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(54) Title: EXTREME HIGH TEMPERATURE TAPE AND BACKINGS THEREOF

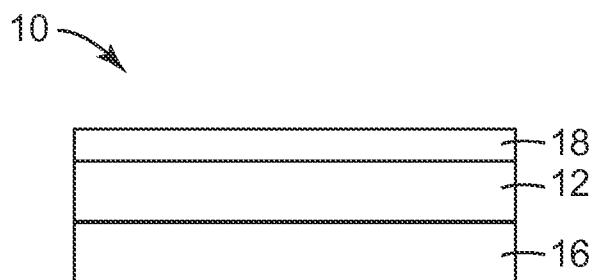


FIG. 1

(57) Abstract: Described herein is a paper-based backing and a tape that may be used in extreme high temperature applications. In one embodiment, the tape comprises (a) a backing comprising a paper and a saturant, wherein the saturant comprises a C2 to C6 (meth)acrylic ester; and (b) an adhesive disposed on the backing, wherein the adhesive comprises a crosslinkable (meth)acrylate polymer and a heat-activatable crosslinking agent, wherein the heat-activatable crosslinking agent is activated at a temperature of at least 80°C. In another embodiment, the backing comprises: (a) a paper and (b) a saturant, wherein the saturant comprises a butyl (meth)acrylic ester wherein the butyl (meth)acrylic ester permeates the paper and wherein the saturant is essentially free of a crosslinker, and the backing has an autoignition temperature of greater than 425°F (218°C).



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EXTREME HIGH TEMPERATURE TAPE AND BACKINGS THEREOF**TECHNICAL FIELD**

Paper-based backings and tapes for extreme high temperature applications are described.

SUMMARY

There is a desire to develop a paper-based backing that is able to withstand extreme high temperatures. There is also a desire to develop a non-silicone-based tape that is able to function when exposed to extreme high temperatures.

In one aspect, a tape is provided comprising: (a) a backing comprising a paper and a saturant, wherein the saturant comprises a C2 to C6 (meth)acrylic ester; and (b) an adhesive disposed on the backing, wherein the adhesive comprises a crosslinkable (meth)acrylate polymer and a heat-activatable crosslinking agent, wherein the heat-activatable crosslinking agent is activated at a temperature of at least 80°C.

In one embodiment, the heat-activatable crosslinking agent is activated at a temperature of at least 160°C.

In one embodiment, the heat-activatable crosslinking agent is selected from at least one of: aluminum acetyl acetonate, a metal salt, an azide, an acetylene, a nitrile, a diene, a dienophile, a blocked polyisocyanate, a polyamine, a polythiol, a glycidyl (meth)acrylate, and a polyol.

In one embodiment, the crosslinkable (meth)acrylate polymer is derived from butyl acrylate and acrylic acid, and optionally an antioxidant.

In another aspect, a backing is provided comprising: (a) a paper and (b) a saturant, wherein the saturant comprises a butyl (meth)acrylic ester wherein the butyl (meth)acrylic ester permeates the paper and wherein the saturant is essentially free of a crosslinker and the autoignition temperature of the backing is greater than 218°C (425°F).

In another aspect, a method of protecting a substrate at a temperature of at least 160°C is described comprising: (i) providing a tape comprising (a) a backing comprising a paper and a saturant, wherein the saturant comprises a C2 to C6 (meth)acrylic ester; and (b) an adhesive disposed on the backing, wherein the adhesive comprises a crosslinkable

(meth)acrylate polymer and a heat-activatable crosslinking agent, wherein the heat-activatable crosslinking agent is activated at a temperature of at least 80°C, wherein the adhesive is in contact with the substrate; (ii) heating the taped substrate to at least 160°C; and (iii) removing the tape from the substrate.

5 The above summary is not intended to describe each embodiment. The details of one or more embodiments of the invention are also set forth in the description below. Other features, objects, and advantages will be apparent from the description and from the claims.

BRIEF DESCRIPTION OF DRAWINGS

10 FIG. 1 is a schematic side-view of a tape according to the present disclosure

DETAILED DESCRIPTION

As used herein, the term

“a”, “an”, and “the” are used interchangeably and mean one or more;

15 “and/or” is used to indicate one or both stated cases may occur, for example A and/or B includes, (A and B) and (A or B);

“crosslinking” refers to connecting two pre-formed polymer chains using chemical bonds or chemical groups in order to increase the cohesive strength of the material;

20 “interpolymerized” refers to monomers that are polymerized together to form a polymer backbone; and

“(meth)acrylate” refers to compounds containing either an acrylate ($\text{CH}_2=\text{CHCO}^-$) or a methacrylate ($\text{CH}_2=\text{CCH}_3\text{CO}^-$) structure or combinations thereof; e.g., butyl(meth)acrylate refers to butylacrylate, butylmethacrylate, and combinations thereof.

25 Also herein, recitation of ranges by endpoints includes the endpoints and all numbers subsumed within that range (e.g., 1 to 10 includes 1 and 10 as well as 1.4, 1.9, 2.33, 5.75, 9.98, etc.).

Also herein, recitation of “at least one” includes all numbers of one and greater (e.g., at least 2, at least 4, at least 10, at least 25, at least 50, at least 100, etc.).

30 Treated papers for high-temperature applications are very often unable to withstand the conditions encountered in powder-coat painting. The paper is weakened enough by the bake cycle that tapes made with such backings cannot be removed from the job without tearing. Products designed for such applications therefore involve film

backings that cannot be readily bent or “curved” and cannot be easily dispensed or torn by hand. A paper (such as a crepe paper)-based backing that could be curved and torn by hand and that could survive such temperatures would be an advance.

Powder paint is rapidly replacing liquid paints due to environmental concerns. With this painting technique the paint powder is attracted to a surface, like cold rolled steel, by electrostatic forces. Then very high temperatures are used to fuse the powder into a continuous film. Typically temperatures up to approximately 218°C (425°F) are used to solidify the paint film. At these temperatures, standard tapes comprising a paper-based backing and rubber adhesive no longer function. The paper-based backings degrade and readily break, and the rubber-based adhesives degrade, leaving residue. The solution for protecting tapes to perform at extreme high temperatures has been served by polyethylene terephthalate (PET) film coated with silicone-based pressure sensitive adhesives (PSAs). Silicone PSAs show little adhesion build during the baking process and the PET film is strong. The disadvantages of silicone are higher costs, and the non-obvious residue left behind. Small fragments of silicone adhesive are not visible to the naked eye, and are non-tactile. However, this small amount of low surface energy material may affect wet out and adhesion of any subsequent paint coating.

When using conventional acrylic based PSAs at an extreme high temperature, controlling the strong adhesion build that occurs at such temperatures is important. Usual acrylic PSAs grow strongly in adhesion during heating, leading to failures such as cohesive failure during removal, and excessively high removal forces. During the painting operation the paint may cover the tape, and besides removing strongly bonded adhesive, the paper backing must also pull through any over-coated paint that has been fused into one continuous layer.

The present disclosure is directed to a tape, specifically a removable protecting tape such as a masking tape that performs after exposure to extreme high temperatures.

