linear block copolymer of the formula $L-(G)_m$, wherein L is a rubbery block comprising a polymerized olefin, a polymerized conjugated diene, a hydrogenated derivative of a polymerized conjugated diene, or any combinations thereof; and wherein m is 1 or 2. The present disclosure also relates to a method of manufacturing such a pressure sensitive adhesive and uses thereof.

RUBBER-BASED PRESSURE-SENSITIVE ADHESIVE

Cross Reference To Related Application

This application claims the benefit of EP Patent Application No. 14193225.1, filed November 14, 2014, the disclosure of which is incorporated by reference herein in its entirety.

Technical Field

The present disclosure relates generally to the field of pressure sensitive adhesives (PSA), more specifically to the field of rubber-based pressure sensitive adhesives and multilayer rubber-based pressure sensitive adhesive assemblies. The present disclosure also relates to a method of manufacturing such pressure sensitive adhesives and assemblies and uses thereof.

Background

Adhesives have been used for a variety of marking, holding, protecting, sealing and masking purposes. Adhesive tapes generally comprise a backing, or substrate, and an adhesive. One type of adhesive which is particularly preferred for many applications is represented by pressure sensitive adhesives.

Pressure-sensitive tapes are virtually ubiquitous in the home and workplace. In its simplest configuration, a pressure-sensitive tape comprises an adhesive and a backing, and the overall construction is tacky at the use temperature and adheres to a variety of substrates using only moderate pressure to form the bond. In this fashion, pressure-sensitive tapes constitute a complete, self-contained bonding system.

Pressure sensitive adhesives (PSAs) are well known to one of ordinary skill in the art, and according to the Pressure-Sensitive Tape Council, PSAs are known to possess properties including the following: (1) aggressive and permanent tack, (2) adherence with no more than finger pressure, (3) sufficient ability to hold onto an adherend, and (4) sufficient cohesive strength. Materials that have been found to function well as PSAs include polymers designed and formulated to exhibit the requisite viscoelastic properties resulting in a desired balance of tack, peel adhesion, and shear holding power. PSAs are characterized by being normally tacky at room temperature (e.g., 20°C). PSAs do not embrace compositions merely because they are sticky or adhere to a surface.

These requirements are assessed generally by means of tests which are designed to individually measure tack, adhesion (peel strength), and cohesion (shear holding power), as noted in A.V. Pocius in Adhesion and Adhesives Technology: An Introduction, 2nd Ed., Hanser Gardner Publication, Cincinnati, OH, 2002. These measurements taken together constitute the balance of properties often used to characterize a PSA.

With broadened use of pressure-sensitive tapes over the years, performance requirements have become more demanding. Shear holding capability, for example, which originally was intended for applications supporting modest loads at room temperature, has now increased substantially for many applications in terms of operating temperature and load. Many applications require pressure sensitive adhesives to support a load at elevated temperatures, typically in the range of from 70°C to 120°C, for which high cohesive strengths are required. Similarly, an increased need has arisen for pressure sensitive adhesives having improved and versatile adhesion characteristics; in particular with respect to peel forces and shear resistance on various types of difficult to adhere surfaces, such as in particular the so-called low surface energy (LSE) and medium surface energy (MSE) substrates.

In addition to increasing performance requirements with regard to pressure sensitive adhesives, volatile organic compounds (VOC) reduction regulations are becoming increasingly important in particular for various kind of interior applications (occupational hygiene and occupational safety) such as, for example, in the construction market or in the automotive or electronics industries. Known acrylate-based pressure sensitive adhesives typically contain notable amounts of low molecular weight organic residuals, such as un-reacted monomers arising from their polymerization process, polymerization initiator residuals, contaminations from raw materials or degradation products formed during the manufacturing process. These low molecular weight residuals qualifying as VOC may diffuse out of the adhesive tape and can be potentially harmful. Known acrylate-based pressure sensitive adhesives, if not crosslinked, also generally suffer from lack of cohesive strength and excessive tendency to flow. This aspect may render the application and processability of uncrosslinked acrylate-based pressure sensitive adhesives particularly problematic, especially when made by a hotmelt process.

The reduction of organic solvent usage in the manufacturing process of pressure sensitive adhesives has quickly emerged as one straightforward means to reduce the overall VOC levels. The use of specific scavengers for organic contaminants, as described in WO 01/44400 (Yang), is another alternative way to achieve reduced VOC levels. However, the solutions for reducing overall VOC levels known from the prior art are often associated with increased manufacturing complexity and production costs.

The pressure sensitive adhesive materials known from the prior art do not often provide sufficient tack to various types of substrate, including the so-called LSE and MSE substrates, in combination with reduced VOC level characteristics. In particular, the overall VOC levels observed do often not fulfill the requirements for various kind of interior applications such as, for example, in the construction market or in the automotive or electronics industries. Partial solutions have been described, for example, in US 2003/0082362 A1 (Khandpur et al.) and in US 2004/0082700 A1 (Khandpur et al.).

Without contesting the technical advantages associated with the pressure sensitive adhesives known in the art, there is still a need for a stable and cost-effective pressure sensitive adhesive providing reduced overall VOC levels whilst providing excellent and versatile adhesion characteristics, in particular with respect to various types of substrate, including LSE and MSE substrates. Other

advantages of the pressure sensitive adhesives, assemblies and methods of the disclosure will be apparent from the following description.

Summary

According to one aspect, the present disclosure relates to a pressure sensitive adhesive comprising:

- a) a multi-arm block copolymer of the formula Q_n -Y, wherein:
 - (i) Q represents an arm of the multi-arm block copolymer and each arm independently has the formula G-R,
 - (ii) n represents the number of arms and is a whole number of at least 3, and
 - (iii) Y is the residue of a multifunctional coupling agent,wherein each R is a rubbery block comprising a polymerized conjugated diene, a hydrogenated derivative of a polymerized conjugated diene, or any combinations thereof; and each G is a glassy block comprising a polymerized monovinyl aromatic monomer;
- b) a polymeric plasticizer having a weight average molecular weight M_w of at least 10.000 g/mol;
- c) at least one hydrocarbon tackifier, wherein the hydrocarbon tackifier(s) have a Volatile Organic Compound (VOC) value of less than 1000 ppm, when measured by thermogravimetric analysis according to the weight loss test methods described in the experimental section; and
- d) optionally, a linear block copolymer of the formula L-(G)_m, wherein L is a rubbery block comprising a polymerized olefin, a polymerized conjugated diene, a hydrogenated derivative of a polymerized conjugated diene, or any combinations thereof; and wherein m is 1 or 2.

In another aspect, the present disclosure is directed to a multilayer pressure sensitive adhesive assembly comprising a pressure sensitive adhesive as described above and a backing layer adjacent to the pressure sensitive adhesive.

According to still another aspect, the present disclosure is directed to a method of manufacturing a pressure sensitive adhesive (or a multilayer pressure sensitive adhesive assembly) as described above, which comprises the steps of:

- a) compounding the multi-arm block copolymer, the polymeric plasticizer, at least one hydrocarbon tackifier; optionally, a linear block copolymer, optionally, a crosslinking agent which is preferably selected from the group of multifunctional (meth)acrylate compounds; and wherein the hydrocarbon tackifier(s) have a Volatile Organic Compound (VOC) value of less than 1000 ppm, less than 800 ppm, less than 600 ppm, less than 400 ppm or even less than 200 ppm, when measured by thermogravimetric analysis according to the weight

loss test methods described in the experimental section; thereby forming a pressure sensitive adhesive formulation; and

- b) optionally, crosslinking the pressure sensitive adhesive formulation, preferably with actinic radiation, more preferably with e-beam irradiation.

According to yet another aspect, the present disclosure relates to the use of a pressure sensitive adhesive or a multilayer pressure sensitive adhesive assembly as described above for industrial applications, preferably for interior applications, more preferably for construction market applications, automotive applications or electronic applications.

Detailed Description

According to a first aspect, the present disclosure relates to a pressure sensitive adhesive comprising:

- a) a multi-arm block copolymer of the formula Q_n-Y , wherein:
 - (i) Q represents an arm of the multi-arm block copolymer and each arm independently has the formula G-R,
 - (ii) n represents the number of arms and is a whole number of at least 3, and
 - (iii) Y is the residue of a multifunctional coupling agent,wherein each R is a rubbery block comprising a polymerized conjugated diene, a hydrogenated derivative of a polymerized conjugated diene, or combinations thereof; and each G is a glassy block comprising a polymerized monovinyl aromatic monomer;
- b) a polymeric plasticizer having a weight average molecular weight M_w of at least 10,000 g/mol;
- c) at least one hydrocarbon tackifier, wherein the hydrocarbon tackifier(s) have a Volatile Organic Compound (VOC) value of less than 1000 ppm, when measured by thermogravimetric analysis according to the weight loss test methods described in the experimental section; and
- d) optionally, a linear block copolymer of the formula $L-(G)_m$, wherein L is a rubbery block comprising a polymerized olefin, a polymerized conjugated diene, a hydrogenated derivative of a polymerized conjugated diene, or any combinations thereof; and wherein m is 1 or 2.

In the context of the present disclosure, it has been surprisingly found that a pressure sensitive adhesive comprising a multi-arm styrenic block copolymer of the formula described above, a polymeric plasticizer having a weight average molecular weight M_w of at least 10,000 g/mol and at least one hydrocarbon tackifier, wherein the hydrocarbon tackifier(s) have a Volatile Organic Compound (VOC) value of less than 1000 ppm, when measured by thermogravimetric analysis according to the weight loss test methods described in the experimental section, provides excellent characteristics and performance as

to overall VOC levels reduction. In some advantageous aspects, the pressure sensitive adhesives as described herein are characterized by very low or even substantial absence of perceptible odor.

In addition, the pressure sensitive adhesives as described herein provide surprisingly good overall balance of adhesive and cohesive characteristics (in particular with respect to peel forces and static shear resistance) on various types of substrate, including LSE and MSE substrates, and in particular on automotive clear coats. In some aspects, the pressure sensitive adhesives according to the present disclosure are characterized by further providing excellent characteristics and performance as to overall fogging levels reduction. The low fogging characteristics typically translate into improved resistance of outgassed components to condensation, as well as improved thermal stability of the corresponding pressure sensitive adhesive.

As such, the pressure sensitive adhesives according to the present disclosure are particularly suited for (industrial) interior applications, more in particular for construction market applications, automotive applications or electronic applications. In the context of automotive applications, the pressure sensitive adhesives as described herein may find particular use for adhering, for example, automotive body side mouldings, weather strips or rearview mirrors. In some aspects, the pressure sensitive adhesives according to the present disclosure are provided with advantageous low fogging characteristics, which are particularly suited for electronic applications.

In the context of the present disclosure, the expression “low surface energy substrates” is meant to refer to those substrates having a surface energy of less than 34 dynes per centimeter. Included among such materials are polypropylene, polyethylene (e.g., high density polyethylene or HDPE, low density polyethylene or LDPE, LLDPE), and blends of polypropylene (PP) such as, for example a blend of polypropylene (PP)/ ethylene propylene diene terpolymer (EPDM)/ thermoplastic polyolefin (TPO).

In the context of the present disclosure, the expression “medium surface energy substrates” is meant to refer to those substrates having a surface energy comprised between 34 and 70 dynes per centimeter, typically between 34 and 60 dynes per centimeter, and more typically between 34 and 50 dynes per centimeter. Included among such materials are polyamide 6 (PA6), acrylonitrile butadiene styrene (ABS), polycarbonate (PC)/ABS blends, PC, polyvinyl chloride (PVC), polyamide (PA), polyurethane (PUR), thermoplastic elastomer (TPE), polyoxymethylene (POM), polystyrene (PS), poly(methyl methacrylate) (PMMA), clear coat surfaces, in particular clear coats for vehicles like a car or coated surfaces for industrial applications and composite materials such as fiber reinforced plastics.

The surface energy is typically determined from contact angle measurements as described, for example, in ASTM D7490-08.

The pressure sensitive adhesive according to the present disclosure comprises a multi-arm block copolymer of the formula Q_n -Y, wherein:

- (i) Q represents an arm of the multi-arm block copolymer and each arm independently has the formula G-R,
- (ii) n represents the number of arms and is a whole number of at least 3, and

(iii) Y is the residue of a multifunctional coupling agent, wherein each R is a rubbery block comprising a polymerized conjugated diene, a hydrogenated derivative of a polymerized conjugated diene, or any combinations thereof; and each G is a glassy block comprising a polymerized monovinyl aromatic monomer.

In a typical aspect, a rubbery block exhibits a glass transition temperature (T_g) of less than room temperature. In some aspects, the T_g of the rubbery block is less than about 0°C, or even less than about -10°C. In some aspects, the T_g of the rubbery block is less than about -40°C, or even less than about -60°C.

In a typical aspect, a glassy block exhibits a T_g of greater than room temperature. In some embodiments, the T_g of the glassy block is at least about 40°C, at least about 60°C, at least about 80°C, or even at least about 100°C.

The terms “glass transition temperature” and “T_g” are used interchangeably and refer to the glass transition temperature of a material or a mixture. Unless otherwise indicated, glass transition temperature values are determined by Differential Scanning Calorimetry (DSC).

In a particular aspect of the present disclosure, the multi-arm styrenic block copolymer for use herein is such that n ranges from 3 to 10 or even from 3 to 5. In some other aspects, n is 4, while in some other executions, n is equal to 6 or more.

Suitable rubbery blocks R for use herein comprise polymerized conjugated dienes, hydrogenated derivatives of a polymerized conjugated diene, or combinations thereof. In some typical aspects, the rubbery block of at least one arm comprises a polymerized conjugated diene selected from the group consisting of isoprene, butadiene, ethylene butadiene copolymers, hydrogenated derivatives of polyisoprene or polybutadiene, and combinations or mixtures thereof. According to an advantageous aspect, the rubbery blocks of each arm comprise a polymerized conjugated diene selected from the group consisting of isoprene, butadiene, ethylene butadiene copolymers, hydrogenated derivatives of polyisoprene or polybutadiene, and any combinations or mixtures thereof.

According to a preferred aspect of the pressure sensitive adhesive according to the present disclosure, at least one of the rubbery blocks of the multi-arm block copolymer comprises a conjugated diene selected from the group consisting of isoprene, butadiene, and any combinations thereof. More preferably, each of the rubbery blocks of the multi-arm block copolymer comprises a conjugated diene selected from the group consisting of isoprene, butadiene, and any combinations or mixtures thereof.

According to a particularly advantageous aspect of the pressure sensitive adhesive according to the present disclosure, at least one arm of the multi-arm block copolymer is selected from the group consisting of styrene-isoprene-styrene, styrene-butadiene-styrene, styrene-ethylene-butylene-styrene, styrene-ethylene-propylene-styrene, and combinations thereof. More preferably, each arm of the multi-arm block copolymer is selected from the group consisting of styrene-isoprene-styrene, styrene-butadiene-styrene, styrene-ethylene-butylene-styrene, styrene-ethylene-propylene-styrene, and any combinations thereof. Even more preferably, each arm of the multi-arm block copolymer is selected

from the group consisting of styrene-isoprene-styrene, styrene-butadiene-styrene, and any combinations thereof.

Suitable glassy blocks G for use herein comprise a polymerized monovinyl aromatic monomer. In some typical aspects, the glassy block of at least one arm comprises a monovinyl aromatic monomer selected from the group consisting of styrene, styrene-compatible blends, and any combinations thereof. According to an advantageous aspect, the glassy blocks of each arm comprise a monovinyl aromatic monomer selected from the group consisting of styrene, styrene-compatible blends, and any combinations thereof.

According to an advantageous execution of the present disclosure, the multi-arm block copolymer for use herein is a (multi-arm) star block copolymer. In a more advantageous aspect of the pressure sensitive adhesive according to the present disclosure, the multi-arm block copolymer is a polymodal block copolymer. As used herein, the term "polymodal" means that the copolymer comprises endblocks having at least two different molecular weights. Such a block copolymer may also be characterized as having at least one "high" molecular weight endblock, and at least one "low" molecular weight endblock, wherein the terms high and low are used relative to each other. In some particular aspects, the ratio of the number average molecular weight of the high molecular weight endblock, $(M_n)_H$, relative to the number average molecular weight of the low molecular weight endblock, $(M_n)_L$, is at least about 1.25.

In some particular aspects, $(M_n)_H$ ranges from about 5000 to about 50000. In some embodiments, $(M_n)_H$ is at least about 8000, and in some aspects at least about 10000. In some aspects, $(M_n)_H$ is no greater than about 35000. In some aspects, $(M_n)_L$ ranges from about 1000 to about 10000. In some aspects, $(M_n)_L$ is at least about 2000, and, in some aspects, at least about 4000. In some aspects, $(M_n)_L$ is less than about 9000, and, in some aspects, less than about 8000.

According to another beneficial aspect, the multi-arm block copolymer is an asymmetric block copolymer. As used herein, the term "asymmetric" means that the arms of the block copolymer are not all identical. Generally, a polymodal block copolymer is an asymmetric block copolymer (i.e., a polymodal asymmetric block copolymer) as not all arms of a polymodal block copolymer are identical since the molecular weights of the end blocks are not all the same. In some aspects, the block copolymers of the present disclosure are polymodal, asymmetric block copolymers.

Multi-arm block copolymers for use herein are described, for example, in US 7,163,741 B1 (Khandpur et al.). Methods of making multi-arm block copolymers, in particular polymodal asymmetric, block copolymers are described in, e.g., U.S. Patent No. 5,296,547 (Nestegard et al.), or in U.S. Patent No. 5,393,787 (Nestegard et al.), the content of which is herewith incorporated by reference.

Generally, the multifunctional coupling agent for use herein may be any polyalkenyl coupling agent or other material known to have functional groups that can react with carbanions of the living polymer to form linked polymers. The polyalkenyl coupling agent may be aliphatic, aromatic, or heterocyclic. Exemplary aliphatic polyalkenyl coupling agents include, but are not limited to, polyvinyl

and polyalkyl acetylenes, diacetylenes, phosphates, phosphites, and dimethacrylates (e.g., ethylene dimethacrylate). Exemplary aromatic polyalkenyl coupling agents include but are not limited to, polyvinyl benzene, polyvinyl toluene, polyvinyl xylene, polyvinyl anthracene, polyvinyl naphthalene, and divinylidurene. Exemplary polyvinyl groups include, but are not limited to, divinyl, trivinyl, and tetravinyl groups. In some aspects, divinylbenzene (DVB) may be used, and may include ortho-divinyl benzene, meta-divinyl benzene, para-divinyl benzene, and mixtures thereof. Exemplary heterocyclic polyalkenyl coupling agents include, but are not limited to, divinyl pyridine, and divinyl thiophene. Other exemplary multifunctional coupling agents include, but are not limited to, silicon halides, polyepoxides, polyisocyanates, polyketones, polyanhydrides, and dicarboxylic acid esters.

According to a typical aspect, the multi-arm block copolymer as described above is used for example in amounts of up to 80 wt%, based on the weight of the pressure sensitive adhesive. In some exemplary aspects, the amount of multi-arm block copolymer can be for example, in the range of from 20 wt% to 80 wt%, from 20 wt% to 70 wt%, from 25 wt% to 60 wt%, or even from 25 wt% to 50 wt%, based on the weight of the pressure sensitive adhesive.

