Abstract: A curable adhesive comprises (A) at least one urethane (meth)acrylate resin having an average of about 1 to about 1.6 (meth)acrylate groups per resin molecule, and (B) at least one tackifier, the adhesive having sufficient precure tack where the loop tack of the uncured adhesive is at least 4.3 g/cm². The adhesive can further comprise (C) at least one initiator, or (D) at least one other curable resin, or (E) at least one additive, or a mixture of any of the foregoing components (C), (D) and (E). The adhesive has adhesion performance before and after curing that is compatible with high speed industrial processes to include labeling of containers such as beverage containers.
Title: (METH)ACRYLATE RESIN CURABLE ADHESIVE

Field of the Invention
The present invention relates to a curable (meth)acrylate based adhesive that is useful in various applications including the label and tape industry.

Background
Curable adhesives including (meth)acrylate based adhesives are especially useful for sealant, coating and attachment purposes in numerous industrial applications and processes. Curable adhesives can offer advantages in terms of reduced energy consumption, environmental and occupational safety compliance, and compatibility in high speed industrial processes. Because of these advantages, curable adhesives having unique and/or improved properties are constantly being sought for existing as well as new applications.

The present invention relates to a curable (meth)acrylate based adhesive that combines performance properties prior to curing of: a reduced application temperature due to a lower inherent viscosity, good tack and surface wetting, with the performance properties after curing of: good peel strength and good shear type adhesive strength. The inventive adhesive is especially useful for high speed industrial processes, such as bottle labeling.

Summary
The present invention is directed to a curable adhesive comprising (A) at least one urethane (meth)acrylate resin, and (B) at least one tackifier, wherein the urethane (meth)acrylate resin has an average of about 1 to about 1.6 (meth)acrylate groups per resin molecule, and the adhesive has a sufficient precure tack, wherein the loop tack of the uncured adhesive is at least 4.3 g/cm².
In an embodiment of the invention, the curable adhesive comprises (A) at least one urethane (meth)acrylate resin and (B) at least one tackifier, and may further comprise (C) at least one initiator, or (D) at least one other curable resin, or (E) at least one additive, or a mixture of two or more of the foregoing components (C), (D) and (E).

In another embodiment of the invention, a curable adhesive comprises (A) at least one urethane (meth)acrylate resin, (B) at least one tackifier, and (C) at least one initiator, wherein the urethane (meth)acrylate resin an average of about 1 to about 1.6 (meth)acrylate groups per resin molecule and is prepared from a polyol and an organic polyisocyanate. The adhesive has a sufficient precure tack, wherein the loop tack of the uncured adhesive is at least 5.7 g/cm².

In an additional embodiment of the invention, a curable adhesive comprises (A) at least one urethane (meth)acrylate resin, (B) at least one tackifier, and (C) at least one photoinitiator, wherein the urethane (meth)acrylate resin has an average of about 1 to about 1.6 (meth)acrylate groups per resin molecule and is prepared from a polyol and an organic polyisocyanate. The adhesive has a sufficient precure tack, wherein the loop tack of the uncured adhesive is at least 5.7 g/cm².

**Detailed Description**

The (meth)acrylate resin curable adhesive of this invention comprises (A) at least one urethane (meth)acrylate resin and (B) at least one tackifier wherein the adhesive has sufficient precure tack to effectively bond adherents before the adhesive is cured. The term "resin" means a composition comprising at least one monomer, a least one oligomer, at least one polymer, or a mixture or two or more thereof. The term "(meth)acrylate" means that a methacrylate group, an acrylate group, or a mixture of methacrylate and acrylate groups can be present. The term "(meth)acrylate resin" means that the resin can comprise a methacrylate-containing resin, an acrylate-containing resin, both methacrylate-containing and acrylate-containing resin, or a mixture of any of the foregoing resins.

In several embodiments of the invention, the at least one urethane (meth)acrylate resin (A) and the at least one tackifier (B) are respectively
present in the adhesive on a weight basis in a ratio of about 1:1 to about 10:1; about 1.25:1 to about 9:1; or about 1.5:1 to about 8:1.

In an embodiment of the invention, the uncured adhesive is sufficiently fluid at the temperature of application to effectively wet out the surface of adherents. In another embodiment, the uncured adhesive has a viscosity of about 6,000 mPa-s or less at the temperature of application, wherein the temperature of application is 107°C or less.