FIG. 1 depicts one exemplary embodiment of a tape according to the present disclosure. Tape **10** comprises backing **12** and adhesive layer **16**, which is fixedly attached to backing **12**. Optional top coat layer **18** is in contact with backing **12** opposite the adhesive layer.

In the present disclosure, both the backing and the adhesive are formulated to function at the extreme high temperatures experienced, for example, during a powder

coating application. As used herein extreme high temperature refers to a temperature of 218°C (425°F) or higher or even 232°C (450°F) or higher.

Backing

5 The backings of the present disclosure comprise a paper and a saturant. The paper of the present disclosure may be selected from a wide variety of papers as will be apparent to those skilled in this art. Such papers, will, however, be predominantly composed of cellulose papermaking fibers, preferably long Kraft fibers, although other additives conventionally used in papermaking may be included. Examples of such additives are
10 various fillers such as titanium dioxide, clay, and the like.

Exemplary papers include: crepe paper, such as those having an elongation of about 4% to about 25%, such as creped NBSK from Northern Bleached Softwood Kraft; and non-crepe paper (i.e., paper that does not comprise a crepe pattern or is flat).

15 The basis weight of the paper web will vary widely depending upon the particular application, but normally will be in the range from about 30 grams per square meter to 75 grams per square meter or even in the range from about 35 grams per square meter to 60 grams per square meter, although heavier or lighter papers can be use if desired. Also, the paper can be composed of two or more plies of such paper. The paper should contain
20 enough wet strength resin so that it will maintain its integrity after absorbing a minimum of about two times its own weight of water.

Papers of the present disclosure may have a thickness of between at least 50, 60, 70, 80, 90, or even 100 µm (micrometers), and no more than 150, 175, 200, 220, or even 230 µm.

25 In tape applications, the paper is generally saturated to provide additional properties, such as toughness, strength, fold-ability, tear, and delamination resistance. Paper typically has an autoignition temperature of between 218 to 246°C (424 to 474°F).

30 In the present disclosure, the paper is saturated with a saturant (or a saturating composition) to enable the paper to perform after exposure to extreme high temperatures. As used herein, a saturant is a composition, which permeates (or penetrates through) the paper, such that when a cross section of the backing is viewed perpendicular to the thickness of the paper, the saturant is present across substantially the thickness (e.g.,

across more than 50%, more than 75%, more than 90 % of the thickness or even across the entire thickness) of the paper.

Saturants for the backing include a C2 to C6 (meth)acrylic ester. Exemplary (meth)acrylic esters include: ethyl(meth)acrylate, propyl (meth)acrylate,
5 butyl(meth)acrylate, pentyl (meth)acrylate, and hexyl(meth)acrylate.

The saturant may also comprise comonomers, however, the saturant comprises between at least 40, 45, 50, 55, 60, or even 65%; and at most 70, 75, 80, 85, 90, 95, 99, or even 99.5% of the C2 to C6 (meth)acrylic ester by weight relative to the total monomers in the saturant.

10 Such comonomers may include vinyl unsaturated acids, acrylamides, 2-hydroxy ethyl acrylate, and combinations thereof. Exemplary comonomers include: (meth)acrylic acid, itaconic acid, acrylamide, N,N-dimethylacrylamide, and isooctyl acrylamide.

Styrene and/or butadiene may be added to a (meth)acrylate saturant to improve the performance at extreme high temperatures. In one embodiment of the present disclosure,
15 the saturant is essentially free of styrene and butadiene. In other words, the saturant comprises less than 5, 2, 1, or even 0.5% total of styrene and butadiene relative to the total amount of monomers used in the saturant.

In one embodiment, the saturant comprises a low amount (less than 10, 8, or even 6%) of acrylonitrile relative to the total amount of monomers used in the saturant). In
20 some embodiments, the saturant comprises no acrylonitrile.

In one embodiment, substantially no crosslinking agents are added to the saturant. In other words, less than 5, 2, 1, 0.5% or even 0% by weight of crosslinking agents may be present in the saturant.

In one embodiment, a crosslinking agent may be added to the saturant. This may
25 be especially preferable if the saturant is solvent-based.

In addition to other monomers, the saturant composition may also include other ingredients such as fillers including titanium dioxide and clay in an amount of at most 50% by total weight, or even at most 33% by total weight. Other additives such as antioxidants, pigments and the like may also be included. The saturant composition may
30 be applied as a latex or from solution as will be understood by those skilled in this art.

The saturant may be applied in a range of from at least 25, 30, 35, or even 40 % by weight; and at most 60, 70, 75, 80, 90, or even 95 % by weight versus the weight of the paper.

Because the backings of the present disclosure may be used at extreme high
5 temperatures, the backings of the present disclosure should have an autoignition temperature of greater than 204 °C (400°F), 218 °C (425°F), 232 °C (450°F), or even greater than 246 °C (470°F).

The saturant may be water-based or solvent-based, however a water-based saturant is preferred, for example, for cost and handling purposes.

10 The paper may be saturated with the saturant using techniques known in the art. For example, the paper may be sprayed with the saturant, dipped or soaked in the saturant, bead coated, or passed through a bath of saturant. In one preferred embodiment, saturant is applied to both major planes of the paper. Rollers, blades, or squeegees may be used to remove excess saturant from the impregnated paper. The saturated paper is then dried to
15 form a backing. After drying, an adhesive may then be applied to the backing.

For example, the application of the saturant by means of a saturant bath can be carried out in a known fashion, for example, by passing a train of paper through a trough filled with the saturant. The train of paper can also be sufficiently permeated by roller
application, spraying, or coating with a doctor blade. The amount of saturant to be applied
20 can be readily adjusted by varying, for example, the concentration and/or the viscosity of the saturant composition or the nip roll pressure. This amount depends on the requirements of the ultimate field of use and the desired final quality and is generally between 30 and 150 percent by weight, preferably between 40 and 80 percent by weight of the paper. Drying can follow directly after treatment with the impregnating bath.

25 According to a particularly advantageous embodiment, impregnation with the saturant bath can take place using an impregnation arrangement in which a train of paper passing there-through is first pre-impregnated by roller application. In order to de-aerate the pre-impregnated train, the latter is then led over a so-called "breathing section" (in which it remains for several seconds). After air has been removed from the train in this
30 manner, a full impregnation in a saturant bath can be carried out. Subsequently, excess saturant is squeezed out between rolls or wiped off with blades and in this way the desired amount of resin to be applied is attained. In special cases, in which a particularly full

impregnation or impregnation on one side only is sought for, a process according to German Offenlegungsschrift No. 25 50 980 (Neumann filed on November 13, 1975), which employs a vacuum arrangement is available.

From the immersion apparatus, the impregnated train is then led through a dryer having one or preferably several drying zones, without coming into contact with other objects. The rate of transport of the train depends on the length of the drying zone or zones as well as on the drying temperature. In general, the drying temperature is between 60° C and 150° C. When several drying zones are present, zones having step-wise differing temperatures are often employed, beginning with the lowest temperature. As drying arrangements which do not involve contact, jet-suspension dryers are advantageously employed. Subsequent to, or interposed in, the drying step, an arrangement can be present for the application of a coating or finish.

The completed train can subsequently be cut to the desired shape or can be rolled up into rolls.