In some advantageous aspects, the pressure sensitive adhesive of the present disclosure may optionally comprise a linear block copolymer of the formula $L-(G)_m$, wherein L represents a rubbery block, G represents a glassy block, and m, the number of glassy blocks, is 1 or 2. Suitable rubbery blocks L for use herein comprise a polymerized olefin, a polymerized conjugated diene, a hydrogenated derivative of a polymerized conjugated diene, or any combinations thereof; and wherein m is 1 or 2. In the context of the present disclosure, it has been surprisingly found that the addition of a linear block copolymer as described above may provide various beneficial effects to the (co)polymeric precursor of the pressure sensitive adhesive and to the resulting pressure sensitive adhesive. In particular, the addition of a linear block copolymer as described above may advantageously impact the processability of the (co)polymeric precursor of the pressure sensitive adhesive due to the viscosity lowering effect of this compound, which in turn results in pressure sensitive adhesives provided with an improved visual and aesthetic appearance. Also, the presence of a linear block copolymer as described above may additionally provide the resulting pressure sensitive adhesive with an improved tack performance.

In some aspects, m is one, and the linear block copolymer is a diblock copolymer comprising one rubbery block L and one glassy block G. In some aspects, m is two, and the linear block copolymer comprises two glassy endblocks and one rubbery midblock, i.e., the linear block copolymer is a triblock copolymer.

In some aspects, the rubbery block L comprises a polymerized conjugated diene, a hydrogenated derivative of a polymerized conjugated diene, or any combinations thereof. In some aspects, the conjugated dienes comprise 4 to 12 carbon atoms. Exemplary conjugated dienes include, but are not limited to, butadiene, isoprene, ethylbutadiene, phenylbutadiene, piperylene, pentadiene, hexadiene, ethylhexadiene, and dimethylbutadiene. The polymerized conjugated dienes may be used individually or as copolymers with each other. Preferably, the rubbery block L of the linear block copolymer comprises

a conjugated diene selected from the group consisting of isoprene, butadiene, and any combinations thereof. In some other aspects, the rubbery block L comprises a polymerized olefin, such as, for example, isobutylene.

In some aspects, at least one glassy block G comprises a polymerized monovinyl aromatic monomer. In some other aspects, both glassy blocks of a triblock copolymer comprise a polymerized monovinyl aromatic monomer. In some other aspects, the linear block copolymer comprises two glassy blocks. According to still another aspect, the monovinyl aromatic monomers comprise 8 to 18 carbon atoms. Exemplary monovinyl aromatic monomers include, but are not limited to, styrene, vinylpyridine, vinyl toluene, alpha-methyl styrene, methyl styrene, dimethylstyrene, ethylstyrene, diethyl styrene, t-butylstyrene, di-n-butylstyrene, isopropylstyrene, other alkylated-styrenes, styrene analogs, and styrene homologs. In some aspects, the monovinyl aromatic monomer is selected from the group consisting of styrene, styrene-compatible monomers or monomer blends, and any combinations thereof.

As used herein, "styrene-compatible monomers or monomer blends" refers to a monomer or blend of monomers, which may be polymerized or copolymerized, that preferentially associate with polystyrene or with the polystyrene endblocks of a block copolymer. The compatibility can arise from actual copolymerization with monomeric styrene; solubility of the compatible monomer or blend, or polymerized monomer or blend in the polystyrene phase during hot melt or solvent processing; or association of the monomer or blend with the styrene-rich phase domain on standing after processing.

In some other aspects, the linear block copolymer is a diblock copolymer. In some aspects, the diblock copolymer is selected from the group consisting of styrene-isoprene, and styrene-butadiene. In some aspects, the linear block copolymer is a triblock copolymer. In some aspects, the triblock copolymer is selected from the group consisting of styrene-isoprene-styrene, styrene-butadiene-styrene, styrene-ethylene-butylene-styrene, styrene-ethylene-propylene-styrene, styrene-isobutylene-styrene, and any combinations thereof. Diblock and triblock copolymers are commercially available, e.g., those under the trade name VECTOR available from Dexco Polymer LP, Houston, Texas; and those available under the trade name KRATON available from Kraton Polymers U.S. LLC, Houston, Texas. As manufactured and/or purchased, triblock copolymers may contain some fraction of diblock copolymer as well.

In a particular aspect of the pressure sensitive adhesive according to the present disclosure, the hydrocarbon tackifier(s) for use herein have a Volatile Organic Compound (VOC) value of less than 800 ppm, less than 600 ppm, less than 400 ppm or even less than 200 ppm, when measured by thermogravimetric analysis according to the weight loss test method described in the experimental section.

According to a preferred aspect, the hydrocarbon tackifier(s) for use herein have a Volatile Fogging Compound (FOG) value of less than 1500 ppm, less than 1000 ppm, less than 800 ppm, less than 600 ppm, or even less than 500 ppm, when measured by thermogravimetric analysis according to the weight loss test methods described in the experimental section. In the context of the present disclosure, it has been surprisingly found that a pressure sensitive adhesive comprising a rubber-based

elastomeric material and at least one hydrocarbon tackifier, wherein the hydrocarbon tackifier(s) have a Volatile Fogging Compound (FOG) value of less than 1500 ppm, less than 1000 ppm, less than 800 ppm, less than 600 ppm, or even less than 500 ppm, when measured by thermogravimetric analysis according to the weight loss test method described in the experimental section, provide excellent characteristics and performance as to resistance of outgassed components to condensation and/or thermal stability of the corresponding pressure sensitive adhesive. Pressure sensitive adhesives provided with advantageous low fogging characteristics are particularly suited for electronic applications.

Preferably still, the hydrocarbon tackifier(s) for use herein have an outgassing value of less than 1 wt%, less than 0.8 wt%, less than 0.6 wt%, less than 0.5 wt%, less than 0.4 wt%, less than 0.3 wt%, less than 0.2 wt% or even less than 0.1 wt%, when measured by weight loss analysis according to the oven outgassing test method described in the experimental section. In the context of the present disclosure, it has been surprisingly found that a pressure sensitive adhesive comprising a rubber-based elastomeric material and at least one hydrocarbon tackifier, wherein the hydrocarbon tackifier(s) have an outgassing value of less than 1 wt%, less than 0.8 wt%, less than 0.6 wt%, less than 0.5 wt%, less than 0.4 wt%, less than 0.3 wt%, less than 0.2 wt% or even less than 0.1 wt%, when measured by weight loss analysis according to the oven outgassing test method described in the experimental section, provide excellent thermal stability.

Any hydrocarbon tackifiers typically included in conventional pressure-sensitive adhesive compositions may be used in the context of the present disclosure, as long as they fulfill the above-detailed VOC requirements and preferably the above-detailed FOG level requirements too. Useful hydrocarbon tackifiers are typically selected to be miscible with the (co)polymeric material. Suitable hydrocarbon tackifier(s) for use herein may be easily identified by those skilled in the art, in the light of the present disclosure.

Either solid or liquid hydrocarbon tackifiers may be added, although solid hydrocarbon tackifiers are preferred. Solid tackifiers generally have a number average molecular weight (Mw) of 10,000 grams per mole or less and a softening point above about 70°C. Liquid tackifiers are viscous materials that have a softening point of about 0°C to about 20°C.

Suitable tackifying resins may include terpene resins such as polyterpenes (e.g., alpha pinene-based resins, beta pinene-based resins, and limonene-based resins) and aromatic-modified polyterpene resins (e.g., phenol modified polyterpene resins); coumarone-indene resins; and petroleum-based hydrocarbon resins such as C5-based hydrocarbon resins, C9-based hydrocarbon resins, C5/C9-based hydrocarbon resins, and dicyclopentadiene-based resins. These tackifying resins, if added, can be hydrogenated to lower their color contribution to the particular pressure-sensitive adhesive composition. Combinations of various tackifiers can be used if desired, as long as they fulfill the above-detailed VOC requirements and preferably the above-detailed FOG level requirements too.

Tackifiers that are hydrocarbon resins can be prepared from various petroleum-based feed stocks. There feedstocks can be aliphatic hydrocarbons (mainly C5 monomers with some other

monomers present such as a mixture of trans-1,3-pentadiene, cis-1,3-pentadiene, 2-methyl-2-butene, dicyclopentadiene, cyclopentadiene, and cyclopentene), aromatic hydrocarbons (mainly C9 monomers with some other monomers present such as a mixture of vinyl toluenes, dicyclopentadiene, indene, methylstyrene, styrene, and methylenes), or mixtures thereof. Tackifiers derived from C5 monomers are referred to as C5-based hydrocarbon resins while those derived from C9 monomers are referred to as C9-based hydrocarbon resins. Some tackifiers are derived from a mixture of C5 and C9 monomers or are a blend of C5-based hydrocarbon tackifiers and C9-based hydrocarbon tackifiers. These tackifiers can be referred to as C5/C9-based hydrocarbon tackifiers. Any of these resins can be partially or fully hydrogenated to improve their color, their thermal stability or their process compatibility.

The C5-based hydrocarbon resins are commercially available from Eastman Chemical Company under the trade designations PICCOTAC and EASTOTAC, from Cray Valley under the trade designation WINGTACK, from Neville Chemical Company under the trade designation NEVTAC LX, and from Kolon Industries, Inc. under the trade designation HIKOREZ. The C5-based hydrocarbon resins are commercially available from Eastman Chemical with various degrees of hydrogenation under the trade designation EASTOTACK.

The C9-based hydrocarbon resins are commercially available from Eastman Chemical Company under the trade designation PICCO, KRISTLEX, PLASTOLYN, PICCOTAC, and ENDEX, from Cray Valley under the trade designations NORSOLENE, from Ruetgers N.V. under the trade designation NOVAREZ, and from Kolon Industries, Inc. under the trade designation HIKOTAC. These resins can be partially or fully hydrogenated. Prior to hydrogenation, the C9-based hydrocarbon resins are often about 40 percent aromatic as measured by proton Nuclear Magnetic Resonance. Hydrogenated C9-based hydrocarbon resins are commercially available, for example, from Eastman Chemical under the trade designations REGALITE and REGALREZ that are 50 to 100 percent (e.g., 50 percent, 70 percent, 90 percent, and 100 percent) hydrogenated. The partially hydrogenated resins typically have some aromatic rings.

Various C5/C9-based hydrocarbon tackifiers are commercially available from Arakawa under the trade designation ARKON, from Zeon under the trade designation QUINTONE, from Exxon Mobil Chemical under the trade designation ESCOREZ, and from Newport Industries under the trade designations NURES and H-REZ. In the context of the present disclosure, suitable hydrocarbon tackifiers for use herein may be advantageously selected among those C5/C9-based hydrocarbon tackifiers commercially available from Exxon Mobil Chemical under the trade designation ESCOREZ.

According to a preferred aspect of the pressure sensitive adhesive of the present disclosure, the hydrocarbon tackifier for use herein is selected from the group consisting of aliphatic hydrocarbon resins, cycloaliphatic hydrocarbon resins, aromatic modified aliphatic and cycloaliphatic resins, aromatic resins, hydrogenated hydrocarbon resins, terpene and modified terpene resins, terpene-phenol resins, rosin esters, and any combinations or mixtures thereof.

In an advantageous aspect of the present disclosure, the tackifying resin is selected from the group consisting of C5-based hydrocarbon resins, C9-based hydrocarbon resins, C5/C9-based hydrocarbon resins, and any combinations or mixtures thereof. In another advantageous aspect, the tackifying resin is selected from the group consisting of hydrogenated terpene resins, hydrogenated rosin resins, hydrogenated C5-based hydrocarbon resins, hydrogenated C9-based hydrocarbon resins, hydrogenated C5/C9-based hydrocarbon resins, and any combinations or mixtures thereof.

According to an advantageous aspect, the pressure sensitive adhesive according to the present disclosure comprises a first hydrocarbon tackifier having a Volatile Organic Compound (VOC) value of less than 1000 ppm, when measured by thermogravimetric analysis according to the weight loss test methods described in the experimental section, wherein the first hydrocarbon tackifier has preferably a Tg of at least 60°C, and wherein preferably the first hydrocarbon tackifier is primarily compatible with the rubbery blocks.

In an advantageous aspect, the first hydrocarbon tackifier is primarily compatible with at least some of the rubbery blocks. In some aspects, the first hydrocarbon tackifier is primarily compatible with the rubbery block of the linear block copolymer and each rubbery block of a multi-arm block copolymer.

As used herein, a tackifier is “compatible” with a block if it is miscible with that block. Generally, the miscibility of a tackifier with a block can be determined by measuring the effect of the tackifier on the Tg of that block. If a tackifier is miscible with a block, it will alter (e.g., increase) the Tg of that block. A tackifier is “primarily compatible” with a block if it is at least miscible with that block, although it may also be miscible with other blocks. For example, a tackifier that is primarily compatible with a rubbery block will be miscible with the rubbery block, but may also be miscible with a glassy block.

Generally, resins having relatively low solubility parameters tend to associate with the rubbery blocks; however, their solubility in the glassy blocks tends to increase as the molecular weights or softening points of these resins are lowered.

Exemplary first hydrocarbon tackifiers that are primarily compatible with the rubbery blocks are advantageously selected from the group consisting of polymeric terpenes, hetero-functional terpenes, coumarone-indene resins, rosin acids, esters of rosin acids, disproportionated rosin acid esters, hydrogenated, C5 aliphatic resins, C9 hydrogenated aromatic resins, C5/C9 aliphatic/aromatic resins, dicyclopentadiene resins, hydrogenated hydrocarbon resins arising from C5/C9 and dicyclopentadiene precursors, hydrogenated styrene monomer resins, and any blends thereof.

According to another advantageous aspect, the pressure sensitive adhesive according to the present disclosure may optionally comprise a second hydrocarbon tackifier having a Volatile Organic Compound (VOC) value of less than 1000 ppm, when measured by thermogravimetric analysis according to the weight loss test methods described in the experimental section, wherein the second hydrocarbon tackifier has preferably a Tg of at least 60°C, and wherein preferably the second hydrocarbon tackifier is primarily compatible with the glassy blocks.

In the context of the present disclosure, it has been surprisingly found that the addition of a second hydrocarbon tackifier which is primarily compatible with the glassy blocks, may advantageously impact the high temperature shear performance of the pressure sensitive adhesive. The presence of a second hydrocarbon tackifier which is primarily compatible with the glassy blocks may also lead to provide improved adhesion performance in particular on critical substrates, such as, for example, critical paint substrates and critical clear coat systems, in particular automotive critical clear coat systems.

In a preferred aspect, the second hydrocarbon tackifiers that are primarily compatible with the glassy blocks are advantageously selected from the group consisting of coumarone-indene resins, rosin acids, esters of rosin acids, disproportionated rosin acid esters, C9 aromatics, styrene, alpha-methyl styrene, pure monomer resins and C9/C5 aromatic-modified aliphatic hydrocarbons, and blends thereof.

In some aspects of the pressure sensitive adhesive according to the present disclosure, the first and/or the second hydrocarbon tackifier has a Tg of at least 65°C, or even at least 70°C. In some aspects, both the first and the second hydrocarbon tackifier have a Tg of at least 65°C, or even at least 70°C.

In some aspects of the pressure sensitive adhesive according to the present disclosure, the first and/or the second hydrocarbon tackifier has a softening point of at least about 115°C, or even at least about 120°C. In some aspects, both the first and the second hydrocarbon tackifier have a softening point of at least about 115°C, or even at least about 120°C.

According to a typical aspect of the pressure sensitive adhesive according to the present disclosure, the ratio of the total weight of all block copolymers to the total weight of all hydrocarbon tackifiers ranges from 2.4:1 to 1:2.4, from 2.0:1 to 1:2.0, from 1.5:1 to 1:1.5, from 1.2:1 to 1:1.2, from 1.15:1 to 1:1.15, or even from 1.1:1 to 1:1.1.

According to a typical aspect of the pressure sensitive adhesive, any of the hydrocarbon tackifiers may be used for example in amounts of up to 80 wt%, based on the weight of the pressure sensitive adhesive. In some aspects, the tackifiers can be used in amounts up to 70 wt%, up to 60 wt%, up to 55 wt%, up to 50 wt%, or even up to 45 wt%, based on the weight of the pressure sensitive adhesive. The amount of tackifiers can be for example, in the range of from 5 wt% to 60 wt%, from 5 wt% to 50 wt%, from 10 wt% to 45 wt%, or even from 15 wt% to 45 wt%, based on the weight of the pressure sensitive adhesive.

The pressure sensitive adhesive according to the present disclosure further comprises a polymeric plasticizer having a weight average molecular weight Mw of at least 10.000 g/mol. Any polymeric plasticizers typically known by those skilled in the art may be used in the context of the present disclosure as long as they fulfill the above weight average molecular weight requirement.

The use of polymeric plasticizers having a weight average molecular weight Mw of at least 10.000 g/mol, may advantageously impact the overall shear performance of the pressure sensitive adhesive, in particular the shear performance at elevated temperature (typically at 70°C). Additionally, polymeric plasticizers having a weight average molecular weight Mw of at least 10.000 g/mol have been found to provide excellent characteristics and performance as to reduction of VOC and FOG levels.

Useful polymeric plasticizers for use herein are typically selected to be miscible with the other components in the composition such as the (co)polymeric material and any optional additives. Suitable polymeric plasticizers for use herein may be easily identified by those skilled in the art, in the light of the present disclosure. Typical examples of polymeric plasticizers that can be used herein include, but are not limited to, those selected from the group consisting of polyisobutylenes, polyisoprenes, polybutadienes, amorphous polyolefins and copolymers thereof, silicones, polyacrylates, oligomeric polyurethanes, ethylene propylene copolymers, any combinations or mixtures thereof.

Advantageously, the polymeric plasticizer(s) for use herein, have a Volatile Organic Compound (VOC) value of less than 1000 ppm, less than 800 ppm, less than 600 ppm, less than 400 ppm or even less than 200 ppm, when measured by thermogravimetric analysis according to the weight loss test method described in the experimental section.

Advantageously still, the polymeric plasticizer(s) for use herein, have a Volatile Fogging Compound (FOG) value of less than 2500 ppm, less than 2000 ppm, less than 1500 ppm, less than 1000 ppm, less than 800 ppm, less than 600 ppm, or even less than 500 ppm, when measured by thermogravimetric analysis according to the weight loss test method described in the experimental section.

Yet advantageously still, the polymeric plasticizer(s) for use herein, have an outgassing value of less than 1 wt%, less than 0.8 wt%, less than 0.6 wt%, less than 0.5 wt%, less than 0.4 wt%, less than 0.3 wt%, less than 0.2 wt% or even less than 0.1 wt%, when measured by weight loss analysis according to the oven outgassing test method described in the experimental section.

According to an advantageous aspect, the polymeric plasticizer has a weight average molecular weight Mw of at least 20.000 g/mol, at least 30.000 g/mol, or even at least 50.000 g/mol. Advantageously still, the polymeric plasticizer has a weight average molecular weight Mw of 100.000 g/mol or less, less than 90.000 g/mol, less than 80.000 g/mol, less than 70.000 g/mol, or even less than 60.000 g/mol.