In embodiments of the invention, the curable adhesive comprising the at least one urethane (meth)acrylate resin (A) and the at least one tackifier (B) can further comprise (C) at least one initiator, or (D) at least one other curable resin, or (E) at least one additive, or a mixture of two or more of the foregoing components (C), (D) and (E). The mixture of components can comprise two or more materials of the same component type, such as for example, two or more initiators, or the mixture can comprise one or more materials from two or more different component types, such as for example, one or more initiators and one or more other curable resins.

The curable adhesive is curable by a polymerization process comprising a free radical polymerization process. The free radical polymerization process can include initiation thermally, by an air oxidation reaction, by particle radiation such as electron beam, by electromagnetic radiation such as visible or ultraviolet, or a combination of any of the foregoing initiation methods. In several embodiments of the invention, the initiator comprises a photoinitiator, an ultraviolet photoinitiator, or a free radical ultraviolet photoinitiator. The curable adhesive of the present invention can also include curable components such as epoxides, oxethanes and lactams, which are curable by processes such as a cationic polymerization process. The components of the curable adhesive of this invention as well as the starting materials and intermediates to these components are available from adhesive suppliers or can be formed by known methods of preparation as described hereinbelow.

(A) Urethane (Meth)acrylate Resin

Component (A) comprises a urethane (meth)acrylate resin that can be formed by reacting a polyol-containing composition with an organic
polyisocyanate in an equivalent ratio of about 0.9 to about 1.1 hydroxy groups: to about 2 or more isocyanate (-NCO) groups, to form a urethane-isocyanate intermediate. The formation of the urethane-isocyanate intermediate is followed by reaction of the intermediate with a hydroxyalkyl (meth)acrylate or with a hydroxyalkyl (meth)acrylate and an alcohol to form a urethane (meth)acrylate resin.

Alternatively, as described in U.S. Patent Publication No. US 2004/0010111, a hydroxyalkyl (meth)acrylate or a hydroxyalkyl (meth)acrylate and an alcohol can be reacted with an excess of an organic polyisocyanate in an equivalent ratio of about 0.9 to about 1.1 hydroxy groups: to about 2 or more isocyanate (-NCO) groups, to form a urethane-isocyanate intermediate. The formation of the urethane-isocyanate intermediate is followed by reaction of the intermediate with a polyol-containing composition in an equivalent ratio of about 0.9 to about 1.1 isocyanate groups: to about 0.9 to about 1.1 polyol hydroxy groups, to form a urethane (meth)acrylate resin. In several embodiments of the invention, the urethane (meth)acrylate resin can contain an average of less than 1, 1, more than 1, about 1 to about 1.6, about 1.05 to about 1.6, about 1.1 to about 1.5, about 1.2 to about -1.4, or greater than 1.6 methacrylate groups or acrylate groups or a combination of both groups.

The polyol-containing composition can contain 2 or more hydroxy groups, and can be monomeric or oligomeric or polymeric or a mixture thereof. The polyol-containing composition can comprise an aliphatic polyol having 2 or more carbon atoms, such as for example, ethylene glycol, glycerol, di(ethylene glycol) and di(propylene glycol)s, a polyether polyol having 2 or more ether groups and usually 6 or more carbon atoms to include poly(ethylene glycol)s and polypropylene glycol)s, polyalkoxylated polyols, such as for example, tri(ethylene glycol) and tri(propylene glycol)s and a polyethoxylated glycol or polyethoxylated glycerol, a polyester polyol having 2 or more ester groups and prepared from one or more polycarboxylic acids and one or more polyhydric alcohols, or a mixture of any of the foregoing polyol-containing compositions. The polyol-containing composition can have a molecular weight of at least 60; about 60 to about 10,000; about 300 to about 8,000; about 500 to about 7,000; about 700 to about 6,000; about 300 to about 6,000; or about 500 to about 3,000.
In an embodiment of the invention, the polyol-containing composition comprises a polyether polyol, a polyester polyol, or a mixture of any of the foregoing polyols. In several embodiments, the polyol-containing composition is a polyester or polyether diol having a molecular weight of at least 150; about 150 to about 10,000; about 300 to about 6,000; about 1,000 to about 5,000; or about 500 to about 3,000.