Adhesive

The saturated paper may then be coated with an adhesive. To be used in an extreme high temperature application, the adhesive must show sufficient properties, including sufficient adhesiveness, low adhesion build, and removability, before and after exposure to extreme high temperatures. The adhesive of the present disclosure comprises one or more crosslinkable (meth)acrylate polymer and a heat-activatable crosslinking agent.

The crosslinkable (meth)acrylate polymer may comprise interpolymerized monomers of (meth)acrylate, such as (meth)acrylate ester monomers, (meth)acrylamide monomers, or (meth)acrylic acid monomers.

(Meth)acrylate ester monomers may include the esters of either acrylic acid or methacrylic acid with non-tertiary alcohols such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 3-methyl-1-butanol, 1-hexanol, 2-hexanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 2-ethyl-1-butanol, 3,5,5-trimethyl-1-hexanol, 3-heptanol, 1-octanol, 2-octanol, isooctyl alcohol, 2-ethyl-1-hexanol, 3,7-dimethylheptanol, 3,7-dimethylhept-3-eneol, 1-decanol, 1-

dodecanol, 1-tridecanol, 1-tetradecanol, citronellol, dihydrocitronellol, 1-octadecanol, and the like.

(Meth)acrylamide monomers may include: acrylamide with or without additional organic groups instead of hydrogen on the nitrogen atom, and methacrylamide with or without additional organic groups instead of hydrogen on the nitrogen atom. The organic groups may include: alkyl, aryl, alkylaryl, alkanol, alkylamine, alkyl or aryl ethers, alkyl or aryl esters, urethane, or other groups.

(Meth)acrylic acid monomers may include acrylic acid or methacrylic acid or their salts.

The (meth)acrylate monomer may be present in an amount of 80 to 99 parts by weight based on 100 parts total monomer content used to prepare the crosslinkable (meth)acrylate polymer. Preferably (meth)acrylate monomer may be present in an amount of 85 to 95 parts by weight based on 100 parts total monomer content. (Meth)acrylates may make up most of the crosslinkable (meth)acrylate polymer.

A dispersing agent such as a hydrocarbon, ester (e.g., ethyl acetate), ketone (e.g., methyl ethyl ketone), or other solvent in which both the crosslinkable (meth)acrylate polymer and the heat-activatable crosslinking agent are soluble, may be necessary to ensure homogeneous dispersion of the heat-activatable crosslinking agent in the crosslinkable (meth)acrylate polymer.

Additional monomers also may be included, such as described below, to provide particular properties. For example, acid-functionalized monomers or other polar monomers.

Useful acid-functionalized monomers include, but are not limited to, those selected from ethylenically unsaturated carboxylic acids, ethylenically unsaturated sulfonic acids, ethylenically unsaturated phosphonic acids, and combinations thereof. Examples of such compounds include those selected from itaconic acid, fumaric acid, crotonic acid, citraconic acid, maleic acid, oleic acid, β -carboxyethyl (meth)acrylate, 2-sulfoethyl methacrylate, styrene sulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, vinylphosphonic acid, and combinations thereof.

Due to their availability, acid-functionalized monomers of the acid functional copolymer are generally selected from ethylenically unsaturated carboxylic acids. When even stronger acids are desired, acidic monomers include the ethylenically unsaturated

sulfonic acids and ethylenically unsaturated phosphonic acids. The acid-functionalized monomer is generally used in amounts of 1 to 15 parts by weight, preferably 1 to 7 parts by weight, based on 100 parts by weight total monomer.

Other polar comonomers may also be included to impart useful properties in the substantially linear copolymer, such as resistance to oils.

Examples of other useful polar copolymerizable monomers include, but are not limited to those selected from the group consisting of hydroxyalkyl acrylates, acrylamides, substituted acrylamides, N-vinyl lactams, acrylonitrile, dimethylaminoethylmethacrylate, and combinations thereof.

Representative examples of the other useful polar monomers include, but are not limited to 2-hydroxyethyl (meth)acrylate; N-vinylpyrrolidone; N-vinylcaprolactam; acrylamide; mono- or di-N-alkyl substituted acrylamides such as t-butyl acrylamide dimethylaminoethyl acrylamide and N-octyl acrylamide; poly(alkoxyalkyl) (meth)acrylates including 2-(2-ethoxyethoxy)ethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 2-methoxyethoxyethyl (meth)acrylate, 2-methoxyethyl methacrylate, polyethylene glycol mono(meth)acrylates; alkyl vinyl ethers, including vinyl methyl ether; and combinations thereof. Preferred polar monomers include those selected from the group consisting of 2-hydroxyethyl (meth)acrylate and N-vinylpyrrolidinone. The polar monomer may be present in amounts of 0 to 10 parts by weight, preferably 1 to 7 parts by weight, based on 100 parts by weight total monomer.

When used, vinyl monomers useful in the substantially linear copolymer include but are not limited to vinyl esters (e.g., vinyl acetate, vinyl propionate, and vinyl butyrate), styrene, substituted styrene (e.g., α -methyl styrene), vinyl halide, and combinations thereof. A preferred monomer with a high T_g (glass transition temperature) is vinyl acetate for reasons of availability. Such vinyl monomers are generally used at 0 to 5 parts by weight, preferably 1 to 5 parts by weight, based on 100 parts by weight total monomer.

A heat-activatable crosslinking agent is added to the crosslinkable (meth)acrylate polymer to obtain an adhesive having sufficient performance properties at extreme high temperatures. The heat-activatable crosslinking agent of the present disclosure is activated at a temperature of at least 80°C, 100°C, 125°C, 150°C, 160°C, 170 °C, 180 °C, or even 190°C. The heat-activatable crosslinking agent provides for the crosslinking of the crosslinkable (meth)acrylate polymer. In one embodiment, the activation may occur by a

compound having an activation temperature, such that when the activation temperature is reached, the compound reacts with the crosslinkable (meth)acrylate polymer. In another embodiment, the activation may occur by unblocking a crosslinking-active group. For example a heat-activatable crosslinking agent containing a ketoxime blocked isocyanate will lose the ketoxime group under elevated temperature and leave the isocyanate moiety to react with the crosslinkable (meth)acrylate polymer. In another example, aluminum acetyl acetonate will lose the acetyl acetonate groups and leave aluminum to react with the crosslinkable (meth)acrylate polymer.

Although not wanting to be limited by theory, it is believed that by using an adhesive, which may be thermally crosslinked during its ultimate end use (e.g., heated following coating with powder paint), it is possible to prevent unacceptable adhesion build during exposure to extreme high temperatures.

In one embodiment, the pressure sensitive adhesive may comprise not only a heat-activatable crosslinking agent, which is activated during end use (e.g., powder coat painting), but also another crosslinking agent, (herein referred to as the preliminary crosslinking agent). The preliminary crosslinking agent is activated during manufacturing of the adhesive and/or the tape, and is used to control the initial properties of the adhesive tape (i.e., balance of adhesion and shear to a substrate, roll unwind force, etc.). These preliminary crosslinking agents may comprise any crosslinking agents known to those of ordinary skill in the art, such as those activated thermally or by high energy radiation (i.e., gamma, UV, or electron beam). If the preliminary crosslinking agent is thermally activated, the crosslinking agent is activated at a temperature below the maximum temperature experienced during the manufacture of the adhesive and/or tape, whereas the heat-activated crosslinking agent is activated at a temperature above the maximum temperature experienced during the manufacture of the adhesive and/or tape.