The weight average molecular weight Mw of the polymeric plasticizer may be determined by any methods known to the skilled person, for example Gel Permeation Chromatography (GPC) also known as Size Exclusion Chromatography (SEC) or by light scattering techniques. Unless otherwise stated, the weight average molecular weight Mw of the polymeric plasticizers is measured by light scattering according to ASTM D4001-13.

In another advantageous aspect of the pressure sensitive adhesive of the present disclosure, the polymeric plasticizer has a weight average molecular weight Mw comprised between 30.000 g/mol and 80.000 g/mol or even between 30.000 g/mol and 60.000 g/mol.

According to a particularly preferred execution of the pressure sensitive adhesive of the present disclosure, the polymeric plasticizer is a polyisobutylene plasticizer. Typical examples of polyisobutylene plasticizers that can be used herein include, but are not limited to, those selected among

those commercially available from BASF under the trade designation OPPANOL, in particular OPPANOL B series.

According to a typical aspect, the polymeric plasticizers are used for example in amounts of up to 40 wt%, based on the weight of the pressure sensitive adhesive. In some aspects, the polyisobutylene plasticizers may be used in amounts up to 35 wt%, up to 30 wt%, or up to 25 wt%, based on the weight of the pressure sensitive adhesive. The amount of polymeric plasticizers can be for example, in the range of from 1 wt% to 40 wt%, from 2 wt% to 30 wt%, or even from 5 wt% to 30 wt%, or even from 5 wt% to 25 wt%, based on the weight of the pressure sensitive adhesive.

According to another typical aspect of the pressure sensitive adhesive, the total amount of the polymeric plasticizers is of no greater than 20 wt%, no greater than 18 wt%, no greater than 15 wt%, or even no greater than 12 wt%, expressed as a percent by weight based on the total weight of the pressure sensitive adhesive. In some other aspects, the total amount of the polymeric plasticizers is of no less than 6 wt%, or even no less than 7 wt%, expressed as a percent by weight based on the total weight of the pressure sensitive adhesive. In still some other aspects, the total amount of the polymeric plasticizers is comprised between 2 and 20 wt%, between 4 and 15 wt%, or even between 6 and 15 wt%, expressed as a percent by weight based on the total weight of the pressure sensitive adhesive.

In some aspects, the pressure sensitive adhesive of the present disclosure may further comprise, as an optional ingredient, a filler material. Such fillers may be advantageously used, for example, to increase the mechanical stability of the pressure sensitive adhesive and may also increase its shear and peel force resistance.

Any filler material commonly known to those skilled in the art may be used in the context of the present disclosure. Typical examples of filler material that can be used herein include, but are not limited to, those selected from the group consisting of expanded perlite, microspheres, expandable microspheres, ceramic spheres, zeolites, clay fillers, glass beads, hollow inorganic beads, silica type fillers, hydrophobic silica type fillers, hydrophilic silica type fillers, fumed silica, fibers, in particular glass fibers, carbon fibers, graphite fibers, silica fibers, ceramic fibers, electrically and/or thermally conducting particles, nanoparticles, in particular silica nanoparticles, and any combinations thereof.

In a typical aspect of the present disclosure, the pressure sensitive adhesive is free of any filler material selected from the group consisting of microspheres, expandable microspheres, preferably pentane filled expandable microspheres, gaseous cavities, glass beads, glass microspheres, glass bubbles and any combinations or mixtures thereof. More typically, the pressure sensitive adhesive is free of any filler material selected from the group consisting of expandable microspheres, glass bubbles, and any combinations or mixtures thereof.

When present, the filler material for use herein may be used in the pressure sensitive adhesive, in any suitable amounts. In some exemplary aspects, the filler material is present in amounts up to 30 parts by weight, up to 25 parts by weight, or even up to 20 parts by weight of the pressure sensitive adhesive.

In some other exemplary aspects, this amount is typically of at least 1 part by weight, or at least 3 parts by weight of the pressure sensitive adhesive.

Accordingly, in some exemplary aspects, the filler material is present in amounts in a range of from 1 to 20 parts by weight, from 3 to 15 parts by weight, or even from 5 to 13 parts by weight of the pressure sensitive adhesive. In some other exemplary aspects, the filler material is present in amounts in a range of from 1 to 20 parts by weight, from 2 to 15 parts by weight, or even from 2 to 10 parts by weight of the pressure sensitive adhesive.

The pressure sensitive adhesive of the present disclosure may further comprise, as an optional ingredient, a crosslinking additive (also referred to as crosslinking agent). A crosslinker may be used to increase the cohesive strength and the tensile strength of the polymeric material. Suitable crosslinking additives for use herein may have multiple (meth)acryloyl groups.

Crosslinkers with multiple (meth)acryloyl groups can be di(meth)acrylates, tri(meth)acrylates, tetra(meth)acrylates, penta(meth)acrylates, and the like. These crosslinkers can be formed, for example, by reacting (meth)acrylic acid with a polyhydric alcohol (i.e., an alcohol having at least two hydroxyl groups). The polyhydric alcohol often has two, three, four, or five hydroxyl groups. Mixtures of crosslinkers may also be used.

In many aspects, the crosslinkers contain at least two (meth)acryloyl groups. Exemplary crosslinkers with two acryloyl groups include, but are not limited to, 1,2-ethanediol diacrylate, 1,3-propanediol diacrylate, 1,9-nonanediol diacrylate, 1,12-dodecanediol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, butylene glycol diacrylate, bisphenol A diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, tetraethylene glycol diacrylate, tripropylene glycol diacrylate, polyethylene glycol diacrylate, polypropylene glycol diacrylate, polyethylene/polypropylene copolymer diacrylate, polybutadiene di(meth)acrylate, propoxylated glycerin tri(meth)acrylate, and neopentylglycol hydroxypivalate diacrylate modified caprolactone.

Exemplary crosslinkers with three or four (meth)acryloyl groups include, but are not limited to, trimethylolpropane triacrylate (e.g., commercially available under the trade designation TMPTA-N from Cytec Industries, Inc., Smyrna, GA and under the trade designation SR-351 from Sartomer, Exton, PA), trimethylolpropane trimethacrylate (e.g., commercially available under the trade designation SR-350 from Sartomer, Exton, PA), pentaerythritol triacrylate (e.g., commercially available under the trade designation SR-444 from Sartomer), tris(2-hydroxyethylisocyanurate) triacrylate (e.g., commercially available under the trade designation SR-368 from Sartomer), a mixture of pentaerythritol triacrylate and pentaerythritol tetraacrylate (e.g., commercially available from Cytec Industries, Inc., under the trade designation PETIA with an approximately 1:1 ratio of tetraacrylate to triacrylate and under the trade designation PETA-K with an approximately 3:1 ratio of tetraacrylate to triacrylate), pentaerythritol tetraacrylate (e.g., commercially available under the trade designation SR-295 from Sartomer), di-trimethylolpropane tetraacrylate (e.g., commercially available under the trade designation SR-355 from Sartomer), and ethoxylated pentaerythritol tetraacrylate (e.g., commercially available under the trade

designation SR-494 from Sartomer). An exemplary crosslinker with five (meth)acryloyl groups includes, but is not limited to, dipentaerythritol pentaacrylate (e.g., commercially available under the trade designation SR-399 from Sartomer).

In some aspects, the crosslinkers are polymeric materials that contain at least two (meth)acryloyl groups. For example, the crosslinkers can be poly(alkylene oxides) with at least two acryloyl groups (e.g., polyethylene glycol diacrylates commercially available from Sartomer such as SR210, SR252, and SR603) or poly(urethanes) with at least two (meth)acryloyl groups (e.g., polyurethane diacrylates such as CN9018 from Sartomer). As the higher molecular weight of the crosslinkers increases, the resulting acrylic copolymer tends to have a higher elongation before breaking. Polymeric crosslinkers tend to be used in greater weight percent amounts compared to their non-polymeric counterparts.

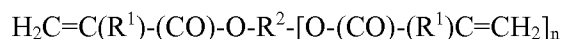
In still other methods of crosslinking, thermal crosslinkers may be used, optionally in combination with suitable accelerants and retardants. Suitable thermal crosslinkers for use herein include, but are not limited to, isocyanates, more particularly trimerized isocyanates and/or sterically hindered isocyanates that are free of blocking agents, or else epoxide compounds such as epoxide-amine crosslinker systems. Advantageous crosslinker systems and methods are described, for example, in the descriptions of DE202009013255 U1, EP 2 305 389 A1, EP 2 414 143 A1, EP 2 192 148 A1, EP 2 186 869, EP 0 752 435 A1, EP 1 802 722 A1, EP 1 791 921 A1, EP 1 791 922 A1, EP 1 978 069 A1, and DE 10 2008 059 050 A1, the relevant contents of which are herewith incorporated by reference. Particularly advantageous crosslinker systems and methods are described in EP 0 752 435 A1 and EP 1 978 069 A1. Suitable accelerants and retardant systems for use herein are described, for example, in the description of US-A1- 2011/0281964, the relevant content of which is herewith explicitly incorporated by reference. Suitable thermal crosslinkers for use herein include epoxy cyclohexyl derivatives, in particular epoxy cyclohexyl carboxylate derivatives, with particular preference to (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate, commercially available from Cytec Industries Inc. under tradename UVACURE 1500. According to a particular aspect, the rubber-based elastomeric material for use herein may comprise (co)polymers or copolymers crosslinkable with epoxide groups. Correspondingly, at least part of the monomers or comonomers used may advantageously be functional monomers crosslinkable with epoxide groups. Monomers with acid groups (especially carboxylic, sulphonic or phosphonic acid groups) and/or hydroxyl groups and/or acid anhydride groups and/or epoxide groups and/or amine groups, in particular monomers containing carboxylic acid groups, may be suitably used. Suitable functional monomers are described e.g. in US 2005/0288436 A1.

The crosslinking additive, if present, may be used for example in amounts of up to 40 wt%, based on the weight of the pressure sensitive adhesive. In some aspects, the crosslinking additive may be used in amounts up to 20 wt%, up to 15 wt%, up to 10 wt%, or up to 5 wt%, based on the weight of the pressure sensitive adhesive. The amount of crosslinking additive can be for example, in the range of from 0.1 wt% to 10 wt%, from 0.5 wt% to 8 wt%, from 1 wt% to 6 wt%, or even from 2 wt% to 5 wt%, based on the weight of the pressure sensitive adhesive.

Aside from thermal, moisture or photosensitive crosslinking additives, crosslinking may also be achieved using high energy electromagnetic radiation, such as gamma or e-beam radiation.

In an advantageous aspect of the present disclosure, the crosslinking additive for use herein is activated/activatable with actinic radiation, more preferably with e-beam irradiation. In a more preferred aspect, the crosslinking additive is selected from the group of multifunctional (meth)acrylate compounds. Exemplary multifunctional (meth)acrylate compounds preferably comprise at least two (meth)acryloyl groups, in particular three or four (meth)acryloyl groups, more in particular three (meth)acryloyl groups.

In another advantageous aspect, the multifunctional (meth)acrylate compound has the following Formula:



wherein R^1 is hydrogen or methyl; n is 1, 2, 3 or 4; and R^2 is an $(n + 1)$ -valent radical of an alkane, aromatic compound, heteroalkane, or any combination thereof such as, for example, an alkylene, arylene, heteroalkylene, or any combinations thereof.

According to still another advantageous aspect, the crosslinking additive for use herein is a multifunctional (meth)acrylate compound selected from the group consisting of 1,6-hexanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, and any combinations or mixtures thereof.

In a particularly advantageous aspect, the pressure sensitive adhesive according to the present disclosure is crosslinked, preferably with actinic radiation, more preferably with e-beam irradiation. According to one preferred aspect, the pressure sensitive adhesive is crosslinked with e-beam irradiation, wherein the e-beam irradiation dose is preferably comprised between 50 kGy and 150 kGy. In a further particular aspect, the e-beam irradiation is performed from both sides so as to get a symmetric irradiation profile within the pressure sensitive adhesive.

In the context of the present disclosure, it has been surprisingly found that crosslinking the pressure sensitive adhesive formulation as described above, in particular with actinic radiation, and preferably with e-beam irradiation, provides a pressure sensitive adhesive characterized with excellent static shear performance both at room temperature and high temperature (e.g., 70°C or even 90°C).

While performing e-beam irradiation based crosslinking, finding a suitable e-beam irradiation dose in conjunction with selecting a suitable e-beam acceleration tension will be well within the practice of those skilled in the art. Suitable acceleration tensions are typically selected and adapted to the coating weight of the corresponding pressure sensitive adhesive formulation layer. Exemplary e-beam acceleration tensions are typically comprised between 140 and 300 kV for pressure sensitive adhesive layers with a coating weight between 25 and 1200g/m². When irradiated from both sides, the pressure sensitive adhesive layers may have a coating weight up to 1800g/m².

Advantageously, the pressure sensitive adhesives of the present disclosure may be crosslinked using an e-beam irradiation dose comprised between 50 kGy and 150 kGy.

According to one particular aspect, the pressure sensitive adhesive according to the present disclosure comprises:

- a) from 20 wt% to 80 wt%, from 20 wt% to 70 wt%, from 25 wt% to 60 wt%, or even from 25 wt% to 50 wt% of the multi-arm block copolymer, based on the weight of the pressure sensitive adhesive;
- b) from 20 wt% to 70 wt%, from 25 wt% to 60 wt%, or even from 25 wt% to 50 wt% of the hydrocarbon tackifier(s), based on the weight of the pressure sensitive adhesive;
- c) from 2 wt% to 20 wt%, from 4 wt% to 15 wt%, or even from 6 wt% to 15 wt% of the polymeric plasticizer, based on the weight of the pressure sensitive adhesive;
- d) optionally, from 3 wt% to 40 wt%, from 5 wt% to 30 wt%, or even from 10 wt% to 25 wt% of linear block copolymer, based on the weight of the pressure sensitive adhesive; and
- e) optionally, from 0.1 wt% to 10 wt%, from 0.5 wt% to 8 wt%, from 1 wt% to 6 wt%, or even from 2 wt% to 5 wt% of a crosslinking additive, based on the weight of the pressure sensitive adhesive foam, and wherein the crosslinking additive is preferably selected from the group of multifunctional (meth)acrylate compounds.

As will be apparent to those skilled in the art in the light of the present disclosure, other additives may optionally be included in the pressure sensitive adhesive to achieve any desired properties. Such additives include, but are not limited to, further tackifiers, pigments, toughening agents, reinforcing agents, fire retardants, antioxidants, polymerization initiators, and various stabilizers. The additives are typically added in amounts sufficient to obtain the desired end properties.

According to a particular aspect, the pressure sensitive adhesive of the present disclosure is a hot melt pressure sensitive adhesive. As used herein, a hot melt pressure sensitive adhesive is a polymer or blended polymeric material with a melt viscosity profile such that it can be coated on a substrate or carrier in a thin layer at a process temperature significantly above normal room temperature, but retains useful pressure-sensitive adhesive characteristics at room temperature.

The pressure-sensitive adhesive compositions of the present disclosure can be manufactured using methods known in the art. As a way of example, they can be made by dissolving the block copolymers, suitable tackifiers, any plasticizer(s), and any other additives in a suitable solvent, creating a solvent-based adhesive. The adhesive may then be coated onto a substrate (e.g., release liner, tape backing, core, or panel) using conventional means (e.g., knife coating, roll coating, gravure coating, rod coating, curtain coating, spray coating, air knife coating). In some aspects, the adhesive is then dried to remove at least some of the solvent. In some advantageous aspects, substantially all of the solvent is removed.

In some alternative executions, the pressure-sensitive adhesive is prepared in a substantially solvent-free process (i.e., the adhesive contain no greater than about 10 wt. % solvent, in some aspects, no greater than about 5 wt. % solvent, and in some aspects no greater than 1 wt. % solvent or even no

greater than trace amounts of solvent (i.e., essentially no solvent). In some aspects, the pressure sensitive adhesive may contain residual solvents, e.g., adhesives may be prepared in solvent, and the solvent is removed prior to subsequent processing, e.g., coating. Generally, the residual solvent is present as no greater than about 5%, in some aspects, no greater than about 1%, or even no greater than trace amounts of solvent (i.e., essentially no solvent). Such substantially solvent-free processes are known and include, e.g., compounding by calendaring or roll milling, and extruding (e.g., single screw, twin screw, disk screw, reciprocating single screw, pin barrel single screw, etc.). Commercially available equipment such as BRABENDER or BANBURY internal mixers are also available to batch mix the adhesive compositions. After compounding, the adhesive may be coated through a die into a desired form, such as a layer of adhesive, or it may be collected for forming at a later time.

In some aspects, solvent-based adhesives may be used. In some aspects, such adhesives comprise at least about 20% by weight solvent, in some aspects, at least about 40% by weight, at least about 50% by weight, or even at least about 60% by weight solvent. Any known method of coating and drying solvent based adhesives may be used.

According to an advantageous aspect, the pressure sensitive adhesive according to the present disclosure is in the form of a layer having a thickness of less than 1500 micrometers (μm), less than 1000 μm , less than 800 μm , less than 600 μm , less than 400 μm , less than 200 μm , less than 150 μm , or even less than 100 μm . Advantageously still, the pressure sensitive adhesive is in the form of a layer having a thickness comprised between 20 and 1500 μm , between 20 and 1000 μm , between 20 and 500 μm , between 30 and 400 μm , between 30 and 250 μm , between 40 and 200 μm , or even between 50 and 150 μm .

The pressure sensitive adhesive of the present disclosure may take the form of a single layer construction, and consist essentially of a pressure sensitive adhesive layer. Such a single pressure sensitive adhesive layer can be advantageously used as double-sided adhesive tape.

According to another aspect, then present disclosure is directed to a multilayer pressure sensitive adhesive assembly comprising a pressure sensitive adhesive as described above and a backing layer adjacent to the pressure sensitive adhesive. The pressure sensitive adhesive assembly according to the present disclosure may have a design or configuration of any suitable kind, depending on its ultimate application and the desired properties, and provided it comprises at least a pressure sensitive adhesive as described above.

According to an exemplary aspect, the pressure sensitive adhesive assembly of the present disclosure may take the form of a multilayer construction comprising two or more superimposed layers, i.e., the first pressure sensitive adhesive layer and adjacent layers such as, for example, a backing layer and/or further pressure sensitive adhesive layers. Such adhesive multilayer constructions or tapes may be advantageously used as a dual-layer adhesive tape to adhere two objects to one another. In that context,

suitable backing layers for use herein may or may not exhibit at least partial pressure sensitive adhesive characteristics.

Accordingly, in one particular aspect, the multilayer pressure sensitive adhesive assembly according to the present disclosure comprises a backing layer having a first major surface and a second major surface; and a first pressure sensitive adhesive skin layer bonded to the first major surface, wherein the first pressure sensitive adhesive skin layer comprises a pressure sensitive adhesive as described above.

In some other executions, the multilayer pressure sensitive adhesive assembly further comprises a second pressure sensitive adhesive skin layer bonded to the second major surface. Such a pressure sensitive adhesive assembly reflects a three-layer design, in which the backing layer may be sandwiched between, for example, two pressure sensitive adhesive layers. In some aspects of the multilayer pressure sensitive adhesive assembly, the first pressure sensitive adhesive skin layer and the second pressure sensitive adhesive skin layer are the same adhesive, and comprise a pressure sensitive adhesive as described above. In some alternative aspects, the first pressure sensitive adhesive skin layer and the second pressure sensitive adhesive skin layer each independently comprise a pressure sensitive adhesive as described above.