The organic polyisocyanate has 2 or more isocyanate groups, and can comprise an aliphatic polyisocyanate, an aromatic polyisocyanate, or a mixture of any of the foregoing polyisocyanates. Aliphatic polyisocyanates comprise polyisocyanates in which all the isocyanate groups are attached to an aliphatic moiety. Useful aliphatic polyisocyanates comprise, for example, trans-1,4-cyclohexanediisocyanate, 1,6-diisocyanatohexane, isophorone diisocyanate, 1,3-bis(isocyanatomethyl)cyclohexane and 1,3-bis(1-isocyanato-1-methyl ethyl)benzene. Aromatic polyisocyanates comprise polyisocyanates in which 1 or more of the isocyanate groups are attached directly to an aromatic ring. Useful aromatic polyisocyanates comprise, for example, 1,4-phenylene diisocyanate and tolylene-2,4-diisocyanate. In one embodiment, the organic polyisocyanate is an aliphatic diisocyanate.

The polyol-containing composition and organic polyisocyanate can be reacted in an equivalent ratio of about 1, or about 0.9 to about 1.1 hydroxy groups: to about 1 to about 2, or about 1.8 to about 2.2, or 1.8 to greater than 2 isocyanate groups; wherein a 1:1 ratio favors formation of a polyurethane and a 1:2 or greater than 2 ratio favors formation of monomeric and oligomeric species. In one embodiment, a polyether diol is reacted with an aliphatic diisocyanate in an equivalent ratio of about 1 hydroxy group: to about 1.8 to about 2.2 isocyanate groups. The urethane-isocyanate intermediate, formed from the reaction of the polyol-containing composition and organic polyisocyanate, can be reacted with a hydroxyalkyl (meth)acrylate. The hydroxyalkyl (meth)acrylate can comprise a hydroxyalkyl methacrylate, a hydroxyalkyl acrylate, or a mixture of any of the foregoing hydroxyalkyl esters. The hydroxyalkyl group of the hydroxyalkyl (meth)acrylate can contain 2 or more carbon atoms, or about 2 to about 20 carbon atoms, or about 2 to about 10 carbon atoms.
Useful hydroxyalkyl (meth)acrylates comprise, for example, hydroxyethyl acrylate and hydroxyethyl methacrylate. The urethane-isocyanate intermediate can be reacted with the hydroxyalkyl (meth)acrylate to give a urethane (meth)acrylate resin having an average of about 0.1 or more (meth)acrylate groups per resin molecule. The urethane-isocyanate intermediate and hydroxyalkyl (meth)acrylate can be reacted on an equivalent basis in a ratio of less than 1 to greater than 1 isocyanate group:1 OH group. In several embodiments, the hydroxyalkyl (meth)acrylate is reacted with the urethane-isocyanate intermediate to yield a urethane epoxy (meth)acrylate resin having an average of about 1 to about 1.6, or about 1.05 to about 1.6, or about 1.1 to about 1.5, or about 1.2 to about 1.4 (meth)acrylate groups on the urethane (meth)acrylate resin molecule. In a further embodiment, the urethane-isocyanate intermediate is reacted with a hydroxyalkyl acrylate in an equivalent ratio that gives a urethane acrylate resin having an average of about 1 to about 1.6, or about 1.05 to about 1.6 acrylate groups per resin molecule. In another embodiment, a urethane-isocyanate intermediate, formed from reaction of about 1.8 to about 2.2 moles of an aliphatic diisocyanate with 1 mole of a polyether diol, is reacted with a hydroxyalkyl acrylate in an equivalent ratio that gives a urethane acrylate resin having an average of about 1 to about 1.6, or about 1.05 to about 1.6, or about 1.3 acrylate groups per resin molecule. In one embodiment, a polyether diol is reacted with an aliphatic diisocyanate in an equivalent ratio of about 1 hydroxy group: to about 1.8 to about 2.2 isocyanate groups to form a urethane-isocyanate intermediate. The intermediate is then reacted with a hydroxyalkyl acrylate to give a urethane acrylate resin having about 1 to about 1.6, or about 1.05 to about 1.6 acrylate groups per resin molecule. The urethane acrylate resin is reacted with an alcohol to convert the remaining unreacted isocyanate groups to alkyl urethane or alkyl carbamate groups. The alcohol can comprise one or more monohydric aliphatic alcohols having 1 or more carbon atoms, or about 1 to about 20 carbon atoms, or about 1 to about 12 carbon atoms. The urethane (meth)acrylate resin (A) can have a number average molecular weight of at least 500, or about 500 to about 30,000, or about 750 to about 25,000, or about 1,000 to about 20,000, or about 1,500 to about 16,000.
The urethane (meth)acrylate resin (A) can have a Brookfield viscosity at ambient temperature near 25°C of at least 17,000, or at least 20,000, or at least 23,000 cP (centipoise) or mPa-s (millipascal-second) (1 cP = 1 mPa-s). The urethane (meth)acrylate resin (A) can have a Brookfield viscosity at ambient temperature near 25°C of 15,000-250,000; 20,000-200,000; 24,000-150,000 cP or mPa-s.