The heat-activatable crosslinking agent is activated during end use and is used to control the adhesion properties of the adhesive tape during and after use. The temperature needed to activate the heat-activatable crosslinking agent and initiate crosslinking of the crosslinkable (meth)acrylate polymer must be higher than the temperatures experienced during the manufacture and coating of the adhesive. Therefore, the polymerization temperatures reached and coating process used will dictate which heat-activatable crosslinking agent to select. For example, if a solvent coating method is used to coat the

adhesive, a heat-activatable crosslinking agent having an activation temperature of at least 80°C may be used since solvent removal can often be done at temperatures lower than 80°C. If an extrusion method, typically solventless, is used to coat the adhesive, a heat-activatable crosslinking agent having an activation temperature of at least 160°C may be necessary.

The heat-activatable crosslinking agent of the present disclosure is a molecule comprising a covalent bonding group, a molecule comprising an ionic bonding group, or a combination thereof.

Exemplary molecules comprising an ionic bonding group are selected from at least one of: aluminum acetyl acetate, and other metal salts.

Exemplary molecules comprising a covalent bonding group are selected from at least one of: an azide, an acetylene, a nitrile, a diene, a dienophile, a blocked polyisocyanate (such as an epsilon caprolactam-blocked polyisocyanate), a multifunctional crosslinker (such as polyamines or polythiol), a glycidyl (meth)acrylate, a polyol (such as 1,6 -hexanediol or butanediol), and combinations thereof.

Isocyanate groups can be blocked by alcohols, oximes, lactams and the like, and combinations thereof. Examples include 3,5-dimethylpyrazole, 2,6-dimethyl-4-heptanone oxime, methyl ethyl ketoxime, 2-heptanone oxime, 1,2,4-triazole, epsilon-caprolactam, nonylphenol, t-butanol, propylene glycol, isopropanol, methanol, n-butanol, n-hexanol, and n-pentanol. The blocking agent is chosen to meet activation temperature requirements. In addition, internal blocking can be used which involves forming an uretdione or a cyclic urea structure, which when heated can revert to isocyanate.

Exemplary types of crosslinking systems that may be used include: (i) the reaction of an aluminum acetyl acetate and acids; (ii) the reaction of an azide and an acetylene as described in U.S. Publ. No. 2010-0125120 (Crandall et al. filed on November 14, 2008; (iii) the reaction of an azide and a nitrile as described in W.O. Publ. No. 2010-014274 (Manzara et al. filed on July 31, 2008); and (iv) a Diels-Alder reaction of a conjugated diene and a substituted alkene (or dienophile).

The heat-activatable crosslinking agent may be a separate molecule from the crosslinkable (meth)acrylate polymer or the heat-activatable crosslinking agent may be incorporated into the crosslinkable (meth)acrylate polymer (see for example U.S. Appl. No. 12/943116, Manzara et al. filed on November 11, 2009).

In one embodiment, the adhesive of the present disclosure comprises at least two, or even three heat-activatable crosslinking agents, for example, a blocked polyisocyanate and a polyol.

The adhesive compositions can include any of the adjuvants commonly employed in curable polymer formulations. An organic or inorganic filler may be added to the composition to improve physical properties, such as tensile strength, density, and modulus. Fillers include: carbon black; silica; or other mineral fillers such as hydrotalcite, or barium sulfate, and combinations thereof.

In some embodiments tackifiers and plasticizers may also be added to the adhesive composition. Tackifiers, include for example, rosin, rosin derivatives, hydrogenated rosin derivatives, polyterpene resins, phenolic resins, coumarone-indene resins, poly-t-butyl styrene and combinations thereof. Plasticizers include for example, hydrocarbon oils, hydrocarbon resins, polyterpenes, rosin esters, phthalates, phosphate esters, dibasic acid esters, fatty acid esters, polyethers, and combinations thereof.

Other optional additives include, for example, stabilizers (e.g., antioxidants or UV-stabilizers), pigments (e.g., dyes), flame retardants, medicaments, and the like. The use of such additives is well known to those of ordinary skill in the art.

Fibers, glass bubbles, and retro-reflective beads may also be added. Fibers can be of several types, generally polymeric or glass. The former can be nylon, polyester, polyamide, epoxy and the like. Glass fibers fall into two types E- and S-glass. E-glass has good insulation properties and maintains its properties up to 815°C (1500°F). S-glass has a high tensile strength and is stiffer than E-glass. The fiber type is chosen for its compatibility with the substantially linear copolymer and to provide enhanced properties such as tensile and elongation. Glass bubbles are generally used to lower density, add topology to the copolymer coatings or films, reduce cost, and/or to control contact area. A series of glass microbubbles with variation in size and crush strength is available from 3M Co., St. Paul, MN.

The curable adhesive composition can typically be prepared by mixing the crosslinkable (meth)acrylate polymer, the heat-activatable crosslinking agent, and any adjuvants (if desired) in conventional processing equipment. This may be done in a solvent or in a solvent-less environment. The desired amounts of compounding ingredients and other conventional adjuvants or ingredients can be added to the curable adhesive

composition and intimately admixed or compounded therewith by employing any of the conventional mixing devices such as extruders, static mixers, internal mixers, (e.g., Banbury mixers), two roll mills, or any other convenient mixing devices. The temperature of the mixture during the mixing process typically is kept safely below the activation temperature of the heat-activatable crosslinking agent. Thus, the temperature typically should not rise above about 60°C, about 80°C, 100 °C, 125 °C, 150 °C, or even about 160 °C. During mixing, it generally is desirable to distribute the components and adjuvants uniformly.

In one embodiment of this disclosure, the compounded composition may be processed (such as by coating or molding) in a solvent or a solvent-less environment. For example, the crosslinkable (meth)acrylate polymer and the heat-activatable crosslinking agent may be coated without the presence of a solvent, or may be coated in the presence of a solvent. The solvent may be removed, for example, by thermal evaporation. Additionally, the amount of solvent in the compounded adhesive composition may be adjusted, depending on the application so as to obtain a desired viscosity of the composition. For example, in pressure sensitive adhesive applications, the viscosity may be adjusted to obtain a desired flow rate for the process.

The compounded adhesive composition may be crosslinked via thermal activation. Additionally the adhesive can be crosslinked to attain desired initial properties using appropriate crosslinkers or actinic radiation such as UV or electron beam irradiation, while retaining the subsequent crosslinking potential of the heat-activatable crosslinking agent during use.

The PSA compositions of the present invention may be coated by any of a variety of conventional coating techniques known in the art, such as roll coating, spray coating, knife coating, extrusion, die-coating, and the like.

In one embodiment, the adhesive coating layer thickness typically may be in the range of about 0.0025 mm to 0.13 mm (0.1 mil to 5.0 mil), and more typically in the range of about 0.0013 mm to 0.076 mm (0.5 mil to 3.0 mil). Optionally, a release liner may be applied over the adhesive layer if the tape is to be wound into a roll. In another embodiment, the saturated paper may be coated with a release coating on the side opposite the adhesive coating.