In some executions, the multilayer pressure sensitive adhesive assembly according to the present disclosure may advantageously be in the form of a skin/core/skin multilayer assembly, wherein the backing layer is the core layer of the multilayer pressure sensitive adhesive assembly. As used herein, the term “core” may be used interchangeably with the term “backing”.

Any known backing or core may be used herein. Suitable backing layers can be made from plastics (e.g., polypropylene, including biaxially oriented polypropylene, vinyl, polyolefin such as polyethylene, polyurethanes, polyurethane acrylates, polyesters such as polyethylene terephthalate), nonwovens (e.g., papers, cloths, nonwoven scrims), metal foils, foams (e.g., polyacrylic, polyethylene, polyurethane, neoprene), and the like.

According to a preferred aspect of the multilayer pressure sensitive adhesive assembly according to the disclosure, the backing takes the form of a polymeric foam layer. In the context of the present disclosure, the term “polymeric foam” is meant to designate a material based on a polymer and which material comprises voids, typically in an amount of at least 5% by volume, typically from 10% to 80% by volume or from 10% to 65% by volume. The voids may be obtained by any of the known methods such as cells formed by gas. Alternatively, the voids may result from the incorporation of hollow fillers, such as hollow polymeric particles, hollow glass microspheres, hollow ceramic microspheres. According to another alternative aspect, the voids may result from the incorporation of heat expandable microspheres, preferably pentane filled expandable microspheres. The heat expandable microspheres for use herein may be expanded when the polymer melt passes an extrusion die. Polymer mixtures containing expandable microspheres may also be extruded at temperatures below their expansion temperature and expanded in a later step by exposing the tape to temperatures above the expansion

temperature of the microspheres. Alternatively, the voids can result from the decomposition of chemical blowing agents.

A polymeric foam layer typically has a density comprised between 0.30 g/cm³ and 1.5 g/cm³, between 0.35 g/cm³ and 1.10 g/cm³, or even between 0.40 g/cm³ and 0.95 g/cm³. This density is achieved by including voids or cells. Typically, the polymeric foam layer will comprise at least 5% of voids by volume and for example between 15 and 45%, or between 20% and 45% by volume.

The voids or cells in the polymeric foam layer can be created in any of the known manners described in the art and include the use of a gas or blowing agent and/or incorporation of hollow fillers, such as hollow polymeric particles, hollow glass microspheres, hollow ceramic microspheres or expandable microspheres, preferably pentane filled expandable microspheres, into the composition for the polymeric foam layer.

A polymeric foam layer for use herein has for example a thickness comprised between 100 and 6000 micrometers (μm), between 200 and 4000 μm, between 500 and 2000 μm, or even between 800 and 1500 μm. As will be apparent to those skilled in the art, in the light of the present description, the preferred thickness of the polymeric foam layer will be dependent on the intended application.

In some aspects the polymeric foam layer has viscoelastic properties at room temperature. In some other aspects, the foam may comprise a thermoplastic foam. In some other aspects, the foam may comprise a thermoset foam. Exemplary foams are also described in, e.g., the *Handbook of Polymer Foams*, David Eaves, editor, published by Shawbury, Shrewsbury, Shropshire, UK: Rapra Technology, 2004.

Multilayer pressure sensitive adhesive assemblies comprising a backing in the form of a polymeric foam layer, are particularly advantageous when compared to single-layer pressure sensitive adhesives, in that adhesion (quick adhesion) can be adjusted by the formulation of the pressure sensitive adhesive layer (also commonly referred to as the skin layer), while other properties/requirements of the overall assembly such as application issues, deforming issues and energy distribution may be addressed by appropriate formulation of the polymeric foam layer (also commonly referred to as the core layer).

According to a typical aspect of the multilayer pressure sensitive adhesive assembly, the backing layer comprises a polymer base material selected from the group consisting of rubber-based elastomeric materials, polyacrylates, polyurethanes, polyolefins, polyamides, polyesters, polyethers, polyisobutylene, polystyrenes, polyvinyls, polyvinylpyrrolidone, and any combinations, copolymers or mixtures thereof.

In an advantageous aspect, the backing layer comprises a polymer base material selected from the group consisting of rubber-based elastomeric materials. Advantageously, the rubber-based elastomeric material is selected from the group consisting of natural rubbers, synthetic rubbers, thermoplastic elastomeric materials, non-thermoplastic elastomeric materials, thermoplastic hydrocarbon elastomeric materials, non-thermoplastic hydrocarbon elastomeric materials, and any combinations or mixtures thereof.

In some aspects of the multilayer pressure sensitive adhesive assembly, the rubber-based elastomeric material is selected from the group consisting of halogenated butyl rubbers, in particular bromobutyl rubbers and chlorobutyl rubbers; halogenated isobutylene-isoprene copolymers; bromo-isobutylene-isoprene copolymers; chloro-isobutylene-isoprene copolymers; block copolymers; olefinic block copolymers; butyl rubbers; synthetic polyisoprene; ethylene-octylene rubbers; ethylene-propylene rubbers; ethylene-propylene random copolymers; ethylene-propylene-diene monomer rubbers; polyisobutylenes; poly(alpha-olefin); ethylene-alpha-olefin copolymers; ethylene-alpha-olefin block copolymers; styrenic block copolymers; styrene-isoprene-styrene block copolymers; styrene-butadiene-styrene block copolymers; styrene-ethylene-butylene-styrene block copolymers; styrene-ethylene-propylene-styrene block copolymers; styrene-butadiene random copolymers; olefinic polymers and copolymers; ethylene-propylene random copolymers; ethylene-propylene-diene terpolymers, and any combinations or mixtures thereof.

In some preferred aspects, the rubber-based elastomeric material is selected from the group consisting of styrenic block copolymers, and any combinations or mixtures thereof. In a more preferred aspect of the multilayer pressure sensitive adhesive assembly, the rubber-based elastomeric material is selected from the group consisting of styrene-isoprene-styrene block copolymers, styrene-butadiene-styrene block copolymers, styrene-ethylene-butylene-styrene block copolymers, and any combinations or mixtures thereof.

In a still preferred aspect, the rubber-based elastomeric material is selected from the group consisting of styrene-isoprene-styrene block copolymers, styrene-butadiene-styrene block copolymers, and any combinations or mixtures thereof.

In some typical aspects, the backing layer further comprises at least one filler material which is preferably selected from the group consisting of microspheres; expandable microspheres, preferably pentane filled expandable microspheres; gaseous cavities; glass beads; glass microspheres; glass bubbles and any combinations or mixtures thereof; more preferably from the group consisting of expandable microspheres, glass bubbles, and any combinations or mixtures thereof. Preferably, the at least one filler material is selected from the group consisting of expandable microspheres, glass bubbles, and any combinations or mixtures thereof.

In some particular aspects of the pressure sensitive adhesive assembly according to the disclosure, a primer layer may be interposed between the pressure sensitive adhesive layer(s) and the backing (or core) layer. In the context of the present disclosure, any primer compositions commonly known to those skilled in the art may be used. Finding appropriate primer compositions is well within the capabilities of those skilled in the art, in the light of the present disclosure. Useful primers for use herein are described, for example, in U.S. Patent No. 5,677,376 (Groves) and U.S. Patent No. 5,605,964 (Groves), the content of which is herewith incorporated by reference.

In some aspects, the pressure sensitive adhesive assembly according to the present disclosure is crosslinked, preferably with actinic radiation, more preferably with e-beam irradiation. According to one

preferred aspect, the pressure sensitive adhesive assembly is crosslinked with e-beam irradiation, wherein the e-beam irradiation dose is preferably comprised between 50 kGy and 150 kGy.

The thickness of the various pressure sensitive adhesive layer(s) and other optional layer(s) comprised in the pressure sensitive adhesive assembly may vary in wide ranges depending on the desired execution and associated properties. By way of example, the thickness can be independently chosen for each layer between 25 micrometers (μm) and 6000 μm , between 40 μm and 3000 μm , between 50 μm and 3000 μm , between 50 μm and 2000 μm , or even between 50 μm and 1500 μm .

According to the particular execution wherein the multilayer pressure sensitive adhesive assembly takes the form of skin/core type multilayer pressure sensitive adhesive assembly, wherein the backing layer is the core layer of the multilayer pressure sensitive adhesive assembly and the pressure sensitive adhesive layer is the skin layer of the multilayer pressure sensitive adhesive assembly, it is preferred that the pressure sensitive adhesive layer has a lower thickness compared to the backing/core layer. This is particularly advantageous in executions where the multilayer pressure sensitive adhesive assembly takes the form of a polymeric foam pressure sensitive adhesive tape. As a way of example, the thickness of the pressure sensitive adhesive layer may typically be in the range from 20 μm to 250 μm , or even from 40 μm to 200 μm , whereas the thickness of the backing foam layer may typically be in the range from 100 μm to 6000 μm , from 400 μm to 3000 μm , or even from 800 μm to 2000 μm . Such multilayer pressure sensitive adhesive assemblies typically exhibit high peel adhesion. Without wishing to be bound by theory, it is believed such high peel adhesion is caused by a stabilizing effect of the relatively thick polymeric foam layer compared to the pressure sensitive adhesive layer.

According to a particularly advantageous aspect, the pressure sensitive adhesive as described above or the multilayer pressure sensitive adhesive assembly as described above, has a Volatile Organic Compound (VOC) value of less than 2000 ppm, less than 1500 ppm, less than 1000 ppm, less than 800 ppm, less than 600 ppm, less than 500 ppm, less than 400 ppm, or even less than 300 ppm, when measured by thermogravimetric analysis according to the weight loss test method described in the experimental section.

Advantageously still, the pressure sensitive adhesive as described above or the multilayer pressure sensitive adhesive assembly as described above, has a Volatile Organic Compound (VOC) value of less than 2000 ppm, less than 1500 ppm, less than 1000 ppm, less than 800 ppm, less than 600 ppm, less than 500 ppm, less than 400 ppm, or even less than 300 ppm, when measured by thermal desorption analysis according to test method VDA278 (Thermal Desorption Analysis of Organic Emissions for the Characterization of Non-Metallic Materials for Automobiles) from VDA, Association of the German Automobile Industry.

Advantageously still, the pressure sensitive adhesive as described above or the multilayer pressure sensitive adhesive assembly as described above, has a Volatile Fogging Compound (FOG) value of less than 4000 ppm, less than 3000 ppm, less than 2500 ppm, less than 2000 ppm, less than 1500 ppm, less than 1000 ppm, less than 800 ppm, less than 600 ppm, less than 500 ppm, or even less

than 400 ppm, when measured by thermogravimetric analysis according to the weight loss test method described in the experimental section.

Advantageously still, the pressure sensitive adhesive as described above or the multilayer pressure sensitive adhesive assembly as described above, has a Volatile Fogging Compound (FOG) value of less than 4000 ppm, less than 3000 ppm, less than 2500 ppm, less than 2000 ppm, less than 1500 ppm, less than 1000 ppm, less than 800 ppm, less than 600 ppm, less than 500 ppm, or even less than 400 ppm, when measured by thermal desorption analysis according to test method VDA278 (Thermal Desorption Analysis of Organic Emissions for the Characterization of Non-Metallic Materials for Automobiles) from VDA, Association of the German Automobile Industry.

According to another advantageous execution, the pressure sensitive adhesive as described above or the multilayer pressure sensitive adhesive assembly as described above, has a static shear strength value of more than 2000 min, more than 4000 min, more than 6000 min, more than 8000 min, or even more than 10000 min, when measured at 70°C according to the static shear test method described in the experimental section.

According to still another advantageous execution, the pressure sensitive adhesive as described above or the multilayer pressure sensitive adhesive assembly as described above, has a static shear strength value of more than 2000 min, more than 4000 min, more than 6000 min, more than 8000 min, or even more than 10000 min, when measured at 90°C according to the static shear test method described in the experimental section.

The present disclosure is further directed to a method of manufacturing a pressure sensitive adhesive (or a multilayer pressure sensitive adhesive assembly) as described above, which comprises the steps of:

- a) compounding the multi-arm block copolymer, the polymeric plasticizer, at least one hydrocarbon tackifier; optionally, a linear block copolymer, optionally, a crosslinking agent which is preferably selected from the group of multifunctional (meth)acrylate compounds; and wherein the hydrocarbon tackifier(s) have a Volatile Organic Compound (VOC) value of less than 1000 ppm, less than 800 ppm, less than 600 ppm, less than 400 ppm or even less than 200 ppm, when measured by thermogravimetric analysis according to the weight loss test methods described in the experimental section; thereby forming a pressure sensitive adhesive formulation; and
- b) optionally, crosslinking the pressure sensitive adhesive formulation, preferably with actinic radiation, more preferably with e-beam irradiation.

According to an exemplary aspect of the method according to the present disclosure, the method is a solvent-free method. By solvent-free method, it is herein meant to reflect that there is substantially no added solvent during the processing steps of the method of manufacturing the pressure sensitive adhesive.

In a particular aspect, the method of manufacturing a pressure sensitive adhesive comprises a hotmelt processing step, preferably a continuous hotmelt mixing processing step, more preferably a hotmelt extrusion processing step, in particular a twin screw hotmelt extrusion processing step.

According to an advantageous aspect of the method of manufacturing a pressure sensitive adhesive or multilayer pressure sensitive adhesive assembly, the hydrocarbon tackifier(s) and/or the polymeric plasticizer(s), are exposed to minimal heat stress prior to their feeding into the compounding medium. In the context of the present disclosure, it has been indeed found that heat stress at elevated temperatures applied to the hydrocarbon tackifier(s) and/or the polymeric plasticizer(s), for a long period of time may lead to an accelerated thermal and/or oxidative degradation of these ingredients and to the generation of VOCs.

Accordingly, in a preferred aspect of the method of manufacturing a pressure sensitive adhesive or multilayer pressure sensitive adhesive assembly, the hydrocarbon tackifier(s) and the polymeric plasticizer(s), are added to the compounding medium with a drum unloader as feeding equipment.

Alternatively, the hydrocarbon tackifier(s) and/or the polymeric plasticizer(s), are fed into the compounding medium with a single screw feeding extruder. Alternatively still, the hydrocarbon tackifier(s) and/or the polymeric plasticizer(s), are fed into the compounding medium with a kneading equipment having a discharge screw.

According to another advantageous aspect of the method of manufacturing a pressure sensitive adhesive or multilayer pressure sensitive adhesive assembly, the hydrocarbon tackifier(s) and/or the polymeric plasticizer(s) are added into the compounding medium in a solid state by means of volumetric or gravimetric feeders.

In some particular aspects, vacuum is applied to the compounded adhesive melt during the extrusion process. Vacuum can indifferently be applied to the skin compound melt and/or to the core compound melt prior to adding the foaming agent.

According to another exemplary aspect of the method of manufacturing a pressure sensitive adhesive or multilayer pressure sensitive adhesive assembly, a chemical entrainer is added to the compounded adhesive melt and removed later in the extrusion process. Suitable entrainers for use herein are liquids, gases or compounds that release a volatile chemical substance under the action of heat. Advantageously, the used entrainer is capable of entraining further volatiles or last traces of volatiles. Suitable entrainers can be added to the skin PSA melt and or to the core melt and removed later in the extrusion process. In case the entrainer is added to the core compound, the latter is preferably removed before adding the foaming agent.

According to a particular aspect of this method of manufacturing a pressure sensitive adhesive, a precursor of the pressure sensitive adhesive layer is deposited on a substrate and then post cured, preferably with actinic radiation, more preferably with e-beam radiation.

In the context of manufacturing a multilayer pressure sensitive adhesive assembly, the various layers may be prepared separately and subsequently laminated to each other. According to an alternative

exemplary aspect, corresponding precursors of the various layers may be prepared as part of a single process step.

However, the production of the pressure sensitive adhesive and the multilayer pressure sensitive adhesive assembly is not limited to the before mentioned methods. Alternative preparation methods may be easily identified by those skilled in the art, in the light of the present disclosure. As a way of example, the pressure sensitive adhesive or the multilayer pressure sensitive adhesive assembly may be produced by solvent-based methods.

The pressure sensitive adhesive of the present disclosure can be coated/applied upon a variety of substrates to produce adhesive-coated articles. The substrates can be flexible or inflexible and be formed of a polymeric material, paper, glass or ceramic material, metal, or combinations thereof. Suitable polymeric substrates include, but are not limited to, polymeric films such as those prepared from polypropylene, polyethylene, polyvinyl chloride, polyester (polyethylene terephthalate or polyethylene naphthalate), polycarbonate, polymethyl(meth)acrylate (PMMA), cellulose acetate, cellulose triacetate, ethyl cellulose, and polyurethane. Foam backings may be used. Examples of other substrates include, but are not limited to, metal such as stainless steel, metal or metal oxide coated polymeric material, metal or metal oxide coated glass, and the like.

The pressure sensitive adhesives of the present disclosure may be used in any conventionally known article such as labels, tapes, signs, covers, marking indices, display components, touch panels, and the like. Flexible backing materials having microreplicated surfaces are also contemplated.

The pressure sensitive adhesives may be coated/applied on a substrate using any conventional coating techniques modified as appropriate to the particular substrate. For example, pressure sensitive adhesives may be applied/coated to a variety of solid substrates by methods such as roller coating, flow coating, dip coating, spin coating, spray coating knife coating, and die coating. These various methods of coating allow the pressure sensitive adhesives to be placed on the substrate at variable thicknesses thus allowing a wider range of use of the assemblies.

The substrate to which the pressure sensitive adhesive may be applied is selected depending on the particular application. For example, the pressure sensitive adhesive, in particular via its second and/or third pressure sensitive adhesive layer may be applied to sheeting products (e.g., decorative graphics and reflective products), label stock, and tape backings. Additionally, the pressure sensitive adhesive may be applied directly onto other substrates such as a metal panel (e.g., automotive panel) or a glass window so that yet another substrate or object can be attached to the panel or window.

Accordingly, the pressure sensitive adhesive of the present disclosure may find a particular use in the automotive manufacturing industry (e.g., for attachment of exterior trim parts or for weatherstrips), in the construction industry, in the solar panel construction industry, or in the electronic industry (e.g., for the fixation of displays in mobile hand held devices).

As such, the pressure sensitive adhesives according to the present disclosure are particularly suited for (industrial) interior applications, more in particular for construction market applications,

automotive applications or electronic applications. In the context of automotive applications, the pressure sensitive adhesives as described herein may find particular use for adhering, for example, automotive body side mouldings, weather strips or rearview mirrors. The pressure sensitive adhesives according to the present disclosure are particularly suitable for adhesion to substrates/panels painted with automotive paint systems comprising a base electrocoat or a pigmented basecoat, and in particular to clear coat surfaces, in particular clear coats for automotive vehicles. The pressure sensitive adhesives according to the present disclosure are particularly suited for adhesion to low energy surfaces, such as polypropylene, polyethylene or copolymers thereof.