Useful urethane (meth)acrylate resins include the aliphatic urethane acrylate oligomer CN3211 which has a viscosity at 25°C of 27,500 cP or mPa-s and is available from Sartomer Company, Inc., and GENOMER™ 4188 which is available from Rahn Corp. and consists of 80 wt. % of a monoacrylate-functional polyester based urethane having a weight average molecular wt. of 8,000 and 20 wt. % of 2-ethylhexyl acrylate. Other useful urethane (meth)acrylate resins include those available from Bomar Specialties Company such as BR-3071, a high molecular weight (greater than 4,000 g/mole) aromatic, polyether-based urethane acrylate having an acrylate functionality of 1 and a viscosity of 92,000 cP or mPa-s at 25°C; BR-3641AA, a high molecular wt. aliphatic, polyether-based urethane acrylate having an acrylate functionality of 1.3 and a viscosity of 24,000 cP or mPa-s at 50°C; and BR-3741AB, a high molecular wt. aliphatic, polyether-based urethane acrylate having an acrylate functionality of 1.3 and a viscosity of 55,000 cP or mPa-s at 50°C. The urethane (meth)acrylate resin (A) is present in the inventive adhesive on a weight basis ranging from about 10% to about 90%, or about 20% to about 90%, or about 25% to about 87%, or about 30% to about 84%.

(B) Tackifier

Component (B) of the invention comprises a tackifier. The tackifier comprises a resin having a relatively low molecular weight and relatively high Tg (glass transition temperature) that can serve as a solvent for the curable (meth)acrylate resins to enhance wet out, peel and adhesion properties of the adhesive. The tackifier resin can comprise monomers, oligomers, polymers, and mixtures thereof. The tackifier can comprise a nonreactive resin, a reactive resin, or a mixture thereof. The tackifier can comprise a natural rosin comprising unsaturated high molecular weight rosin carboxylic acids, a
modified natural rosin comprising hydrogenated high molecular weight rosin carboxylic acids, a polyester comprising rosin esters such as glycerol and pentaerythritol esters of natural and modified natural rosins, aliphatic hydrocarbon resins derived from petroleum or plants, aromatic hydrocarbon resins derived from petroleum or plants, urea-aldehyde condensate resins, and mixtures of two or more of the foregoing materials. The aliphatic hydrocarbon resins comprise unsaturated resins, saturated resins via hydrogenation, and mixtures thereof. The aliphatic hydrocarbon resins comprise resins prepared by the polymerization or copolymerization of aliphatic olefins which comprise monoolefins and/or polyolefins to include C₅ based olefins such as pentadienes, methyl-substituted butenes, butadienes such as isoprene, cyclopentenes, pentenes, dicyclopentadienes, terpenes such as the pinenes, cyclopentadienes, and mixtures thereof. Aliphatic hydrocarbon resins include terpene based resins comprising terpene homopolymers, terpene copolymers, phenol modified terpene resins, and mixtures thereof. The aromatic hydrocarbon resins comprise resins prepared by polymerization or copolymerization of aromatic monomers to include C₉ based aromatic monomers comprising styrene based monomers such as styrene and vinyltoluenes and alpha-methylstyrenes, indenes, and mixtures thereof. The aromatic hydrocarbon resins include resins prepared by copolymerization of aromatic monomers with olefins such as C₅ based olefins, indene-cumarone resins, and mixtures thereof. The urea-aldehyde condensate resins comprise resins prepared by initially condensing urea or a urea derivative with an aldehyde having an acidic hydrogen on the carbon atom adjacent to the -CHO aldehyde group to form oxohexahydropyrimidine based intermediates which are further reacted with formaldehyde and the acidic-hydrogen-containing aldehyde as described in U.S. Patent No. 4,906,727. The urea derivatives include thioureas and alkylene coupled ureas and thioureas such as for example methylenediurea.