In some embodiments, a primer, as is known in the art, is used between the backing and the adhesive layer to improve adhesion between the backing and the adhesive layer. In one embodiment, a primer may not be needed between the backing and the adhesive for example, when the (meth)acrylate polymer of the saturant and the crosslinkable (meth) acrylate polymer of the adhesive are the same (e.g., both butylacrylate).

As previously mentioned, in some embodiments, the tapes of the present disclosure may be used in extreme high temperature applications, such as powder coating applications. In some embodiments, the tape of the present disclosure may be applied to a substrate, such that the adhesive is in contact with the substrate, protecting or masking the substrate. A composition such as a powder coating, may be applied to the taped substrate and the coated taped substrate may be heated to temperatures greater than 160°C, 180°C or even 190°C to react the composition (e.g., fusing the powder coating to form a continuous layer). The tape of the present disclosure then may be removed from the substrate.

Silicone-based adhesive tapes may be cleanly removed from the substrate after use, however, they may leave non-visible contaminants on the substrate surface, which interfere with subsequent processes (such as paint coating). Advantageously, in one embodiment, the tape of the present disclosure, may be cleanly removed from the substrate after use (i.e., no visible presence of backing or adhesive) and if non-visible contaminants remain on the substrate surface, they do not interfere with subsequent processes.

Preferably the cured adhesive of the present disclosure has a peel ratio of 4 or less, or even 5 or less.

EXAMPLES

Advantages and embodiments of this disclosure are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. In these examples, all percentages, proportions and ratios are by weight unless otherwise indicated.

All materials are commercially available, for example from BASF Corporation, Mt. Olive, NJ, or known to those skilled in the art unless otherwise stated or apparent.

These abbreviations are used in the following examples: g = gram, in = inch, kg = kilograms, min = minutes, mol = mole; cm = centimeter, mm = millimeter, ml = milliliter, L = liter, lb = pound, psi = pounds per square inch, pwi = pounds per inch width, ppm = parts per million, MPa = megaPascals, N = Newtons, pph = parts per hundred, and wt = weight.

Backings

Materials

Antioxidant 1	A 50% aqueous dispersion of an antioxidant, tetrakis(methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate))methane, available from Akron Dispersions, Akron, OH available under the trade designation "BOSTEX 537"
Backing 1	Crepe paper having a weight basis of 30 lb. / ream (48.5 g/m ²)
Backing 2	Crepe paper having a weight basis of 34 lb. / ream (55 g/m ²)
Saturant 1:	an aqueous anionic dispersion of an n-butyl acrylate-acrylonitrile-styrene copolymer, ca. 50% solids; available from BASF Corporation, Charlotte, NC under the trade designation "ACRONAL S 504"
Saturant 2	a carboxylated styrene/butadiene dispersion, ca. 51% solids, available from BASF Corporation, Florham Park, NJ under the trade designation "BUTOFAN NS-209"

Saturant 3	an anionic, aqueous acrylate copolymer dispersion of primarily butyl acrylate (46 wt%) with smaller amounts of methyl acrylate, 2-ethylhexyl acrylate, styrene, and acrylamide, and containing internal crosslinking agents, ca. 51% solids, available from BASF Corporation, Charlotte, NC., under the trade designation "ACRONAL NX 3587" to which 1 pph Antioxidant 1 was added
Saturant 4	a self-crosslinking, acrylic, anionic latex based on butyl acrylate/acrylonitrile polymer, ca. 60% solids, and containing approximately 89 wt.% butyl acrylate, available from BASF Corporation, Charlotte, NC., available under the trade designation "ACRONAL OPTIVE 510" to which 1 pph Antioxidant 1 was added.

Test Methods

Tensile Strength and Elongation – After Conditioning at 22°C

Tensile strength and elongation were measured according to ASTM D 3759/D 3795M-05 "Standard Test Method for Breaking Strength and Elongation of Pressure Sensitive Tape" using the following parameters. Conditioning was done for at least 24 hours followed by testing, both at 22°C (71°F) and 50% relative humidity (RH). The samples were cut such that the length was in the machine direction, and the dimensions were 2.54 cm wide by approximately 22.9 cm long (1 in. by approximately 9 in.), the gauge length was 10.2 cm (4 in.), and the crosshead speed was 30.5 cm/minute (12 in./minute). For each example, three samples were evaluated and the average tensile strength and elongation values obtained in pounds/inch (pounds per inch width, piw) and % respectively. Strength values were then converted to N/m.

Tensile Strength and Elongation – After Conditioning at 163°C

Tensile testing was done as described above in "Tensile Strength and Elongation – After Conditioning at 22°C" with the following modifications. Samples were conditioned at 163°C (325°F) for 30 minutes. They were then equilibrated for at least 24 hours followed by testing, both at 22°C (71°F) and 50% RH.

The % retention was calculated as [(average result after conditioning at 163°C) / average result after conditioning at 22°C] x 100.

Tensile Strength and Elongation – After Conditioning at 218°C

Tensile testing was done as described above in “Tensile Strength and Elongation – After Conditioning at 22°C” with the following modifications. Samples were conditioned at 218°C (425°F) for 30 minutes. They were then equilibrated for at least 24 hours followed by testing, both at 22°C (71°F) and 50% RH. The % retention was calculated as [(average result after conditioning at 218°C) / average result after conditioning at 22°C] x 100.

Examples**General Preparation**

For Examples 1A-C and 2A-B in Table 1 below, the saturant solution was diluted with deionized water to a coatable viscosity (approximately 30% solids) and poured into an aluminum pan measuring 24.1 cm by 29.2 cm by 8.9 cm (9.5 by 11.5 by 3.5 in.) (width, length, and depth respectively) to fill it. A sample of paper, measuring 15.2 cm (6 in.) wide by 122 to 152 cm (48 to 60 in.) long, was then immersed in the saturant solution by dipping it in at one end of the pan, moving it to the other end of the pan while keeping it submerged, and then slowly removing it from the solution. The saturated paper (or backing) was then placed on a silicone-treated paper release liner and the top, exposed side of the backing was wiped down one time to remove excess saturant using a rubber squeegee and firm hand pressure. The backing was then removed, the excess saturant wiped from the liner, and the backing placed back on the liner such that the opposite side of the backing was exposed, and the exposed surface squeegeed as before. The wiped backing was then taped down by its end edges to a clean silicone-treated paper release liner, which had been previously taped down by its end edges to a Masonite board. This assembly was placed in a forced air oven set at 74°C (165°F) for 20 to 30 minutes. Upon removal, the backing was allowed to cool before removing it from the release liner. Comparative Example 1 was prepared in a production plant using a continuous process that employed a saturating bath, squeeze rolls, and heated ovens set such that the exit temperature of the saturated paper was 116°C (240°F). Comparative Example 2 was prepared in a production plant using a continuous process that employed a saturating bath, squeeze rolls, and an oven heated at 149°C (300°F).