Accordingly, the present disclosure is further directed to the use of a pressure sensitive adhesive or a multilayer pressure sensitive adhesive assembly as described above for industrial applications, preferably for interior (industrial) applications, more preferably for construction market applications, automotive applications or electronic applications.

In some aspects, the pressure sensitive adhesive or the multilayer pressure sensitive adhesive assembly according to the present disclosure may be particularly useful for forming strong adhesive bonds to low surface energy (LSE) substrates.

However, the use of these adhesives is not limited to low surface energy substrates. The pressure sensitive adhesives and multilayer pressure sensitive adhesive assemblies may, in some aspects, surprisingly bond well to medium surface energy (MSE) substrates. Included among such materials are polyamide 6 (PA6), acrylonitrile butadiene styrene (ABS), PC/ABS blends, PC, PVC, PA, polyurethane, PUR, TPE, POM, polystyrene, poly(methyl methacrylate) (PMMA), clear coat surfaces, in particular clear coats for vehicles like a car or coated surfaces for industrial applications and composite materials like fiber reinforced plastics.

Accordingly, the present disclosure is further directed to the use of a pressure sensitive adhesive foam or a pressure sensitive adhesive assembly as above described for the bonding to a low surface energy substrate and/or a medium surface energy substrate.

The pressure sensitive adhesive may also be provided in the form of a pressure-sensitive adhesive transfer tape in which at least one layer of the pressure sensitive adhesive assembly is disposed on a release liner for application to a permanent substrate at a later time. The pressure sensitive adhesive assembly may also be provided as a single coated or double coated tape in which the pressure sensitive adhesive assembly is disposed on a permanent backing. Backings can be made from plastics (e.g., polypropylene, including biaxially oriented polypropylene, vinyl, polyolefin such as polyethylene, polyurethanes, polyurethane acrylates, polyesters such as polyethylene terephthalate), nonwovens (e.g., papers, cloths, nonwoven scrims), metal foils, foams (e.g., polyacrylic, polyethylene, polyurethane, neoprene), and the like. Polymeric foams are commercially available from various suppliers such as 3M Co., Volttek, Sekisui, and others. For a single-sided tape, the pressure sensitive adhesive is applied to one surface of the backing material and a suitable release material is applied to the opposite surface of the backing material. Release materials are known and include materials such as, for example, silicones,

polyolefins, polycarbamates, polyacrylics, and the like. For double coated tapes, the pressure sensitive adhesive is applied to one surface of the backing material and a pressure sensitive adhesive is disposed on the opposite surface of the backing material. Double coated tapes are often carried on a release liner.

Various items are provided that are pressure sensitive adhesives or a multilayer pressure sensitive adhesive assembly.

Item 1 is a pressure sensitive adhesive comprising:

- a) a multi-arm block copolymer of the formula Q_n -Y, wherein:
 - (i) Q represents an arm of the multi-arm block copolymer and each arm independently has the formula G-R,
 - (ii) n represents the number of arms and is a whole number of at least 3, and
 - (iii) Y is the residue of a multifunctional coupling agent,wherein each R is a rubbery block comprising a polymerized conjugated diene, a hydrogenated derivative of a polymerized conjugated diene, or any combinations thereof; and each G is a glassy block comprising a polymerized monovinyl aromatic monomer;
- b) a polymeric plasticizer having a weight average molecular weight M_w of at least 10,000 g/mol;
- c) at least one hydrocarbon tackifier, wherein the hydrocarbon tackifier(s) have a Volatile Organic Compound (VOC) value of less than 1000 ppm, when measured by thermogravimetric analysis according to the weight loss test methods described in the experimental section; and
- d) optionally, a linear block copolymer of the formula L-(G)_m, wherein L is a rubbery block comprising a polymerized olefin, a polymerized conjugated diene, a hydrogenated derivative of a polymerized conjugated diene, or any combinations thereof; and wherein m is 1 or 2.

Item 2 is the pressure sensitive adhesive of item 1, wherein the hydrocarbon tackifier(s) have a Volatile Organic Compound (VOC) value of less than 800 ppm, less than 600 ppm, less than 400 ppm or even less than 200 ppm, when measured by thermogravimetric analysis according to the weight loss test method described in the experimental section.

Item 3 is a pressure sensitive adhesive according to item 1 or 2, wherein the hydrocarbon tackifier(s) have a Volatile Fogging Compound (FOG) value of less than 1500 ppm, less than 1000 ppm, less than 800 ppm, less than 600 ppm, or even less than 500 ppm, when measured by thermogravimetric analysis according to the weight loss test methods described in the experimental section.

Item 4 is a pressure sensitive adhesive according to any one of the preceding items, wherein the hydrocarbon tackifier(s) have an outgassing value of less than 1 wt%, less than 0.8 wt%, less than 0.6 wt%, less than 0.5 wt%, less than 0.4 wt%, less than 0.3 wt%, less than 0.2 wt% or even less than 0.1

wt%, when measured by weight loss analysis according to the oven outgassing test method described in the experimental section.

Item 5 is a pressure sensitive adhesive according to any one of the preceding items, wherein the polymeric plasticizer has a weight average molecular weight M_w of at least 20.000 g/mol, at least 30.000 g/mol, or even at least 50.000 g/mol.

Item 6 is a pressure sensitive adhesive according to any one of the preceding items, wherein the polymeric plasticizer has a weight average molecular weight M_w of 100.000 g/mol or less, less than 90.000 g/mol, less than 80.000 g/mol, less than 70.000 g/mol, less than 60.000 g/mol, less than 50.000 g/mol, or even less than 40.000 g/mol.

Item 7 is a pressure sensitive adhesive according to any one of the preceding items, wherein the polymeric plasticizer has a weight average molecular weight M_w comprised between 30.000 g/mol and 80.000 g/mol or even between 30.000 g/mol and 60.000 g/mol.

Item 8 is a pressure sensitive adhesive according to any one of the preceding items, wherein the polymeric plasticizer(s), have a Volatile Organic Compound (VOC) value of less than 1000 ppm, less than 800 ppm, less than 600 ppm, less than 400 ppm or even less than 200 ppm, when measured by thermogravimetric analysis according to the weight loss test methods described in the experimental section.

Item 9 is a pressure sensitive adhesive according to any one of the preceding items, wherein the polymeric plasticizer(s), have a Volatile Fogging Compound (FOG) value of less than 2500 ppm, less than 2000 ppm, less than 1500 ppm, less than 1000 ppm, less than 800 ppm, less than 600 ppm, or even less than 500 ppm, when measured by thermogravimetric analysis according to the weight loss test method described in the experimental section.

Item 10 is a pressure sensitive adhesive according to any one of the preceding items, wherein the polymeric plasticizer(s), have an outgassing value of less than 1 wt%, less than 0.8 wt%, less than 0.6 wt%, less than 0.5 wt%, less than 0.4 wt%, less than 0.3 wt%, less than 0.2 wt% or even less than 0.1 wt%, when measured by weight loss analysis according to the oven outgassing test method described in the experimental section.

Item 11 is a pressure sensitive adhesive according to any one of the preceding items, wherein the polymeric plasticizer is a polyisobutylene plasticizer.

Item 12 is a pressure sensitive adhesive according to any one of the preceding items, wherein the multi-arm block copolymer is a star block copolymer.

Item 13 is a pressure sensitive adhesive according to item 8, wherein the multi-arm block copolymer is a polymodal, asymmetric star block copolymer.

Item 14 is a pressure sensitive adhesive according to any one of the preceding items, wherein the rubbery block of the linear block copolymer comprises an olefin selected to be isobutylene or a conjugated diene selected from the group consisting of isoprene, butadiene, and any combinations thereof.

Item 15 is a pressure sensitive adhesive according to any one of the preceding items, wherein the rubbery block of the linear block copolymer comprises a conjugated diene selected from the group consisting of isoprene, butadiene, and any combinations thereof.

Item 16 is a pressure sensitive adhesive according to any one of the preceding items, wherein at least one of the rubbery blocks of the multi-arm block copolymer comprises a conjugated diene selected from the group consisting of isoprene, butadiene, and any combinations thereof, preferably wherein each of the rubbery blocks of the multi-arm block copolymer comprises a conjugated diene selected from the group consisting of isoprene, butadiene, and any combinations thereof.

Item 17 is a pressure sensitive adhesive according to any one of the preceding items, wherein at least one glassy block of the linear block copolymer is a mono vinyl aromatic monomer selected from the group consisting of styrene, styrene-compatible blends, and any combinations thereof.

Item 18 is a pressure sensitive adhesive according to any one of the preceding items, wherein at least one of the glassy blocks of the multi-arm block copolymer is a monovinyl aromatic monomer selected from the group consisting of styrene, styrene-compatible blends, and any combinations thereof, preferably wherein each of the glassy blocks of the multi-arm block copolymer is a monovinyl aromatic monomer selected from the group consisting of styrene, styrene-compatible blends, and any combinations thereof.

Item 19 is a pressure sensitive adhesive according to any one of the preceding items, wherein the linear block copolymer comprises two glassy blocks.

Item 20 is a pressure sensitive adhesive according to any one of the preceding items, wherein the linear block copolymer is selected from the group consisting of styrene-isoprene-styrene, styrene-butadiene-styrene, styrene-ethylene-butylene-styrene, styrene-isobutylene-styrene, styrene-ethylene-propylene-styrene, and any combinations thereof.

Item 21 is a pressure sensitive adhesive according to any one of the preceding items, wherein at least one arm of the multi-arm block copolymer is selected from the group consisting of styrene-isoprene-styrene, styrene-butadiene-styrene, styrene-ethylene-butylene-styrene, styrene-ethylene-propylene-styrene, and combinations thereof, preferably wherein each arm of the multi-arm block copolymer is selected from the group consisting of styrene-isoprene-styrene, styrene-butadiene-styrene, styrene-ethylene-butylene-styrene, styrene-ethylene-propylene-styrene, and any combinations thereof.

Item 22 is a pressure sensitive adhesive according to any one of the preceding items, which comprises a first hydrocarbon tackifier having a Volatile Organic Compound (VOC) value of less than 1000 ppm, when measured by thermogravimetric analysis according to the weight loss test methods described in the experimental section, wherein the first hydrocarbon tackifier has preferably a T_g of at least 60°C, and wherein preferably the first hydrocarbon tackifier is primarily compatible with the rubbery blocks.

Item 23 is a pressure sensitive adhesive according to any one of the preceding items, which further comprises a second hydrocarbon tackifier having a Volatile Organic Compound (VOC) value of

less than 1000 ppm, when measured by thermogravimetric analysis according to the weight loss test methods described in the experimental section, wherein the second hydrocarbon tackifier has preferably a Tg of at least 60°C, and wherein preferably the second hydrocarbon tackifier is primarily compatible with the glassy blocks.

Item 24 is a pressure sensitive adhesive according to item 22 or 23, wherein the first and/or the second hydrocarbon tackifier has a Tg of at least 65°C.

Item 25 is a pressure sensitive adhesive according to any one of items 22 to 24, wherein the first and/or the second hydrocarbon tackifier has a softening point of at least about 115°C, preferably, at least about 120°C.

Item 26 is a pressure sensitive adhesive according to any one of items 22 to 25, wherein the first hydrocarbon tackifier is selected from the group consisting of polymeric terpenes, hetero-functional terpenes, coumarone-indene resins, esters of rosin acids, disproportionated rosin acid esters, hydrogenated rosin acids, C5 aliphatic resins, C9 hydrogenated aromatic resins, C5/C9 aliphatic/aromatic resins, dicyclopentadiene resins, hydrogenated hydrocarbon resins arising from C5/C9 and dicyclopentadiene precursors, hydrogenated styrene monomer resins, and blends thereof.

Item 27 is a pressure sensitive adhesive according to any one of items 22 to 26, wherein the second hydrocarbon tackifier is selected from the group consisting of coumarone-indene resins, rosin acids, esters of rosin acids, disproportionated rosin acid esters, C9 aromatics, styrene, alpha-methyl styrene, pure monomer resins and C9/C5 aromatic-modified aliphatic hydrocarbons, and blends thereof.

Item 28 is a pressure sensitive adhesive according to any one of the preceding items, wherein the number of arms of the multi-arm block copolymer, n, is a whole number from 3 to 5, inclusive, preferably wherein n is 4.

Item 29 is a pressure sensitive adhesive according to any one of the preceding items, wherein the ratio of the total weight of all block copolymers to the total weight of all hydrocarbon tackifiers ranges from 2.4:1 to 1:2.4, from 2:1 to 1:2, from 1.5:1 to 1:1.5, from 1.2:1 to 1:1.2, from 1.15:1 to 1:1.15, or even from 1.1:1 to 1:1.1.

Item 30 is a pressure sensitive adhesive according to any one of the preceding items, wherein the total amount of the polymeric plasticizer is of no greater than 20 wt%, no greater than 18 wt%, no greater than 15 wt%, or even no greater than 12 wt%, expressed as a percent by weight based on the total weight of the pressure sensitive adhesive.

Item 31 is a pressure sensitive adhesive according to any one of the preceding items, wherein the total amount of the polymeric plasticizer is of no less than 6 wt%, or even no less than 7 wt%, expressed as a percent by weight based on the total weight of the pressure sensitive adhesive.

Item 32 is a pressure sensitive adhesive according to any one of the preceding items, wherein the total amount of the polymeric plasticizer is comprised between 2 and 20 wt%, between 4 and 15 wt%, or even between 6 and 15 wt%, expressed as a percent by weight based on the total weight of the pressure sensitive adhesive.

Item 33 is a pressure sensitive adhesive according to any one of the preceding items, which further comprises a crosslinking additive, which is preferably activated with actinic radiation, more preferably with e-beam irradiation.

Item 34 is a pressure sensitive adhesive according to item 33, wherein the crosslinking additive is selected from the group of multifunctional (meth)acrylate compounds.

Item 35 is a pressure sensitive adhesive according to any one of the preceding items, which further comprises a multifunctional (meth)acrylate compound, wherein the multifunctional (meth)acrylate compound preferably comprises at least two (meth)acryloyl groups, in particular three or four (meth)acryloyl groups, more in particular three (meth)acryloyl groups.

Item 36 is a pressure sensitive adhesive according to any one of the preceding items, which is crosslinked, preferably with actinic radiation, more preferably with e-beam irradiation.

Item 37 is a pressure sensitive adhesive according to any one of the preceding items, which is free of any filler material selected from the group consisting of microspheres, expandable microspheres, preferably pentane filled expandable microspheres, expanded microspheres, gaseous cavities, glass beads, glass microspheres, glass bubbles and any combinations or mixtures thereof.

Item 38 is a pressure sensitive adhesive according to any one of the preceding items, which comprises:

- a) from 20 wt% to 80 wt%, from 20 wt% to 70 wt%, from 25 wt% to 60 wt%, or even from 25 wt% to 50 wt% of the multi-arm block copolymer, based on the weight of the pressure sensitive adhesive;
 - b) from 20 wt% to 70 wt%, from 25 wt% to 60 wt%, or even from 25 wt% to 50 wt% of the hydrocarbon tackifier(s), based on the weight of the pressure sensitive adhesive;
 - c) from 2 wt% to 20 wt%, from 4 wt% to 15 wt%, or even from 6 wt% to 15 wt% of the polymeric plasticizer, based on the weight of the pressure sensitive adhesive;
 - d) optionally, from 3 wt% to 40 wt%, from 5 wt% to 30 wt%, or even from 10 wt% to 25 wt% of linear block copolymer, based on the weight of the pressure sensitive adhesive;
- and

optionally, from 0.1 wt% to 10 wt%, from 0.5 wt% to 8 wt%, from 1 wt% to 6 wt%, or even from 2 wt% to 5 wt% of a crosslinking additive, based on the weight of the pressure sensitive adhesive foam, and wherein the crosslinking additive is preferably selected from the group of multifunctional (meth)acrylate compounds.

Item 39 is a pressure sensitive adhesive according to any one of the preceding items, which is a hot melt adhesive.

Item 40 is a pressure sensitive adhesive according to any one of the preceding items, which is a solvent-based adhesive.

Item 41 is a pressure sensitive adhesive according to any one of the preceding items, in the form of layer having a thickness of less than 1500 μm , less than 1000 μm , less than 800 μm , less than 600 μm , less than 400 μm , less than 200 μm , less than 150 μm , or even less than 100 μm .

Item 42 is a pressure sensitive adhesive according to any one of the preceding items, in the form of layer having a thickness comprised between 20 and 1500 μm , between 20 and 1000 μm , between 20 and 500 μm , between 30 and 400 μm , between 30 and 250 μm , between 40 and 200 μm , or even between 50 and 150 μm .

Item 43 is a multilayer pressure sensitive adhesive assembly comprising a pressure sensitive adhesive according to any one of the preceding items and a backing layer adjacent to the pressure sensitive adhesive.

Item 44 is a multilayer pressure sensitive adhesive assembly according to item 43, comprising a backing layer having a first major surface and a second major surface; and a first pressure sensitive adhesive skin layer bonded to the first major surface, wherein the first pressure sensitive adhesive skin layer comprises a pressure sensitive adhesive according to any one of items 1 to 42.

Item 45 is a multilayer pressure sensitive adhesive assembly according to item 44, which further comprises a second pressure sensitive adhesive skin layer bonded to the second major surface.

Item 46 is a multilayer pressure sensitive adhesive assembly according to item 45, wherein the first pressure sensitive adhesive skin layer and the second pressure sensitive adhesive skin layer are the same adhesive.

Item 47 is a multilayer pressure sensitive adhesive assembly according to item 46, wherein the first pressure sensitive adhesive skin layer and the second pressure sensitive adhesive skin layer each independently comprise a pressure sensitive adhesive according to any one of items 1 to 42.

Item 48 is a multilayer pressure sensitive adhesive assembly according to any one of items 45 to 47, which is in the form of a skin/core/skin multilayer pressure sensitive adhesive assembly, wherein the backing layer is the core layer of the multilayer pressure sensitive adhesive assembly.

Item 49 is a multilayer pressure sensitive adhesive assembly according to any one of items 43 to 48, wherein the backing is a foam backing.

Item 50 is a multilayer pressure sensitive adhesive assembly according to any one of items 43 to 49, wherein the backing layer comprises a polymer base material selected from the group consisting of rubber-based elastomeric materials, polyacrylates, polyurethanes, polyolefins, polyamides, polyesters, polyethers, polyisobutylene, polystyrenes, polyvinyls, polyvinylpyrrolidone, and any combinations, copolymers or mixtures thereof.

Item 51 is a multilayer pressure sensitive adhesive assembly according to item 50, wherein the backing layer comprises a polymer base material selected from the group consisting of rubber-based elastomeric materials.

Item 52 is a multilayer pressure sensitive adhesive assembly according to item 51, wherein the rubber-based elastomeric material is selected from the group consisting of natural rubbers, synthetic rubbers, thermoplastic elastomeric materials, non-thermoplastic elastomeric materials, thermoplastic hydrocarbon elastomeric materials, non-thermoplastic hydrocarbon elastomeric materials, and any combinations or mixtures thereof.