Useful tackifiers comprise the aliphatic C₅ petroleum hydrocarbon resin Wingtack® 95 Flake, which is available from Sartomer Company, Inc. and has a number average molecular wt. of 1,100 g/mole, an onset T_g of 49°C and an FTIR olefinic ratio of 0.23; the rosin ester SYLVALITE® RE 80HP, which is available from Arizona Chemical and has a Brookfield viscosity at 125°C of
1,270 cP or mPa-s; the low molecular weight polystyrene resin Piccolastic® A75 from Eastman; and the urea-aldehyde condensate resin Laropal® A81 from BASF. The tackifier is present in the adhesive on a weight basis from about 5% to about 60%, or about 8% to about 50%, or about 5% to about 40%, or about 10% to about 40%.

(C) Initiator

The curable adhesive in one embodiment of the invention can be cured by free radical polymerization of unsaturates in the absence of an initiator by exposing the adhesive to short wave electromagnetic radiation or particle radiation such as for example, x-rays, gamma rays or electron beam radiation. In another embodiment, the curable adhesive comprises an initiator (C). The initiator serves to catalyze or promote a polymerization reaction of the polymerizable adhesive components to effect curing of the adhesive. The initiator can comprise a thermal initiator, an oxidative initiator or drier, a photoinitiator, or a combination of any of the foregoing initiators. The thermal initiator is normally activated by heating it above ambient temperature from about 30°C to about 200°C to form free radicals, which initiate free radical polymerization of unsaturates. The thermal initiator can include, for example, organic peroxides and organic azo compounds. The oxidative initiator or drier catalyzes or promotes air oxidation and cross-linking of unsaturates at ambient or elevated temperatures. The oxidative initiator can include for example metal salts and carbodiimides. The photoinitiator comprises a free radical photoinitiator, a cationic photoinitiator, or a combination thereof. In several embodiments, initiator comprises a photoinitiator, a free radical photoinitiator, or a combination of a free radical initiator and a cationic photoinitiator. Photoinitiators are generally activated by exposure to electromagnetic radiation to include infrared, visible, ultraviolet (or UV), and combinations thereof. In several embodiments, the initiator is a UV-activated photoinitiator, a UV-activated free radical photoinitiator, or a combination of UV-activated free radical and cationic photoinitiators. Free radical photoinitiators can be activated by exposure to electromagnetic radiation including, for example, UV to form free radicals which initiate free radical polymerization of unsaturates such as (meth)acrylate-containing resins.
Cationic photoinitiators can be activated by exposure to electromagnetic radiation including, for example, UV to form cations which initiate cationic catalyzed type polymerizations such as an epoxide polymerization. The UV-activated free radical photoinitiator can comprise at least one photoinitiator of the type that undergoes a unimolecular bond cleavage reaction to form free radicals including where the cleavage is alpha-cleavage or beta-cleavage, at least one photoinitiator and one cointiator of the type that undergoes a bimolecular bond cleavage reaction to form free radicals, or combinations thereof. Free radical photoinitiators of the unimolecular bond cleavage type can comprise benzoyl type photoinitiators including benzoin ethers and benzil ketals and alpha-dialkoxyacetophenones and alpha-hydroxyalkylphenones and alpha-halogeno-acetophenones, amino-ketones, acyl-phosphine oxides, or mixtures thereof.

Useful unimolecular type free radical photoinitiators include, for example, 2-hydroxy-2-methylpropiophenone and/or butyrophenone and the commercial UV-activated free radical photoinitiators SARCURE® SR1 135 from Sartomer Company, Inc. which is a three-photoinitiator-blend of 2,4,6-trimethyl benzoyl diphenyl phosphate oxide and oligo [2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl]propanone] and methylbenzophenone derivatives, Genocure® LTM from Rahn Corp, the 1-hydroxycyclohexyl phenyl ketone based photoinitiator Esacure® KS300 from Sartomer, the oligomeric photoinitiator oligo [2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl]propanone] from Sartomer, the photoinitiators KIP 150 and KIP 100F and KL 200 from Lamberti, and the 4-phenylbenzophenone based photoinitiator Genocure® PBZ from Rahn. Free radical photoinitiators of the bimolecular bond cleavage type can comprise as the photoinitiator at least one of a benzophenone or a thioxanthone or a titanocene and as the cointiator at least one of an alcohol or an ether or an amine having an abstractable alpha-hydrogen. Useful bimolecular type free radical photoinitiators and cointiators include for example benzophenone and tetrahydrofuran. The UV-activated cationic photoinitiator can comprise a photoinitiator of the type comprising a sulfonium salt, an iodonium salt, or mixtures thereof including, for example, the SARCAT® CD 1010, 1011 and 1012 series of photoinitiators available from Sartomer. Selection of a UV-activated photoinitiator and the amount of the
photoinitiator is generally based on the emission characteristics and intensity of the UV source and on the spectral sensitivity of the photoinitiator. The commercially available photoinitiators can be used individually or in combinations depending on the requirements for an adhesive and service conditions. Generally, oligomeric photoinitiators are used in adhesive applications involving high temperatures and/or extended times at temperatures above ambient.