Comparative Example 1

Backing 1 was impregnated with Saturant 1 and dried as described in the “General Preparation” above. The saturant resin content of the backing was determined, which is reported as the approximate percent weight of the saturant in the backing per the weight of the input paper. The backing was evaluated for its tensile properties at room and elevated temperatures and the results are shown in Table 1.

Comparative Example 2

Backing 2 was impregnated with Saturant 2 and dried as described in the “General Preparation” above. The saturant resin content of the backing was determined and the backing was evaluated for its tensile properties at room and elevated temperatures. The results are shown in Table 1.

Examples 1A, 1B, and 1C

Backing 2 was impregnated with Saturant 3 and dried as described in the “General Preparation” above. The saturant resin content of the backing was determined and the backing was evaluated for its tensile properties at room and elevated temperatures. The results are shown in Table 1.

Examples 2A and 2B

Backing 2 was impregnated with Saturant 4 and dried as described in the “General Preparation” above. The saturant resin content of the backing was determined and the backing was evaluated for its tensile properties at room and elevated temperatures. The results are shown in Table 1.

Table 1: Results

N.D.: not determined

Ex.	Backing	Saturant Type (approximate wt%)	Tensile Properties									
			72 F (23 C)		325 F (163 C)			425 F (218 C)				
			Strength N/m (piw)	% Elongation	Strength N/m (piw)	% Retention	% Elongation	% Retention	Strength N/m (piw)	% Retention	% Elongation	% Retention
CE 1	1	1 (20)	3.00 (26.60)	6.44	24.10 (21.33)	80.2	4.36	67.7	1.24 (11.00)	41.3	1.00	15.5
CE 2	2	2 (49)	3.12 (27.6)	13.9	N.D.	N.D.	N.D.	N.D.	1.18 (10.4)	36.2	2.3	16.5
1A	2	3 (43)	4.18 (37.00)	9.80	3.30 (29.20)	78.9	9.40	95.9	2.43 (21.53)	58.2	5.70	58.2
1B	2	3 (43)	3.03 (26.8)	14.8	N.D.	N.D.	N.D.	N.D.	1.88 (16.6)	61.9	5.7	38.5
1C	2	3 (43)	3.28 (29.0)	16.2	N.D.	N.D.	N.D.	N.D.	1.91 (16.9)	58.3	7.1	43.8
2A	2	4 (43)	2.42 (21.4)	14.2	N.D.	N.D.	N.D.	N.D.	1.66 (14.7)	68.7	7.7	54.2
2B	2	4 (43)	2.51 (22.2)	14.6	N.D.	N.D.	N.D.	N.D.	1.51 (13.4)	60.4	5.6	38.4

Adhesives
Materials

BA	Butyl acrylate monomer, available from BASF Corporation, Mt. Olive, NJ.
2-EHA	2-ethylhexyl acrylate monomer, available from BASF Corporation, Mt. Olive, NJ.
AA	Acrylic acid monomer, available from Arkema, Incorporated, Philadelphia PA.
TMPTA	1,1,1-Trimethylolpropane Triacrylate; a liquid, non-nitrosoamine retarded crosslinking agent, available as Saret 519HP from Sartomer, Exton, PA.
IOTG	Isooctyl thioglycolate
AeBP	4-(2-Hydroxyethoxy)benzophenone acrylate, a difunctional monomer that is copolymerizable with acrylate monomers and contains a radiation sensitive hydrogen abstracting group which provides crosslinking upon exposure to high intensity radiation, eg. e-beam (see US 5,773,485), 3M Company, St. Paul, MN.
BLI	an epsilon-Caprolactam-blocked polyisocyanate, having an NCO-content of 10.1-10.8% by weight, a Tg of approximately 51°C, and an unblocking temperature of 170-180°C, available from Evonik Degussa Corporation, Parsippany, NJ available under the trade designation "VESTAGON B 1065".
HD	1,6-hexanediol, available from BASF Corporation, Freeport, TX.
AO 2	Pentaerythritol Tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate; an antioxidant, available from Ciba Specialty Chemicals, Incorporated, Tarrytown, NY available under the trade designation "IRGANOX 1010".
Photoinitiator	2,2-dimethoxy-2-phenylacetophenone; a photoinitiator, available from Ciba Specialty Chemicals, Incorporated, Tarrytown, NY available under the trade designation "IRGANOX 651".
AO 3	Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate, an antioxidant, available from Ciba Specialty Chemicals, Incorporated, Tarrytown, NY available under the trade designation "IRGANOX 1076".
Film A	Ethylene/vinyl acetate copolymer film having a thickness of 0.0635 millimeters, available as VA-24 from Pliant Corporation, Dallas, TX.
Cold Rolled Steel	B952 P60 DIW, unpolished, measuring 20.3 cm long by 10.2 cm wide by 0.81 mm thick (8 inches by 4 inches by 0.032 inches), used as received, ACT Test Panels LLC, Hillsdale, MI.
BPI	A blocked polyisocyanate, having an NCO-content of 11.2% by weight, and an unblocking temperature of 120°C, available from Evonik Degussa Corporation, Parsippany, NJ available under the trade designation "VESTAGON EP-BE 9030".

Test Methods

Peel Adhesion Strength – Initial (at Room Temperature)

Single coated pressure sensitive tape samples, measuring 2.54 cm (width) by 25.4 cm (length) (1 in. by 10 in.), were conditioned and tested as described below at approximately 23°C and 50% RH. A tape sample was conditioned for at least 24 hours after which it was adhered to a cold rolled steel test substrate surface by rolling a 2.04 kilogram (kg) rubber-faced roller back and forth over the sample two times. After a 20 minute dwell the peel adhesion force was measured using a Model 3M90 Slip/Peel tester (IMASS, Incorporated, Accord, Massachusetts) at an angle of 90° and a peel rate of 30.5 centimeters/minute (cm/min) (12 in./min.). Two or three samples were evaluated for peel adhesion strength and the average of the results was recorded in ounces/inch then converted and reported in N/decimeter (N/dm).

Peel Adhesion Strength – Post Bake

Cold rolled steel substrates having single coated pressure sensitive tape samples thereon were prepared as described above and placed in a forced air oven set at 218°C for 30 minutes. After removal from the oven and cooling overnight at approximately 23°C and 50% RH, they were evaluated for peel adhesion strength as described previously.

Peel Ratio

The peel ratio was calculated as follows: (post bake peel adhesion strength / initial peel adhesion strength).

Examples 3-22 and Comparative Examples CE-3 to CE-12

Adhesive Preparation I

Generally, two sheets of Film A were heat sealed on the lateral edges and the bottom to form a rectangular pouch having a width of approximately 4.6 cm (1.8 in.) on a liquid form, fill, and seal machine. The pouch was then filled with a pressure sensitive adhesive (PSA) composition having components A-E as given in Table 1 below. In addition, all the compositions contained 0.15 parts Photoinitiator per hundred parts of the sum of A-C (hereinafter written as “0.15 pph Photoinitiator based on the sum of A-C”)

and 0.40 pph AO 3 based on the sum of A-C. In Table 2, components A-C are given in parts by weight (pbw), and components D and E are given in pph based on the sum total of A-C. Prior to filling the pouch, nitrogen gas was bubbled through the PSA composition. The filled package was then heat sealed at the top in the cross direction through the monomer to form a pouch having a length of approximately 14 cm (5.5 in.), a thickness of approximately 0.625 cm (0.25 in.), and containing approximately 25 gm of PSA composition. The pouch was then placed in a water bath that was maintained at about 16°C (60°F) and exposed to ultraviolet radiation at an intensity of about 4.55 mW/cm² for approximately 21 minutes. The radiation was supplied from lamps having about 90% of the emissions between 300 and 400 nanometers (nm), and a peak emission at 351 nm.