Item 53 is a multilayer pressure sensitive adhesive assembly according to item 51 or 52, wherein the rubber-based elastomeric material is selected from the group consisting of halogenated butyl rubbers, in particular bromobutyl rubbers and chlorobutyl rubbers; halogenated isobutylene-isoprene copolymers; bromo-isobutylene-isoprene copolymers; chloro-isobutylene-isoprene copolymers; block copolymers; olefinic block copolymers; butyl rubbers; synthetic polyisoprene; ethylene-octylene rubbers; ethylene-propylene rubbers; ethylene-propylene random copolymers; ethylene-propylene-diene monomer rubbers; polyisobutylenes; poly(alpha-olefin); ethylene-alpha-olefin copolymers; ethylene-alpha-olefin block copolymers; styrenic block copolymers; styrene-isoprene-styrene block copolymers; styrene-butadiene-styrene block copolymers; styrene-ethylene-butylene-styrene block copolymers; styrene-ethylene-propylene-styrene block copolymers; styrene-butadiene random copolymers; olefinic polymers and copolymers; ethylene-propylene random copolymers; ethylene-propylene-diene terpolymers, and any combinations or mixtures thereof.

Item 54 is a multilayer pressure sensitive adhesive assembly according to any one of items 51 to 53, wherein the rubber-based elastomeric material is selected from the group consisting of styrene-isoprene-styrene block copolymers, styrene-butadiene-styrene block copolymers, styrene-ethylene-butylene-styrene block copolymers, and any combinations or mixtures thereof.

Item 55 is a multilayer pressure sensitive adhesive assembly according to any one of items 51 to 53, wherein the rubber-based elastomeric material is selected from the group consisting of styrene-isoprene-styrene block copolymers, styrene-butadiene-styrene block copolymers, styrene-isobutylene-styrene block copolymers, and any combinations or mixtures thereof.

Item 56 is a multilayer pressure sensitive adhesive assembly according to any one of items 51 to 55, wherein the backing layer further comprises at least one filler material which is preferably selected from the group consisting of microspheres; expandable microspheres, preferably pentane filled expandable microspheres; expanded microspheres; gaseous cavities; glass beads; glass microspheres; glass bubbles and any combinations or mixtures thereof; more preferably from the group consisting of expandable microspheres, glass bubbles, and any combinations or mixtures thereof.

Item 57 is a multilayer pressure sensitive adhesive assembly according to item 56, wherein the at least one filler material is selected from the group consisting of expandable microspheres, expanded microspheres, glass bubbles, and any combinations or mixtures thereof.

Item 58 is a pressure sensitive adhesive or a multilayer pressure sensitive adhesive assembly according to any one of the preceding items, which has a Volatile Organic Compound (VOC) value of less than 2000 ppm, less than 1500 ppm, less than 1000 ppm, less than 800 ppm, less than 600 ppm, less

than 500 ppm, less than 400 ppm, or even less than 300 ppm, when measured by thermogravimetric analysis according to the weight loss test method described in the experimental section.

Item 59 is a pressure sensitive adhesive or a multilayer pressure sensitive adhesive assembly according to any one of the preceding items, which has a Volatile Organic Compound (VOC) value of less than 2000 ppm, less than 1500 ppm, less than 1000 ppm, less than 800 ppm, less than 600 ppm, less than 500 ppm, less than 400 ppm, or even less than 300 ppm, when measured by thermal desorption analysis according to test method VDA278.

Item 60 is a pressure sensitive adhesive or a multilayer pressure sensitive adhesive assembly according to any one of the preceding items, which has a Volatile Fogging Compound (FOG) value of less than 4000 ppm, less than 3000 ppm, less than 2500 ppm, less than 2000 ppm, less than 1500 ppm, less than 1000 ppm, less than 800 ppm, less than 600 ppm, less than 500 ppm, or even less than 400 ppm, when measured by thermogravimetric analysis according to the weight loss test method described in the experimental section.

Item 61 is a pressure sensitive adhesive or a multilayer pressure sensitive adhesive assembly according to any one of the preceding items, which has a Volatile Fogging Compound (FOG) value of less than 4000 ppm, less than 3000 ppm, less than 2500 ppm, less than 2000 ppm, less than 1500 ppm, less than 1000 ppm, less than 800 ppm, less than 600 ppm, less than 500 ppm, or even less than 400 ppm, when measured by thermal desorption analysis according to test method VDA278.

Item 62 is a pressure sensitive adhesive or a multilayer pressure sensitive adhesive assembly according to any one of the preceding items, which has a static shear strength value of more than 2000 min, more than 4000 min, more than 6000 min, more than 8000 min, or even more than 10000 min, when measured at 70°C according to the static shear test method described in the experimental section.

Item 63 is a pressure sensitive adhesive or a multilayer pressure sensitive adhesive assembly according to any one of the preceding items, which has a static shear strength value of more than 2000 min, more than 4000 min, more than 6000 min, more than 8000 min, or even more than 10000 min, when measured at 90°C according to the static shear test method described in the experimental section.

Item 64 is a method of manufacturing a pressure sensitive adhesive (or a multilayer pressure sensitive adhesive assembly) according to any one of items 1 to 63, which comprises the steps of:

- a) compounding the multi-arm block copolymer, the polymeric plasticizer, at least one hydrocarbon tackifier; optionally, a linear block copolymer, optionally, a crosslinking agent which is preferably selected from the group of multifunctional (meth)acrylate compounds; and wherein the hydrocarbon tackifier(s) have a Volatile Organic Compound (VOC) value of less than 1000 ppm, less than 800 ppm, less than 600 ppm, less than 400 ppm or even less than 200 ppm, when measured by thermogravimetric analysis according to the weight loss test methods described in the experimental section; thereby forming a pressure sensitive adhesive formulation; and

b) optionally, crosslinking the pressure sensitive adhesive formulation, preferably with actinic radiation, more preferably with e-beam irradiation.

Item 65 is a method according to item 64, which is a solvent-free method.

Item 66 is a method according to any one of item 64 or 65, which comprises a hotmelt processing step, preferably a continuous hotmelt mixing processing step, more preferably a hotmelt extrusion processing step, in particular a twin screw hotmelt extrusion processing step.

Item 67 is a method for manufacturing a multilayer pressure sensitive adhesive assembly according to any one of items 64 to 66, which comprises the step of hotmelt extruding the backing layer, wherein the backing layer is preferably a foam backing.

Item 68 is a method according to item 67, whereby a first pressure sensitive adhesive skin layer is bonded to the first major surface of the backing layer immediately after hotmelt extruding the backing layer.

Item 69 is a method according to item 68, whereby a second pressure sensitive adhesive skin layer is bonded to the second major surface of the backing layer immediately after hotmelt extruding the backing layer, and preferably simultaneously with the step of bonding the first pressure sensitive adhesive skin layer to the first major surface of the backing layer.

Item 70 is the use of a pressure sensitive adhesive or a multilayer pressure sensitive adhesive assembly according to any one of items 1 to 63 for industrial applications, preferably for interior applications, more preferably for construction market applications, automotive applications or electronic applications.

Item 71 is the use of a pressure sensitive adhesive or a multilayer pressure sensitive adhesive assembly according to any one of items 1 to 63 for the bonding to a low surface energy substrate and/or a medium surface energy substrate.

EXAMPLES

The present disclosure is further illustrated by the following examples. These examples are merely for illustrative purposes only and are not meant to be limiting on the scope of the appended claims.

Test Methods applied:

TGA test method

The TGA (Thermogravimetric Analysis) measurements are performed with a Q5000IR equipment from Texas Instruments. The samples are weighed in a platinum pan and placed with an auto sampler in the oven of the apparatus. The nitrogen flow through the oven is 25mL/min, the nitrogen flow through the balance is 10mL/min. The temperature is equilibrated at 30°C and is held for 15 minutes. Then the temperature is increased to 90°C with a ramp of 60°C/min. The 90°C are then held for

30 minutes. In a next step, the temperature is increased to 120°C with a ramp of 60°C/min. The 120°C are held for 60 minutes. The weight losses during 30 minutes at 90°C (VOC analysis) and during 60 minutes at 120°C (FOG analysis) are recorded.

The test is then completed by increasing the temperature to 800°C with a ramp of 10°C/min. Then, the temperature is equilibrated at 600°C, the oven is purged with air and the temperature is increased to 900°C with a ramp of 10°C/min.

Oven Outgassing test method

A measure for the outgassing of raw material samples is accomplished by weighing 10 g of the selected raw material into an aluminum cup with a precision of 0.1 mg. Prior to this step, the aluminum cup is already weighed out with a precision in the range of 0.1 mg. The weighed-in test sample is then placed into a forced air oven for 2 hours at 120°C or 2 hours at 160°C. Once the sample is removed from the oven, it is allowed to cool at ambient temperature (23°C +/- 2°C) for 30 minutes before weighing the filled aluminum cup again. The weight loss of the sample before and after oven drying is calculated and recorded in %.

Thermal desorption analysis of organic emissions according to VDA test method 278

VDA method 278 is a test method used for the determination of organic emissions from non-metallic trim components used to manufacture the interior of motor vehicles (VDA stands for “Verband der Automobilindustrie”, the German Association of Automobilists). The method classifies the emitted organic compounds into two groups:

VOC value – the sum of volatile and semi-volatile compounds up to n-C₂₅ and

FOG value – the sum of the semi-volatile and heavy compounds from n-C₁₄ to n-C₃₂

For measuring the VOC and FOG values, adhesive samples of 30mg +/- 5mg are weighed directly into empty glass sample tubes. The volatile and semi-volatile organic compounds are extracted from the samples into the gas stream and are then re-focused onto a secondary trap prior to injection into a GC for analysis. An automated thermal desorber (Markes International Ultra-UNITY system) is hereby used for the VDA 278 testing.

The test method comprises two extraction stages:

- 1) VOC analysis, which involves desorbing the sample at 90°C for 30 minutes to extract VOCs up to n-C₂₅. This is followed by a semi-quantitative analysis of each compound as µg toluene equivalents per gram of sample.
- 2) FOG analysis, which involves desorbing the sample at 120°C for 60 minutes to extract semi-volatile compounds ranging from n-C₁₄ to n-C₃₂. This is followed by semi-quantitative analysis of each compound as µg hexadecane equivalents per gram of sample.

The VOC values expressed are the average of two measurements per sample. The higher value of the measurements is indicated as the result, as described in the VDA278 test method. In order to

determine the FOG value, the second sample is retained in the desorption tube after the VOC analysis and reheated to 120°C for 60 minutes.

90°-Peel-test at 300 mm/min (according to FINAT Test Method No. 2, 8th edition 2009)

90° Peel Test for single layer pressure sensitive adhesive films

The pressure sensitive adhesive films are laminated prior to testing on a 50 µm thick PET backing (commercially available as Hostaphan RN 50). The hereby obtained pressure sensitive adhesive strips are cut out in the machine direction from the pressure sensitive adhesive film sample material to provide test strips with a width of 12.7 mm and a length > 120 mm.

For test sample preparation, the adhesive coated side of each PSA assembly strip is placed, after the liner is removed, with its adhesive side down on a clean test panel using light finger pressure. Next, the test samples are rolled twice with a standard FINAT test roller (weight 2 kg) at a speed of approximately 10 mm per second to obtain intimate contact between the adhesive mass and the surface. After applying the pressure sensitive adhesive assembly strips to the test panel, the test samples are allowed to dwell for 24 hours at ambient room temperature (23°C +/- 2°C, 50% relative humidity +/-5%) prior to testing.

For peel testing, the test samples are in a first step clamped in the lower movable jaw of a Zwick tensile tester (Model Z020 commercially available from Zwick/Roell GmbH, Ulm, Germany). The pressure sensitive adhesive film strips are folded back at an angle of 90° and their free ends grasped in the upper jaw of the tensile tester in a configuration commonly utilized for 90° measurements. The tensile tester is set at 300 mm per minute jaw separation rate. Test results are expressed in Newton per 12.7 mm or Newton per 0.5 inch (N/12.7mm or N/0.5in). The quoted peel values are the average of two 90°-peel measurements.

90°-Peel for multilayer pressure sensitive adhesive assemblies

Multilayer pressure sensitive adhesive assembly strips according to the present invention and having a width of 10 mm and a length > 120 mm are cut out in the machine direction from the sample material.

For test sample preparation, the liner is first removed from the one adhesive side and placed on an aluminum strip having the following dimension 22 x 1.6 cm, 0.13 mm thickness. Then, the adhesive coated side of each PSA assembly strip is placed, after the liner is removed, with its adhesive side down on a clean test panel using light finger pressure. Next, the test samples are rolled twice with a standard FINAT test roller (weight 6.8 kg) at a speed of approximately 10 mm per second to obtain intimate contact between the adhesive mass and the surface. After applying the pressure sensitive adhesive assembly strips to the test panel, the test samples are allowed to dwell for 24 hours at ambient room temperature (23°C +/- 2°C, 50% relative humidity +/-5%) prior to testing.

For peel testing, the test samples are in a first step clamped in the lower movable jaw of a Zwick tensile tester (Model Z020 commercially available from Zwick/Roell GmbH, Ulm, Germany). The multilayer pressure sensitive adhesive film strips are folded back at an angle of 90° and their free ends grasped in the upper jaw of the tensile tester in a configuration commonly utilized for 90° measurements. The tensile tester is set at 300 mm per minute jaw separation rate. Test results are obtained in Newton per 10 mm (N/10 mm) and converted in Newton per half inch (N/0.5in or N/12.7mm) for comparison purpose with the single layer pressure sensitive adhesive constructions. The quoted peel values are the average of two 90°-peel measurements.

Static Shear-Test @ RT with 500g (according to FINAT Test Method 8, 8th edition 2009)

The test is carried out at ambient room temperature (23°C +/- 2°C and 50% +/- 5% relative humidity). The pressure sensitive adhesive films according to the disclosure are laminated on a 50 µm thick PET backing (commercially available as Hostaphan RN50). Test specimens are cut out of the sample material having a dimension of 13 mm by 175 mm. The liner is then removed and the adhesive strips are adhered onto Ceramic Clear 5 (CC5) plates with an overlap of 12.7 x 25.4 mm. A loop is prepared at the end of the test strip in order to hold the specified weight. Next, the test samples are rolled down four times with a standard FINAT test roller (weight 2 kg) at a speed of approximately 10 mm per second to obtain intimate contact between the adhesive mass and the surface. After applying the pressure sensitive adhesive assembly strips to the test panel, the test samples are allowed to dwell for 24 hours at ambient room temperature (23°C +/- 2°C, 50% relative humidity +/-5%) prior to testing.

Each sample is then placed into a vertical shear-stand (+2° disposition) providing automatic time logging. A 500g weight is hung into the loop. The time until failure is measured and recorded in minutes. Target value is 10,000 minutes. Two samples are measured for each construction. A recorded time of “>10000” indicates that the adhesive did not fail after 10,000 minutes.

Static shear test @ 70°C or 90°C with 500g (FINAT Test Method No. 8, 8th edition 2009)

The test is carried out at 70°C or 90°C. The pressure sensitive adhesive film is laminated on a 50 µm thick PET backing (commercially available as Hostaphan RN50). Test specimens are cut out of the sample material having a dimension of 13 mm by 175 mm. The liner is then removed and the adhesive strips are adhered onto Ceramic Clear 5 (CC5) plates with an overlap of 12.7 x 25.4 mm. A loop is prepared at the end of the test strip in order to hold the specified weight. Next, the test samples are rolled down four times with a standard FINAT test roller (weight 2 kg) at a speed of approximately 10 mm per second to obtain intimate contact between the adhesive mass and the surface. After applying the pressure sensitive adhesive assembly strips to the test panel, the test samples are allowed to dwell for 24 hours at ambient room temperature (23°C +/- 2°C, 50% relative humidity +/-5%) prior to testing.

Each sample is then placed into a vertical shear-stand (+2° disposition) at 70°C or 90°C provided with automatic time logging. After 10 minutes dwell time in the oven, a 500g weight is hung into the loop. The time until failure is measured and recorded in minutes. Target value is 10,000 minutes. Two samples are measured for each construction. A recorded time of “>10000” indicates that the adhesive did not fail after 10,000 minutes.

Test Substrates used for testing:

The multilayer pressure sensitive adhesives and assemblies according to the present disclosure are tested for their adhesive properties on following substrates:

PP: polypropylene plate (“Kunststoffprüfkörper PP nature”; Fabrikat Simona HWST; 150cm x 50 x 2 mm), available from Rocholl GmbH, Aglatershausen, Germany.

Prior to testing, the PP substrates are cleaned as follows: the PP panels are cleaned first with a dry tissue applied with gentle force to remove any residuals / waxy compounds on the surface and then cleaned with a mixture of isopropyl alcohol: distilled water (1:1) and dried with a tissue.

The adhesive tests are further carried out on the following automotive clear coat panels:

UreGloss clear coat coated panels available from BASF Coatings.

CeramiClear5 (“CC5”) coated panels available from PPG Industries.

The upper listed automotive clear coats include acrylic resins and polyesters used alone or with mixtures of copolymers comprising hydroxy- or glycidyl-functionalities or carbamate acid residues (groups); or copolymers of acrylic acid and methacrylic acid esters with hydroxyl groups, free acid groups and further co-monomers (e.g., styrene). Panels are cut prior to 90 °peel and shear testing to the requested dimension. Before testing, the automotive clear coat coated panels are cleaned with a 1:1 mixture of isopropyl alcohol and distilled water. Test panels are then wiped dry with a paper tissue.

Raw materials used:

The raw materials and commercial adhesive tapes used are summarized in Table 1 below.

Name	Description	Supplier
ACX 7065	Black Acrylic foam tape with a thickness of 1200µm	Tesa
Kraton D1340	Polymodal asymmetric SIS star block copolymer	Kraton Polymers
Kraton D1116	Branched SBS (Styrene-Butadiene) _n block copolymer with 23% Styrene	Kraton Polymers
Kraton D1102	Linear SBS (Styrene-Butadiene-Styrene) triblock copolymer with 29% Styrene and a diblock content of 17%	Kraton Polymers

Kraton D1161	Linear SIS (Styrene-Isoprene-Styrene) triblock copolymer (15% Styrene, 19% Diblock)	Kraton Polymers
Escorez 1304	Aliphatic hydrocarbon resin	Exxon Mobil
Escorez 5615	Aliphatic/aromatic hydrocarbon resin, mid block tackifier	ExxonMobil
Regalite R9100	Partially hydrogenated resin	Eastman
Regalite R1090	Fully hydrogenated resin	Eastman
Regalite 1125	Fully hydrogenated, low molecular weight resin	Eastman
Piccotac 1020E	Liquid aliphatic hydrocarbon resin	Eastman
Novares C120	Indene coumarone resin	Rüttgers
Plastolyn 290	Aromatic hydrocarbon endblock tackifier	Eastman
Plastolyn 290LV	Aromatic hydrocarbon endblock tackifier	Eastman
Plastolyn 5140LV	Aromatic hydrocarbon endblock tackifier	Eastman
Novares C140	Indene coumarone resin	Rüttgers
Novares T140M	Modified C9 Resin	Rüttgers
Norsolene S155	Aromatic resin	Cray Valley
Nyplast 222B	Mineral Oil	Nynas
Glissopal 1000	Polyisobutylene of Mw=1600g/mol	BASF
Glissopal V1500	Polyisobutylene of Mw=4140g/mol	BASF
Oppanol B10N	Polyisobutylene of Mw=36000g/mol	BASF
Oppanol B12N	Polyisobutylene of Mw=51000g/mol	BASF
Glass bubbles K37	Hollow Glass bubbles with a diameter of 85µm	3M
EMS FN100MD	Expandable microspheres	Lehmann & Voss
Irganox 1010	Heat stabilizer	BASF
Irgacure 651	2,2 dimethoxy-2-phenylacetophenone	BASF
Renol-schwarz F- IK	38% Carbon Black Masterbatch in EVA	Clariant
IOA	Isooctyl acrylate is a ester of isooctylalcohol and acrylic acid	3M, Germany
BA	Butyl acrylate	Sigma Aldrich
AA	Acrylic acid	Sigma Aldrich

IOTG	Isooctyl thioglycolate, chain transfer agent	Sigma Aldrich
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Table 1: Raw material list.