In several embodiments of the invention, the curable adhesive comprises a free radical photoinitiator, such as for example a UV-activated free radical photoinitiator, wherein the adhesive can be cured by being exposed for less than 5 minutes, or 3 minutes, or 1 minute to an electromagnetic radiation source, such as for example a UV source, having an intensity of at least 20, or 50, or 80, or 100 mJ/cm² (millijoules per square centimeter) where the (meth)acrylate resin double bonds of the adhesive are at least 60%, or 70%, or 80%, or 90% reacted or consumed. The initiator is optionally present in the inventive adhesive depending on the requirements of the intended area of use and when present can range on a weight basis from about 0.1 to about 15%, or about 0.2 to about 12.5%, or about 0.5 to about 10%, or about 1-8%.

(D) Other Curable Resins

Component (D) of the invention comprises at least one other curable resin in addition to the urethane (meth)acrylate resins of component (A) described hereinabove. The at least one other curable resin of component (D) comprises other (meth)acrylate based resins, epoxy based resins, other curable resins containing one or more double bonds which are polymerizable by a free radical process, and mixtures of any of the foregoing resins. The other (meth)acrylate based resins comprise epoxy (meth)acrylate resins, alkoxylated monool (meth)acrylate resins, (meth)acrylate esters of polyols including polyols based on polyhydric alcohols and polyethers and polyesters, (meth)acrylate esters of monohydric alcohols such as ethyl acrylate and vinyl methacrylate, (meth)acrylic resins comprising (meth)acrylic oligomers or polymers containing a polymerizable (meth)acrylic group, olefin-(meth)acrylic copolymers comprising copolymers of (meth)acrylic acids and/or (meth)acrylate esters of polyols containing one or more double bonds which are polymerizable by a free radical process, and mixtures of any of the foregoing resins.
esters with olefins such as butadiene, (meth)acrylated hydrocarbon oils, (meth)acrylated silicone oils, and mixtures of any of the foregoing resins.

Epoxy (Meth)acrylate Resins

Epoxy (meth)acrylate resins comprise resins which can be formed by first reacting a polyol reagent with a epoxide-containing or epoxide-forming reagent to form an epoxide intermediate. The formation of the epoxide intermediate is followed by reaction of the epoxide intermediate with a hydroxy-containing (meth)acrylic reagent or with a hydroxy-containing (meth)acrylate reagent and a saturated hydroxy-containing nucleophile, an amine-containing nucleophile, or a mixture of any of the foregoing nucleophiles to form an epoxy (meth)acrylate resin, wherein the epoxy (meth)acrylate resin contains essentially no epoxy group and the amine-containing nucleophile has at least one N-H or nitrogen to hydrogen bond. In several embodiments of the invention, the epoxy (meth)acrylate resin contains essentially no epoxy groups per resin molecule, wherein there are on average 0.2 or less, or 0.1 or less, or 0.05 or less, or 0.025 or less, or 0.02 or less epoxy groups per resin molecule. In several embodiments, the epoxy (meth)acrylate resin can contain on average less than 1, or more than 1, or about 1 to about 1.6, or about 1.05 to about 1.6, or about 1 to about 1.5, or about 1.2 to about 1.4, or greater than 1.6 methacrylate groups or acrylate groups or a combination of both groups per resin molecule.