Extrusion

Adhesive pouches were fed into a Leistritz twin screw extruder (Leistritz Corporation, Allendale, NJ) having eight zones, a diameter of 18 mm, and a length:diameter ratio of 36:1. The zone and die temperatures were set depending on the presence or absence of a heat-activatable crosslinking agent. When no heat-activatable crosslinking agent was employed, the barrel zones and die temperatures were set at approximately 149°C (300°F). When a heat-activatable crosslinking agent was used the barrel zones and die temperatures were set at approximately 121°C (250°F). The adhesive pouches were fed via zone 1, component H (TMPTA) via zone 2, and components F and/or G (the heat-activatable crosslinking agents, when present) along with AO 2 via zone 6. The amounts of components F-H are given pph based on the sum total of A-C. The final pressure sensitive adhesive composition was extruded at a rate of 3 lbs per hour to a thickness of between 0.037 mm and 0.062 mm (where 6.15 grains/24 in.² is approximately 0.025 mm (0.001 in)) onto a saturated paper backing prepared as described in Example 1 in Table 1 above. The coated adhesive was then crosslinked by exposure to electron beam irradiation using the parameters given in Table 2. The resulting pressure sensitive adhesive tape was then evaluated for Peel Adhesion Strength Initial and Post Bake, and the Peel Ratio determined as described in the test methods above. The results are shown in Table 2 below.

Table 2

Ex.	A	B	C	D	E	F	G	H	Coating & Process Parameters				Peel (N/dm)		Peel Ratio
									Coating Grains	eBeam Dose (MRads)	eBeam Voltage (kVolts)	eBeam O ₂ (ppm)	Initial	Post Bake	
CE 3	93.7	0.0	6.3	0.050	0.030	0	0	2	12	3	130	50	4.0	41.8	10.2
CE 4	93.7	0.0	6.3	0.050	0.030	0	0	2	12	2	130	50	5.8	58.8	10.2
3	93.7	0.0	6.3	0.050	0.030	1	0	2	12	2	130	50	10.5	32.0	3.0
CE 5	93.7	0.0	6.3	0.050	0.030	0	0	2	12	4	130	50	2.7	35.7	12.8
4	93.7	0.0	6.3	0.050	0.030	1	0	2	12	4	130	50	6.6	19.7	3.0
5	93.7	0.0	6.3	0.050	0.030	1	0	1	12	3	140	50	31.7	27.6	0.9
CE 6	93.7	0.0	6.3	0.050	0.030	0	0	1	12	6	140	50	22.2	67.2	3.0
6	93.7	0.0	6.3	0.050	0.030	1	0	1	12	6	140	50	10.6	23.4	2.2
CE 7	93.7	0.0	6.3	0.050	0.030	0	0	2	9	4	120	50	3.4	11.6	3.5
7	93.7	0.0	6.3	0.050	0.030	1	0	2	9	4	120	50	5.0	7.4	1.5
CE 8	93.7	0.0	6.3	0.050	0.030	0	0	2	15	4	135	50	1.5	53.4	34.4
8	93.7	0.0	6.3	0.050	0.030	1	0	2	15	4	135	50	6.7	25.3	3.8
CE 9	97.0	0.0	3.0	0.071	0.053	0	0	1	12	6	140	550	21.8	73.4	3.4
9	97.0	0.0	3.0	0.071	0.053	1	0	1	12	6	140	550	25.3	54.5	2.2
10	97.0	0.0	3.0	0.071	0.053	3	0	2	12	6	140	550	38.1	51.3	1.4
CE 10	48.0	48.0	4.0	0	0.050	0	0	3	12	6	140	50	4.8	34.0	7.1
CE 11	48.0	48.0	4.0	0	0.050	0	0	1	12	6	140	50	15.5	57.7	3.7
11	48.0	48.0	4.0	0	0.050	1	0	1	12	6	140	50	18.3	32.0	1.8
12	48.0	48.0	4.0	0	0.050	2	0	1	12	6	140	550	54.6	66.5	1.2
CE 12	0	96	4	0	0.03	0	0	1	12	6	140	50	20.9	80.3	3.8
13	0	96	4	0	0.03	0	1	1	12	6	140	550	40.3	70.3	1.8
14	0	96	4	0	0.03	0	4	2	12	2	130	50	22.9	59.0	2.6
15	93.7	0.0	6.3	0.050	0.030	0	4	2	12	4	130	50	13.7	47.0	3.4
16	93.7	0.0	6.3	0.050	0.030	0	4	2	9	4	120	50	3.1	15.7	5.1
17	93.7	0.0	6.3	0.050	0.030	0	4	2	15	4	135	50	13.6	48.3	3.6
18	93.7	0.0	6.3	0.050	0.030	0	4	1	12	3	140	50	10.8	28.6	2.7
19	97.0	0.0	3.0	0.071	0.053	0	4	1.5	12	6	140	550	48.5	110.9	2.3
20	93.7	0.0	6.3	0.050	0.030	1	1	1	12	3	140	50	41.3	44.9	1.1
21	93.7	0.0	6.3	0.050	0.030	1	1	2	12	3	140	50	39.6	51.1	1.3
22	97.0	0.0	3.0	0.071	0.053	2	1	1.5	12	6	140	550	34.6	70.7	2.1

Examples 23 and Comparative Examples CE-13*Adhesive Preparation II*

Generally, two sheets of Film A were heat sealed on the lateral edges and the bottom to form a rectangular pouch having a width of approximately 4.6 cm (1.8 in.) on a liquid form, fill, and seal machine. The pouch was then filled with a pressure sensitive adhesive (PSA) composition having components A, C, D, and E as given in Table 3 below. In addition, all the compositions contained 0.15 parts Photoinitiator per hundred parts of the sum of A and C (hereinafter written as "0.15 pph Photoinitiator based on the sum of A and C") and 0.40 pph AO3 based on the sum of A and C. In Table 3, components A and C are given in parts by weight (pbw), and components D, and E are given in pph based on the sum total of A and C. Prior to filling the pouch nitrogen gas was bubbled through the PSA composition. The filled package was then heat sealed at the top in the cross direction through the monomer to form a pouch having a length of approximately 14 cm (5.5 in.), a thickness of approximately 0.625 cm (0.25 in.), and containing approximately 25 gm of PSA composition. The pouch was then placed in a water bath that was maintained at about 16°C (60°F) and exposed to ultraviolet radiation at an intensity of about 4.55 mW/cm² for approximately 21 minutes. The radiation was supplied from lamps having about 90% of the emissions between 300 and 400 nanometers (nm), and a peak emission at 351 nm.