Screening of raw materials with regard to low VOC:

In order to screen the raw materials in advance concerning their outgassing behavior and thermal stability, an oven outgassing test, as described in the previous test method part, is performed at 120°C and 160°C. Results are provided in Table 2 below.

Raw Material	weight loss 2h 120°C (%)	weight loss 2h 160°C (%)
Regalite 9100	0.15	2.53
Regalite 1090	0.25	4.99
Escorez 5615	0.04	0.21
Escorez 1304	0.06	0.52
Piccotac 1020E	0.20	1.12
Oppanol B10N	0.05	0.22
Oppanol B12N	-	0.07

Table 2

In Table 2, the tackifying hydrocarbon resins Escorez 5615 and Escorez 1304 show a very low outgassing at 120°C and a very good thermal stability at 160°C. In contrast, Regalite R9100 and R1090 show higher outgassing behavior at 120°C and a significant weight loss at 160°C. The weight loss at 160°C provides a good indication of the thermal stability of a raw material and its behavior when processed at high temperatures in a hot melt type process.

Concerning the plasticizers, both of the polyisobutylene resins Oppanol B10N and B12N show very low outgassing behavior when compared to the liquid hydrocarbon resin Piccotac 1020E and excellent heat stability at 160°C. Based on these findings a pre-selection concerning low VOC behavior can be envisaged.

Another way of pre-screening the raw materials concerning their improved low VOC behavior is by TGA (thermogravimetric analysis) measurements, as previously described in the test method section. Results of the TGA measurements are found in Table 3 below, the values are an average of 2 measurements. These include also a comparison to an existing and commercially available acrylic adhesive based foam tape.

Raw Material	Weight loss 30 min at 90°C (in ppm)	Weight loss 60 min at 120°C (in ppm)
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ACX 7065	1974±13	5732±112
Kraton D1340	326±76	234±99
Kraton D1161	669±47	253±101
Regalite 9100	1353±223	10905±1325
Regalite 1090	2409±457	20792±284
Regalite 1125	1472±134	2037±296
Escorez 1304	296±64	1476±155
Escorez 5615	258±153	727±180
Escorez 5340	335±35	590±43
Escorez 5320	334±1	1124±68
Plastolyn R1140	344±15	541±10
Novares C120	1000±29	5849±116
Norsolene S155	840±34	3013±585
Novares C140	757±2	1376±113
Novares T140M	616±2	853±48
Plastolyn 290	731±179	2119±219
Plastolyn 290LV	732±1	912±161
Kristalex 5140LV	493±17	476±7
Nyplast222B	1225±231	16817±1664
Glissopal 1000	8730±622	18363±658
Glissopal V1500	2310±148	4419±206
Oppanol B10N	558±75	1707±274
Oppanol B12N	285±34	538±25

Table 3

From Table 3, the difference in outgassing of polymeric plasticizers in function of their weight average molecular weight M_w can be further seen. While the polyisobutylene plasticizer Oppanol B12N with 51000g/mol has very low outgassing at 90 and 120°C, Glissopal 1000 and V1500 which are polyisobutylenes having a weight average molecular weight M_w of respectively 1600 and 4140g/mol have very high amounts of volatile organic compounds.

Among the mid block tackifiers, the TGA outgassing test clearly shows that for instance Escorez 5615 and Escorez 5340 have by far lower outgassing values and are more heat stable than Regalite 1125, Regalite 9100 or Regalite 1090.

Among the endblock tackifiers, Novarez C140 has lower outgassing behavior than Novares C120. Other very valuable low VOC endblock tackifier alternatives are Novares T140M, Plastolyn 290LV and Kristalex 5140LV.

Current commercially available acrylic based PSA foam tapes exhibit high levels of VOCs and Fog values when analyzed with the TGA test method. The acrylic PSA foam tape ACX 7065 has a weight loss of 1974 ppm after 30 minutes at 90°C and 5732 ppm of weight loss after further 60 minutes at 120°C.

The combination of oven outgassing test results with TGA test results clearly indicates favorable selections of raw materials for low VOC multilayer pressure sensitive adhesives and assemblies.

Preparation of pressure sensitive adhesives (“PSA”) from solvent:

Half of the mass of raw materials as later indicated in Table 4 (in total 50.675g) are weighed in a glass jar. 75g of toluene is then added. The jar is covered with a metal lid and placed on rotating rolls. The mixture is then rolled for 2 days until all the components are dissolved. The solutions are coated on a siliconized paper liner using a knife coater. The wet film is 300µm thick. The toluene is allowed to evaporate from the film for 20 minutes at room temperature (23°C +/- 2°C, 50% relative humidity +/-5%) before the PSA coating is annealed for 3 minutes at 110°C.

Pressure sensitive adhesive tape lamination onto a PET backing

For allowing adhesive testing, the pressure sensitive adhesive layers are laminated onto a PET backing (commercially available as Hostaphan RN 50) having a film thickness of 50µm, resulting in a PSA tape comprising a PET backing.

E-beam experiments

The PSA tapes obtained from solvent coating are also e-beam crosslinked. The adhesive side of the PSA tapes is hereby covered by a 100g/cm² siliconized polyethylene liner. The construction is then irradiated through the liner with an electron beam having an acceleration tension of 245kV and a dose of 75kGy. The nitrogen gap of the setting is adjusted to 30mm.

From the outgassing values of the PSA raw materials in **Error! Reference source not found.** or Table 3, appropriate raw material combinations for making a low VOC pressure sensitive adhesive can be selected. Comparative example C1 is based on a linear SBS polymer Kraton D1102. Ex.1 is based on Kraton D1116 a branched SBS polymer. Pressure sensitive adhesives Ex.2 to Ex.7 are all based on Kraton D1340, a star shaped SIS polymer. Kraton D1161, linear triblock SIS copolymer, is additionally used in Ex.5 to Ex.7 for providing SIS based adhesives comprising a blend of a star shaped SIS polymer with a linear SIS polymer. Hereby Escorez 5615 was chosen as mid block tackifier for Ex.2 to Ex.7 and Oppanol B12N (PIB) as the low outgassing polymeric plasticizer, excluding an end block tackifier. In Ex.8, the star shaped SIS block copolymer Kraton D1340, is compounded with a low outgassing

tackifier blend of Escorez 5615 (mid-block tackifier) and Plastolyn 290LV (end block tackifier) and with the low outgassing plasticizer Oppanol B12N. Finally, Ex.14 describes a PSA construction based on the combination of star shaped SIS Kraton D1340 and star shaped SBS Kraton D1116 formulated with E5615, Plastolyn 290LV and Oppanol B12N. Comparative example C2 is identical in its composition to Ex.8 except that the star shaped Kraton D1340 is exchanged by Kraton D1161, a linear SIS polymer. Irganox 1010 is added as an antioxidant to all examples.

	C1 (parts)	C2 (parts)	Ex.1 (parts)	Ex.2 (parts)	Ex.3 (parts)	Ex.4 (parts)	Ex.5 (parts)	Ex.6 (parts)	Ex.7 (parts)	Ex.8 (parts)	Ex.14 (parts)
D1102	40										
D1116			40								20
D1340				51	46.5	42	35.7	32.6	29.4	45.5	20
D1161		45.5					15.3	14.0	12.6		
Irganox 1010	1.35	1.35	13.5	1.35	1.35	1.35	1.35	1.35	1.35	1.35	1.35
Escorez 5615	40	33.5	40	46	46	46	46	46	46	33.5	40
Plastolyn 290LV	10	10.5	10							10.5	10
Oppanol B12N	10	7.35	10	3	7.5	12	3	7.5	12	7.3	10

Table 4

Preparation of pressure sensitive adhesives (“PSA”) by a hot melt process incl. VDA 278 test results

For VOC and FOG analysis, hot melt extruded samples (Ex.9 – Ex.11) and one comparative example C3 are prepared. The formulations are listed in Table 5 below. The pressure sensitive adhesives are extruded in a twin screw extruder and coated with a rotary rod die to a siliconized release paper. The twin screw extruder is a co-rotating ZSK25 available from Werner & Pfleiderer (Stuttgart, Germany) having 11 heat zones, a screw diameter of 25mm and a L/D (length/diameter) ratio of 46. The temperature profile of the extruder and the extrusion conditions for Ex.9 are described below in Table 6, for Ex.10 in Table 7, for Ex.11 in Table 8 and for comparative example C3 in Table 9.

	Ex.9		Ex.10		Ex.11		C3	
Kraton D1340	31.85	Blend 1	45.5	Blend 2	32.28	Blend 3	32.28	Blend 5
Irganox 1010	1.35		1.35		1.37		1.37	
Kraton D1161	13.65				13.84		13.84	
Carbon Black				0.39	0.39			
Regalite 1125							31.99	Blend

Novares C120							10.66	6
Escorez 5615	44.00		33.5		31.99	Blend 4		
Novares C140					10.66			
Plastolyn 290LV			10.5					
Acrylate polymer (45 IOA/ 45 BA/ 10 AA)					2.03		2.03	
Nyplast 222B							7.45	
Oppanol B12N	7.35		7.35		7.45			

Table 1: Chemical composition of SIS based PSA (in parts).

The acrylate polymer listed in upper Table 5 is used for Ex.11 and C3 and is prepared by mixing 45 parts of isooctyl acrylate (IOA), 45 parts of butyl acrylate (BA), 10 parts of acrylic acid (AA), 0.15 part IRGACURE 651, and 0.06 part of isooctyl thioglycolate (IOTG). Discreet film packages are formed from a packaging film (0.0635 mm thick ethylene vinyl acetate copolymer film sold as VA-24 Film from CT Film, Dallas, Texas). The acrylate composition is sealed into the film packages, which measures approximately 10 centimeters (cm) by 5 cm by 0.5 cm thick. While immersed in a water bath maintained at between about 21°C and about 32°C, the packages are exposed to ultraviolet (UV) radiation having an intensity of about 3.5 milliwatts per square centimeter (mW/sq cm), and a total energy of about 1680 milliJoules per square centimeter (mJ/sqcm). The method of forming the packages and curing are described in Example 1 of U.S. Patent No. 5,804,610.

For Ex.9, Kraton D1340, Kraton D1161 and Irganox 1010 are blended in a tumbling mixer providing Blend 1. Blend 1 is then fed into the twin screw extruder with a throughput of 2.129kg/h in Zone Z1 using a gravimetric weight loss feeder from Brabender. The hydrocarbon tackifier Escorez 5615 is also fed in Zone Z1 using a gravimetric screw feeder from Brabender with a throughput of 2.037kg/h. Oppanol B12N is fed in Zone Z7 with a throughput of 0.340kg/h using a 20L drum unloader (Robatech RMC20). The extruder screw speed is kept at 300rpm. Between the extruder and the die, the adhesive melt is metered by a gear pump (165°C) through a heated hose (170°C), which makes the junction between the extruder and the coating die (185°C). The pressure sensitive adhesive Ex.9 has a thickness of about 90µm.

Zone (Barrel)	Temperature (°C)	Description
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Z1	80	Feeding of Blend 1 (Kraton D1340, Kraton 1161 and Irganox1010) with a throughput of 2.129kg/h using a weight loss feeder from Brabender. Feeding of Escorez 5615 with a throughput of 2.037kg/h using a weight loss feeder from Brabender.
Z2	80	
Z3	95	
Z4	115	
Z5	120	
Z6	128	
Z7	130	Feeding of Oppanol B12N (0.340kg/h) with a 20L drum unloader from Robatech.
Z8	135	
Z9	150	
Z10	160	
Z11	160	
Gear pump	165	
Hose	170	
Rotary rod die	185	Coating of the PSA hot melt. Total throughput 4.506 kg/h.

Table 6: Extrusion conditions for PSA Ex.9.

For Ex.10, Kraton D1340 and Irganox1010 are blended in a tumbling mixer providing Blend 2. Blend 2 is fed into the twin screw extruder in Zone Z2 using a gravimetric weight loss feeder from Brabender. The hydrocarbon tackifier Escorez 5615 is also fed in Zone Z2 using a gravimetric screw feeder from Brabender. Oppanol B12N is fed in Zone Z6 using a 20L drum unloader (Robatech RMC20). A vacuum of 38 mbar is applied in Zone 10 which is equipped with a vacuum port. The extruder screw speed is set at 450rpm. The total throughput is 10kg/h. Between the extruder and the die, the adhesive melt is metered by a gear pump (165°C) through a heated hose (170°C), which makes the junction between the extruder and the coating die (185°C).

Zone (Barrel)	Temperature (°C)	Description
Z1	50	

Z2	30	Feeding of Blend 2 (Kraton D1340 and Irganox1010) using a weight loss feeder from Brabender. Feeding of Escorez 5615 using a weight loss feeder from Brabender.
Z3	50	
Z4	130	Feeding of Plastolyn 290LV using a weight loss feeder from Brabender and a side stuffer from Werner and Pfleiderer.
Z5	160	
Z6	160	Feeding of Oppanol B12N with a 20L drum unloader from Robatech.
Z7	160	
Z8	160	
Z9	160	
Z10	160	Vacuum (38 mbar)
Z11	160	
Gear pump	165	
Hose	170	
Rotary rod die	185	Coating of the PSA hot melt. Total throughput 10 kg/h.

Table 7: Extrusion conditions for PSA Ex.10.

For Ex.11, Kraton D1340, Kraton D1161, Irganox1010 and the Carbon Black MB are blended in a tumbling mixer providing Blend 3. Blend 3 is fed in the twin screw extruder with a throughput of 2.361kg/h in Zone Z1 using a Linden Feeder. The tackifier Blend 4 (Escorez 5615 and Novares C140) is added in Zone Z3 using a vibratory feeder (K-SFS-24 from K-Tron) and a side stuffer from Werner & Pfleiderer with a throughput of 2.104kg/h. The acrylate polymer 45/45/10 IOA/BA/AA is fed in zone Z5 using a single screw extruder. The low outgassing plasticizer Oppanol B12N is fed in Zone Z7 with a throughput of 0.368kg/h using a 20L drum unloader (Robatech RMC20). The screw speed of the twin screw extruder is 300rpm. Between the extruder and the die, the adhesive melt is metered by a gear pump (175°C) through a heated hose (175°C), which makes the junction between the extruder and the coating die (175°C). The pressure sensitive adhesive has a thickness of about 90µm.

Zone (Barrel)	Temperature (°C)	Description
Z1	175	Feeding of Blend 3 (Kraton D1340, Kraton D1161, Irganox1010 and Carbon Black MB) with a throughput of 2.361kg/h using a Linden feeder.

Z2	175	
Z3	175	Feeding of Blend 4 (Escorez 5615 and Novares C140) with a throughput of 2.104kg/h using a vibratory feeder from K-Tron and a side stuffer from Werner & Pfleiderer.
Z4	175	
Z5	175	Feeding of the acrylate polymer (0.100kg/h) using a single screw extruder.
Z6	175	
Z7	175	Feeding of Oppanol B12N (0.368kg/h) using a drum unloader RMC 20.
Z8	175	
Z9	175	
Z10	175	
Z11	175	
Gear pump	175	
Hose	175	
Rotary rod die	175	Coating of the PSA hot melt. Total throughput 4.933 kg/h.

Table 8: Extrusion conditions for PSA Ex.11.

The hot melt comparative pressure sensitive adhesive example C3, is composed of the multi arm block copolymer Kraton D1340, linear block copolymer Kraton D1161, a higher outgassing mid block tackifier Regalite 1125, a higher outgassing second indene coumarone tackifier Novares C120, a higher outgassing mineral oil plasticizer Nyplast 222B and several additives (Irganox 1010, acrylate polymer (45/45/10 2-EHA/BA/AA), Carbon Black Masterbatch).

For making comparative example C3, Kraton D1340, Kraton D1161, Irganox1010 and the Carbon Black MB are blended in a tumbling mixer providing Blend 5. Blend 5 is fed into the twin screw extruder with a throughput of 2.361kg/h in Zone Z1 using a Linden Feeder. The tackifier Blend 6 (Regalite 1125 and Novares C120) is added in Zone Z3 using a vibratory feeder (K-SFS-24 from K-Tron) and a side stuffer from Werner & Pfleiderer with a throughput of 2.104kg/h. The acrylate polymer 45/45/10 IOA/BA/AA is fed in zone Z5 using a single screw extruder. The mineral oil Nyplast 222B is added with a gear pump from Dynatec. The screw speed of the twin screw extruder is set at 300rpm. Between the extruder and the die, the adhesive melt is metered by a gear pump (175°C) through a heated hose (175°C), which makes the junction between the extruder and the coating die (175°C). Comparative pressure sensitive adhesive example C3 has a thickness of about 90µm.

Zone (Barrel)	Temperature (°C)	Description
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Z1	175	Feeding of Blend 5 (Kraton D1340, Kraton D1161, Irganox1010 and Carbon Black MB) with a throughput of 2.361kg/h using a Linden feeder.
Z2	175	
Z3	175	Feeding of Blend 6 (Regalite1125 and Novares C120) with a throughput of 2.104kg/h using a vibratory feeder from K-Tron and a side stuffer from Werner & Pfleiderer.
Z4	175	
Z5	175	Feeding of the acrylate polymer (0.100kg/h) using a single screw extruder.
Z6	175	
Z7	175	Feeding of Nyplast 222B using a Dynatec gear pump.
Z8	175	
Z9	175	
Z10	175	
Z11	175	
Gear pump	175	
Hose	175	
Rotary rod die	175	Coating of the PSA hot melt. Total throughput 4.933 kg/h.

Table 9: Extrusion conditions for comparative example C3.

VOC and Fog levels of Ex.9 to Ex.11 and comparative example C3 are measured according to VDA 278 and are summarized in Table 10 below.

	Ex.9	Ex.10	Ex.11	C3
VOC VDA278 (ppm)	205	522	219	1371
Fog VDA278 (ppm)	804	1204	1684	7553

Table 10: VDA 278 results from hot melt extruded PSAs.

VDA 278 test results of Ex.9 to Ex.11 show that C3 provides especially a strong increase in the VOC and the FOG values resulting from the usage of Nyplast 222B, the midblock tackifier Regalite 1125 and the endblock tackifier Novares C120, which in the low VOC raw materials screening had already shown high TGA weight loss values.

Preparation of multilayer pressure sensitive adhesive (“PSA”) assemblies by hot melt processing of the individual layers and later lamination thereof

A multilayer pressure sensitive adhesive assembly according to the disclosure comprises a foam layer with a first and/or a second pressure sensitive adhesive layer on the opposing sides of the foam layer. The selected formulation for the first and/or second pressure sensitive layer (“skin layer”) for use in a multilayer PSA assembly according to the disclosure is Ex.11 as described above.

For making PSA assemblies according to the disclosure foam layers are also made. The foam layer formulations are described in Table 11 below and are also compounded in a 25 mm co-rotating twin screw extruder (ZSK25 from Werner& Pfleiderer, Stuttgart, Germany) having 11 heat zones and a L/D (length/diameter) ratio of 46.

	Foam 1	Foam 2	
Kraton D1340	35	35	Blend 9
Irganox 1010	1	1	
Escorez 5615	50	50	
Oppanol B12N	15	15	
EMS	3	3	
Glass Bubbles K37	-	6	

Table 11

For the preparation of Foams 1 and 2, the screw speed is set at 350 rpm. Kraton D1340 is blended with Irganox 1010 in a tumbling mixer resulting in Blend 9. Blend 9 is then fed into the twin screw extruder with a throughput of 2.16kg/h in Zone Z1 using a loss in weight feeder (K-Tron). The hydrocarbon resin tackifier Escorez 5615 is added in Zone Z1 as well, using a vibratory feeder (K-SFS-24 from K-Tron) with a throughput of 3.00kg/h. The plasticizer Oppanol B12N is next fed in Zone Z4 with a throughput of 0.90kg/h using a 20L drum unloader (Robatech RMC20). The expandable microspheres FN100MD are added in Zone Z9 with a throughput of 180g/h employing a loss in weight twin screw feeder (MiniTwin from Brabender). Glass bubbles are dosed in zone Z8 with 360g/h using a volumetric twin screw feeder (KT20 from K-Tron) for Foam 2. The expandable microspheres are immediately conveyed by the extruder screws and can only expand after passing the rotary rod dye at the end of the extrusion process, leading to a foam layer.

Between the extruder and the die, the adhesive melt is metered by a gear pump (150°C) and pumped through a heated hose (150°C), which makes the junction between the extruder and the coating die (160°C).

The temperature profile and the extrusion conditions for the foam layers are listed below in Table 12.

Zone (Barrel)	Temperature	Description
Z1	50	Feeding of Blend 9 (Kraton D1340 and Irganox 1010) (2.16kg/h) using a Gravimetric feeder (loss in weight) from K-Tron Feeding of Escorez 5615 (3.00kg/h) using a vibratory feeder from K-Tron.
Z2	50	
Z3	90	
Z4	145	Feeding of Oppanol B12N (0.90 kg/h) using a drum unloader RMC 20 from Robatech.
Z5	150	
Z6	150	
Z7	150	
Z8	135	Feeding of Glass bubbles (360g/h) for Foam 2.
Z9	125	Feeding of EMS FN100MD (180 g/h) gravimetric loss in weight twin screw feeder from Brabender.
Z10	150	
Z11	150	
Gear pump	150	
Hose	150	
Rotary rod die	160	Coating and expansion of the microspheres.

Table 12

Table 13 below provides the structure of two laminated 3-layer pressure sensitive adhesive assemblies where the first and the second pressure sensitive adhesive layers (both skin layer Ex.11) are laminated in a first step onto the opposing sides of the selected foam layer. These laminated 3-layer PSA assemblies are then covered on both sides with two-side silicone-coated polyethylene release liners. The samples are then irradiated through the release liner from both sides with an e-beam dose of 100 kGy under an acceleration tension of 280 kV.

Example	“Skin” layer	Foam layer
Ex.12 (100kGy)	Ex.11	Foam 1

Ex.13 (100kGy)	Ex.11	Foam 2
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Table 13

VOC and Fog levels of Ex.12 (100kGy) and comparative example ACX 7065 are measured according to VDA 278 and are summarized in Table 14 below. The multilayer PSA construction of the present disclosure has very low VOC and Fog values. In contrast, the comparative commercially available acrylic example ACX 7065 has very high VOC and Fog values.

	Comparative acrylic example ACX 7065	Ex.12 (100kGy)
VOC VDA278 (ppm)	2540	352
Fog VDA278 (ppm)	7870	322

Table 14

Mechanical Test Results of the pressure sensitive adhesives and multilayer pressure sensitive adhesive assemblies

90°Peel test results at room temperature (RT)

90° Peel test results at room temperature of the examples are shown in Table 15 below.

Example No	90° Peel to CC5 (N/12.7mm)	90° Peel to PP (N/12.7mm)	90° Peel to Uregloss (N/12.7mm)
Ex.1	15.6	-	-
Ex.1 (75kGy-closed face)	10.6	-	-
Ex.2	18.4	16.9	-
Ex.3	8.1	17.3	-
Ex.4	11.2	17.5	-
Ex.5	17.8	15.6	-
Ex.6	7.2	17.6	-
Ex.7	6.9	19.7	-
Ex.8	18.4	-	-
Ex.8 (75kGy- closed face)	16.4	-	-
Ex.11	16.8	-	-

Ex.12 (100kGy- closed face)	41.9	-	54.1
Ex.13 (100kGy- closed face)	-	-	37.5
Ex.14	9.0	-	-
Ex.14 (75kGy- closed face)	11.8	-	-
C1	9.0	-	-
C1 (75kGy-closed face)	8.8	-	-
C2	10.1	-	-

Table 15

Static Shear Test results @ 70°C and 90°C

Static Shear test results are listed in Table 16 below. Examples that were e-beam crosslinked are indicated in brackets with the selected dose. All e-beam crosslinking was done as closed face e-beaming. This means the sample irradiation took place through the two opposing liners.

	Static Shear at 70°C on CC5 (min)	Failure Mode	Static Shear at 90°C on CC5 (min)	Failure Mode
C1	22	CF	-	-
C1 (75kGy- closed face)	40	CF	9	CF
C2	189	CF	-	
C2 (75kGy- closed face)	-	-	30	CF
Ex.1	5341	CF	-	-
Ex.1 (75kGy- closed face)	>10000	-	>10000	-
Ex.8	>10000		-	-
Ex.8 (75kGy- closed face)	-	-	>10000	-
Ex.10	>10000	-		-

Ex.10 (75kGy- closed face)	>10000	-	>10000	-
Ex.14	9336	CF		
Ex.14 (75kGy- closed face)	>10000		>10000	
Ex.11	>10000	-		-

Table 16

CF denotes cohesive failure.

The peel and 70°C static shear performances of the SBS based PSAs are evaluated on the automotive clear coat CC5. Without e-beam crosslinking, C1, which is strictly based on a linear SBS triblock copolymer, fails in 70°C static shear after 20 minutes with a cohesive failure mode. Ex.1, which is based on a branched styrene butadiene block copolymers shows already a clearly improved 70°C static shear performance of >5000 minutes.

The high temperature static shear performance of the star shaped SBS PSA example Ex.1 could further be improved with e-beam crosslinking. E-beam crosslinking allowed for static shear holding performances at 70°C and at 90°C of greater 10000 minutes for Ex.1 (75kGy). Comparative example C1 (75kGy) failed already after 40 minutes at 70°C and 9 minutes at 90°C with a CF mode.

Generally, the advantage of star shaped SIS block copolymers over linear SIS block copolymers can be seen from the two previous tables (Table 15 and Table 16), for example star shaped based PSA example Ex.8 exhibits very high peel values on CC5 (18.4 N/12.7mm) in comparison to the linear SIS block copolymer based formulation C2 (10.1 N/12.7). However, the main advantage is the increased 70°C static shear performance of star shaped block copolymers versus linear SIS block copolymer based PSAs. C2 holds only 175 minutes in the 70°C static shear experiment whereas Ex.8 exhibits a holding power of greater 10000 minutes.

The advantage of star shaped over linear SIS block copolymers also remains obvious after e-beam crosslinking: C2 (75kGy), although crosslinked with e beam, fails after 30 minutes in the 90°C static shear test whereas Ex.8 (75kGy) remains at high values above 10000 minutes.

Ex.2 to Ex.4 show excellent 90° peel performance on critical LSE substrates such as PP and CC5. In Ex.5 to Ex.7, the star shaped Kraton D1340 rubber is replaced by a 70/30 blend of the star shaped Kraton D1340 with the linear Kraton D1161. The 90°C peel performances on PP is increased when compared to solely Kraton D1340 based constructions because of the softened adhesive.

Ex.14 shows the advantage of combining a star shaped SIS with a star shaped SBS in a low VOC pressure sensitive adhesive construction: Ex.14 only failed after 9336 minutes in the static shear test at 70°C. Further e-beam crosslinking can improve the static shear holding performance at 70°C and 90°C to greater than 10000 minutes for Ex.14 (75kGy- closed face).

Finally, the multilayer pressure sensitive adhesive assemblies of Ex. 12 and Ex. 13 show the highest 90° peel values of all selected examples on CC5 and Uregloss.

CLAIMS

1. A pressure sensitive adhesive comprising:
 - a) a multi-arm block copolymer of the formula Q_n -Y, wherein:
 - (i) Q represents an arm of the multi-arm block copolymer and each arm independently has the formula G-R,
 - (ii) n represents the number of arms and is a whole number of at least 3, and
 - (iii) Y is the residue of a multifunctional coupling agent,wherein each R is a rubbery block comprising a polymerized conjugated diene, a hydrogenated derivative of a polymerized conjugated diene, or any combinations thereof; and each G is a glassy block comprising a polymerized monovinyl aromatic monomer;
 - b) a polymeric plasticizer having a weight average molecular weight M_w of at least 10.000 g/mol;
 - c) at least one hydrocarbon tackifier, wherein the hydrocarbon tackifier(s) have a Volatile Organic Compound (VOC) value of less than 1000 ppm, when measured by thermogravimetric analysis according to the weight loss test methods described in the experimental section; and
 - d) optionally, a linear block copolymer of the formula $L - (G)_m$, wherein L is a rubbery block comprising a polymerized olefin, a polymerized conjugated diene, a hydrogenated derivative of a polymerized conjugated diene, or any combinations thereof; and wherein m is 1 or 2.
2. A pressure sensitive adhesive according to claim 1, wherein the hydrocarbon tackifier(s) have a Volatile Organic Compound (VOC) value of less than 800 ppm, less than 600 ppm, less than 400 ppm or even less than 200 ppm, when measured by thermogravimetric analysis according to the weight loss test method described in the experimental section.
3. A pressure sensitive adhesive according to any one of claim 1 or 2, wherein the hydrocarbon tackifier(s) have a Volatile Fogging Compound (FOG) value of less than 1500 ppm, less than 1000 ppm, less than 800 ppm, less than 600 ppm, or even less than 500 ppm, when measured by thermogravimetric analysis according to the weight loss test methods described in the experimental section.
4. A pressure sensitive adhesive according to any one of the preceding claims, wherein the polymeric plasticizer has a weight average molecular weight M_w of at least 20.000 g/mol, at least 30.000 g/mol, or even at least 50.000 g/mol.

5. A pressure sensitive adhesive according to any one of the preceding claims, wherein the polymeric plasticizer(s), have a Volatile Organic Compound (VOC) value of less than 1000 ppm, less than 800 ppm, less than 600 ppm, less than 400 ppm or even less than 200 ppm, when measured by thermogravimetric analysis according to the weight loss test methods described in the experimental section.
6. A pressure sensitive adhesive according to any one of the preceding claims, wherein the polymeric plasticizer is a polyisobutylene plasticizer.
7. A pressure sensitive adhesive according to any one of the preceding claims, wherein at least one of the glassy blocks of the multi-arm block copolymer is a monovinyl aromatic monomer selected from the group consisting of styrene, styrene-compatible blends, and any combinations thereof, preferably wherein each of the glassy blocks of the multi-arm block copolymer is a monovinyl aromatic monomer selected from the group consisting of styrene, styrene-compatible blends, and any combinations thereof.
8. A pressure sensitive adhesive according to any one of the preceding claims, wherein at least one arm of the multi-arm block copolymer is selected from the group consisting of styrene-isoprene-styrene, styrene-butadiene-styrene, styrene-ethylene-butylene-styrene, styrene-ethylene-propylene-styrene, and combinations thereof, preferably wherein each arm of the multi-arm block copolymer is selected from the group consisting of styrene-isoprene-styrene, styrene-butadiene-styrene, styrene-ethylene-butylene-styrene, styrene-ethylene-propylene-styrene, and any combinations thereof.
9. A pressure sensitive adhesive according to any one of the preceding claims, which is crosslinked, preferably with actinic radiation, more preferably with e-beam irradiation.
10. A pressure sensitive adhesive according to any one of the preceding claims, which comprises:
 - a) from 20 wt% to 80 wt%, from 20 wt% to 70 wt%, from 25 wt% to 60 wt%, or even from 25 wt% to 50 wt% of the multi-arm block copolymer, based on the weight of the pressure sensitive adhesive;
 - b) from 20 wt% to 70 wt%, from 25 wt% to 60 wt%, or even from 25 wt% to 50 wt% of the hydrocarbon tackifier(s), based on the weight of the pressure sensitive adhesive;
 - c) from 2 wt% to 20 wt%, from 4 wt% to 15 wt%, or even from 6 wt% to 15 wt% of the polymeric plasticizer, based on the weight of the pressure sensitive adhesive;
 - d) optionally, from 3 wt% to 40 wt%, from 5 wt% to 30 wt%, or even from 10 wt% to 25 wt% of linear block copolymer, based on the weight of the pressure sensitive adhesive;and

e) optionally, from 0.1 wt% to 10 wt%, from 0.5 wt% to 8 wt%, from 1 wt% to 6 wt%, or even from 2 wt% to 5 wt% of a crosslinking additive, based on the weight of the pressure sensitive adhesive foam, and wherein the crosslinking additive is preferably selected from the group of multifunctional (meth)acrylate compounds.

11. A multilayer pressure sensitive adhesive assembly comprising a pressure sensitive adhesive according to any one of the preceding claims and a backing layer adjacent to the pressure sensitive adhesive.

12. A multilayer pressure sensitive adhesive assembly according to claim 11, comprising a backing layer having a first major surface and a second major surface; and a first pressure sensitive adhesive skin layer bonded to the first major surface, wherein the first pressure sensitive adhesive skin layer comprises a pressure sensitive adhesive according to any one of claims 1 to 10.

13. A multilayer pressure sensitive adhesive assembly according to claim 12, which further comprises a second pressure sensitive adhesive skin layer bonded to the second major surface.

14. A multilayer pressure sensitive adhesive assembly according to claim 13, wherein the first pressure sensitive adhesive skin layer and the second pressure sensitive adhesive skin layer each independently comprise a pressure sensitive adhesive according to any one of claims 1 to 10.

15. A multilayer pressure sensitive adhesive assembly according to any one of claims 11 to 14, wherein the backing is a foam backing.

16. A multilayer pressure sensitive adhesive assembly according to any one of claims 11 to 15, wherein the backing layer comprises a polymer base material selected from the group consisting of rubber-based elastomeric materials, polyacrylates, polyurethanes, polyolefins, polyamides, polyesters, polyethers, polyisobutylene, polystyrenes, polyvinyls, polyvinylpyrrolidone, and any combinations, copolymers or mixtures thereof.

17. A multilayer pressure sensitive adhesive assembly according to claim 16, wherein the backing layer comprises a polymer base material selected from the group consisting of rubber-based elastomeric materials.

18. A pressure sensitive adhesive or a multilayer pressure sensitive adhesive assembly according to any one of the preceding claims, which has a Volatile Organic Compound (VOC) value of less than 2000 ppm, less than 1500 ppm, less than 1000 ppm, less than 800 ppm, less than 600 ppm, less than 500 ppm,

less than 400 ppm, or even less than 300 ppm, when measured by thermogravimetric analysis according to the weight loss test method described in the experimental section.

19. A method of manufacturing a pressure sensitive adhesive or a multilayer pressure sensitive adhesive assembly according to any one of claims 1 to 18, which comprises the steps of:
- a) compounding the multi-arm block copolymer, the polymeric plasticizer, at least one hydrocarbon tackifier; optionally, a linear block copolymer, optionally, a crosslinking agent which is preferably selected from the group of multifunctional (meth)acrylate compounds; and wherein the hydrocarbon tackifier(s) have a Volatile Organic Compound (VOC) value of less than 1000 ppm, less than 800 ppm, less than 600 ppm, less than 400 ppm or even less than 200 ppm, when measured by thermogravimetric analysis according to the weight loss test methods described in the experimental section; thereby forming a pressure sensitive adhesive formulation; and
 - b) optionally, crosslinking the pressure sensitive adhesive formulation, preferably with actinic radiation, more preferably with e-beam irradiation.
20. Use of a pressure sensitive adhesive or a multilayer pressure sensitive adhesive assembly according to any one of claims 1 to 18 for industrial applications, preferably for interior applications, more preferably for construction market applications, automotive applications or electronic applications.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/059144

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09J7/02 C09J153/02
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)
C09J C08F

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 2008/073669 A1 (3M INNOVATIVE PROPERTIES CO [US]; HANLEY KENNETH J [US]; JENNEN JAY M) 19 June 2008 (2008-06-19) paragraph [0080] - paragraph [0100]; claims 1-54 -----	1-20
X	US 2008/070053 A1 (SCHMIERER JEFFREY G [US] ET AL) 20 March 2008 (2008-03-20) paragraph [0031] - paragraph [0036]; claims 1-18; examples 1-7 -----	1-20
X	WO 03/018702 A1 (TESA AG [DE]; KRAWINKEL THORSTEN [DE]) 6 March 2003 (2003-03-06) page 9, line 1 - line 10; claims 1-10; table 1 -----	1-20
X	WO 03/002684 A1 (NAT STARCH CHEM INVEST [US]) 9 January 2003 (2003-01-09) claims 1-10; example F; table 2 -----	1-20

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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- "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

18 January 2016

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2015/059144

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2008073669	A1	19-06-2008	BR PI0719599 A2 17-12-2013
			CA 2671033 A1 19-06-2008
			CN 101547988 A 30-09-2009
			EP 2094801 A1 02-09-2009
			JP 5801533 B2 28-10-2015
			JP 2010512428 A 22-04-2010
			KR 20090094442 A 07-09-2009
			US 2010098962 A1 22-04-2010
			WO 2008073669 A1 19-06-2008
US 2008070053	A1	20-03-2008	AT 493480 T 15-01-2011
			AU 2007297633 A1 27-03-2008
			BR PI0717032 A2 01-10-2013
			CN 101517027 A 26-08-2009
			EP 2064299 A1 03-06-2009
			US 2008070053 A1 20-03-2008
			WO 2008036322 A1 27-03-2008
WO 03018702	A1	06-03-2003	DE 10141379 A1 30-04-2003
			EP 1425359 A1 09-06-2004
			ES 2287307 T3 16-12-2007
			JP 2005501164 A 13-01-2005
			WO 03018702 A1 06-03-2003
WO 03002684	A1	09-01-2003	CA 2421045 A1 09-01-2003
			EP 1453931 A1 08-09-2004
			JP 4494775 B2 30-06-2010
			JP 2004521994 A 22-07-2004
			US 2003065048 A1 03-04-2003
			WO 03002684 A1 09-01-2003