Solvent Coating

The adhesive was dissolved in ethyl acetate to yield a solution comprising 30.9% solids. Components H, I, and J were added to the solvated solution, which was then coated onto a saturated paper backing prepared as described in Example 3 in Table 1 above. Components H-J are given in pph based on the sum total of A and C in Table 3. The coatings were allowed to air dry for approximately 1-2 minutes and were then dried in an oven at 65°C for 10 minutes. The coated adhesive was then crosslinked by exposure to electron beam irradiation using the parameters given in Table 3. The resulting pressure sensitive adhesive tape was then evaluated for Peel Adhesion Strength Initial and Post Bake, and the Peel Ratio determined as described in the test methods above. The results are shown in Table 3 below.

Table 3

	A	C	D	E	I	J	H	Coating & Process Parameters				Peel (N/dm)		Peel Ratio
								Coating Grains	eBeam Dose (MRads)	eBeam Voltage (kVolts)	eBeam O2 (ppm)	Initial	Post Bake	
Ex.	BA	AA	AeBP	IOTG	BPI	Antioxidant 2	TMPTA							
23	93.7	6.3	0.050	0.075	0.16	0.16	0.33	12	5	140	50	38.4	47.9	1.25
CE 13	93.7	6.3	0.050	0.075	0	0.13	0.26	12	5	140	50	31.9	50.9	1.60

Foreseeable modifications and alterations of this invention will be apparent to those skilled in the art without departing from the scope and spirit of this invention. This invention should not be restricted to the embodiments that are set forth in this application for illustrative purposes.

What is claimed is:

1. A article comprising:

5 (a) a backing comprising a paper and a saturant, wherein the saturant comprises a C2 to C6 (meth)acrylic ester; and

(b) an adhesive disposed on the backing, wherein the adhesive comprises a crosslinkable (meth)acrylate polymer and a heat-activatable crosslinking agent, wherein the heat-activatable crosslinking agent is activated at a temperature of at least 80°C.

10 2. The article according to claim 1, wherein the heat-activatable crosslinking agent is activated at a temperature of at least 160 °C.

15 3. The article according to claim 1 or 2, wherein the heat-activatable crosslinking agent is a molecule comprising an ionic bonding group and is selected from at least one of: aluminum acetyl acetate, and other metal salts.

20 4. The article according to claim 1 or 2, wherein the heat-activatable crosslinking agent is a molecule comprising a covalent bonding group and is selected from at least one of: an azide, an acetylene, a nitrile, a diene, a dienophile, a blocked polyisocyanate, a glycidyl (meth)acrylate, and a polyol.

25 5. The article according to claim 4, wherein the blocked polyisocyanate is selected from at least one of: epsilon caprolactam-blocked polyisocyanate and an uretdione.

6. The article according to claim 4, wherein the polyol is selected from at least one of: 1,6-hexanediol and butanediol.

30 7. The article according to claim 1 or 2, wherein the heat-activatable crosslinking agent is a molecule comprising a covalent bonding group and is selected from at least one of: a polyamine and a polythiol.

8. The article according to any one of the previous claims, comprising at least two heat-activatable crosslinking agents.

5 9. The article according to any one of the previous claims, wherein the crosslinkable (meth)acrylate polymer is derived from butyl acrylate and acrylic acid, and optionally an antioxidant.

10 10. The article according to any one of the previous claims, wherein the adhesive is essentially free of solvent.

15 11. A article comprising: (a) a paper and (b) a saturant, wherein the saturant comprises a butyl (meth)acrylic ester wherein the butyl (meth)acrylic ester permeates the paper and wherein the saturant is essentially free of a crosslinker, wherein the autoignition temperature of the backing is greater than 425°F (218°C).

12. The article according to any one of the previous claims, wherein the saturant further comprises a comonomer.

20 13. The article according to claim 12, wherein the comonomer is selected from vinyl unsaturated acids, acrylamides, and 2-hydroxy ethyl acrylate.

25 14. The article according to claim 13, wherein the comonomer is selected from (meth)acrylic acid, itaconic acid, acrylamide, N,N-dimethylacrylamide, and isooctyl acrylamide.

15. The article according to any one of the claims 12-14, wherein the comonomer is 0.5 to 50% by weight relative to total monomers in the saturant.

30 16. The article according to any one of the previous claims, wherein the C2 to C6 ester compound is 45 to 99.5% by weight relative to the total monomers in the saturant.

17. The article according to any one of the previous claims, wherein the saturant is essentially free of styrene and butadiene.

5 18. The article according to any one of the previous claims, wherein the paper is a crepe paper.

19. The article according to any one of the previous claims, wherein the saturant further comprises an antioxidant.

10

20. The article according to any one of the previous claims, wherein the backing comprises 25 to 95 % by weight of the saturant versus the weight of the paper.

21. A method of protecting a substrate at a temperature of at least 160°C comprising:

15 providing a tape comprising (a) a backing comprising a paper and a saturant, wherein the saturant comprises a C2 to C6 (meth)acrylic ester; and

(b) an adhesive disposed on the backing, wherein the adhesive comprises a crosslinkable (meth)acrylate polymer and a heat-activatable crosslinking agent, wherein the heat-activatable crosslinking agent is activated at a temperature of at least 80°C, wherein the
20 adhesive is in contact with the substrate;

heating the taped substrate to at least 160°C;

followed by removing the tape from the substrate.

22. The method according to claim 21, wherein after removing the tape from the substrate,
25 the substrate is substantially free of adhesive.

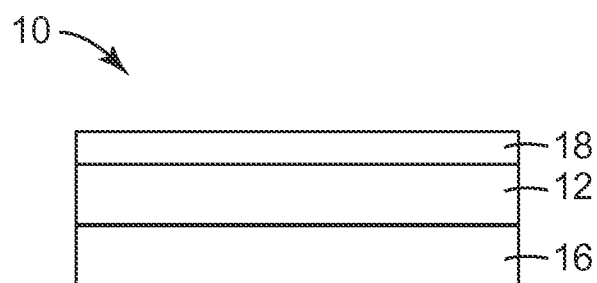


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2011/024496**A. CLASSIFICATION OF SUBJECT MATTER***C09J 133/04(2006.01)i, C09J 7/02(2006.01)i, C09J 7/04(2006.01)i, C09J 11/00(2006.01)i, B05D 5/10(2006.01)i*

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 133/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: article, backing, paper, saturant, acrylate polymer.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2004-0029511 A1 (Don H. Kincaid, Ernest L. Thurber, Eric G. Larson, Gregg D. Dahlke, Chad R. Wold) 12 February 2004 See the whole document.	1-7, 11, 21, 22
A	EP 0622432 A1 (Schurb, Francis A., Ellsworth, Arthur J.) 02 November 1994 See the whole document.	1-7, 11, 21, 22
A	US 05863847 A (De Voe Robert J., Dahlke Gregg D., Harmon Kimberly K., Masmar Craig A.) 26 January 1999 See the whole document.	1-7, 11, 21, 22

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

29 NOVEMBER 2011 (29.11.2011)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2011/024496**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 13, 14
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
claims 13, 14 cite multiple dependent claim 12, and so unclear.
3. ☒ Claims Nos.: 8-10, 12, 15-20
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2011/024496

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