The polyol reagent can have 2 or more hydroxy groups. The polyol reagent can comprise a condensate of a hydroxy-containing aromatic compound and an aldehyde and/or ketone, an aliphatic polyol, or a mixture thereof. The hydroxy-containing aromatic compound can be phenol, a substituted phenol, such as for example, a cresol, a polyhydroxy aromatic compound, such as for example, a catechol, or a mixture thereof. The aldehyde can have one or more carbon atoms to include, for example, formaldehyde. The ketone can have three or more carbon atoms to include, for example, acetone. The hydroxy-containing aromatic compound and aldehyde and/or ketone are generally condensed respectively in a mole ratio of about 1:3:1, 0.5:2:1, 1:2:1, or 2:1 hydroxy:aldehyde/ketone. In one embodiment, the polyol reagent comprises a diol of a bisphenol-aldehyde or
ketone condensate. Useful polyol reagents prepared from hydroxy-containing aromatic compounds include, for example, bisphenol A or 4,4'-isopropylidenediphenol, bisphenol F or bis(4-hydroxyphenyl)methane, and bisphenol E or 4,4'-ethylidenebisphenol. The polyol reagent can comprise aliphatic polyols having 2 or more carbon atoms to include, for example, ethylene glycol, butanediol, and hexanediol. The polyol reagent can also comprise alkoxylates of a reaction product of a hydroxy-containing aromatic compound and aldehyde and/or ketone, alkoxylates of an aliphatic polyol, or mixtures thereof. These alkoxylates can have one or more oxyalkylene units to include, for example, ethoxylates of bisphenol A and ethoxylates of neopentyl glycol.

The epoxide-containing or epoxide-forming reagent can comprise a halogen-containing aliphatic epoxide that can contain one or more epoxide rings and three or more carbon atoms to include, for example, epichlorohydrin and 4-chloro-1,2-epoxybutane.

The polyol reagent and epoxide reagent, wherein the epoxide reagent is the epoxide-containing or epoxide-forming reagent, can be reacted on an equivalent basis in a ratio of less than 1 to greater than 1 polyol OH:1 epoxide group. In an embodiment of the invention, the polyol reagent and epoxide reagent are reacted in a 1:1 equivalent ratio such as, for example, in the reaction of 1 mole of bisphenol A with 2 moles of epichlorohydrin to form as an epoxide intermediate the diglycidyl ether of bisphenol A, which on an equivalent basis is 1 hydroxy group:1 halogen group. The epoxide intermediate can also include reaction products in which the equivalent ratio of polyol reagent to epoxide-containing or epoxide-forming reagent such as a halogen-containing aliphatic epoxide is respectively greater than 1 hydroxy group:1 halogen group, so that the polyol reagent can further react with the epoxide group as described in U.S. Patent No. 5,989,778. In one embodiment, the epoxide intermediate is a reaction product of a polyol reagent and a halogen-containing aliphatic epoxide reacted in respectively an equivalent ratio of 1 hydroxy group:1 halogen group where the polyol reagent is formed from the reaction of a phenol and a ketone in respectively a 2:1 mole ratio. In another embodiment, the epoxide intermediate is formed by reacting bisphenol A with epichlorohydrin in respectively a 1:2 mole ratio. A
useful epoxide intermediate is EPON™ Resin 828, which is available from Resolution Performance Products and has an epoxide equivalent weight of 185-192 per ASTM D 1652.

The hydroxy-containing (meth)acrylic reagent can comprise methacrylic acid, acrylic acid, a hydroxyalkyl methacrylate, a hydroxyalkyl acrylate, or a mixture of any of the foregoing hydroxy-containing (meth)acrylic reagents. The epoxide intermediate and hydroxy-containing (meth)acrylic reagent can be reacted on an equivalent basis in a ratio of less than 1 to greater than 1 epoxide group:1 OH group. The epoxide intermediate and hydroxy-containing (meth)acrylic reagent can be reacted in a ratio that results in on average 0.1 or more (meth)acrylate groups on the epoxy (meth)acrylate resin molecule. In several embodiments of the invention, the hydroxy-containing (meth)acrylic reagent is reacted with the epoxide intermediate to yield an epoxy (meth)acrylate resin having an average of about 1 to about .6, or about 1.05 to about 1.6, or about 1.1 to about 1.5 or about 1.2 to about 1.4 (meth)acrylate groups on the epoxy (meth)acrylate resin molecule. In another embodiment, the epoxide intermediate is reacted with methacrylic acid, acrylic acid, or a mixture thereof in an equivalent ratio where on average there are about 1 to about 1.6, or about 1.05 to about 1.6, or about 1.1 to about 1.5, or about 1.2 to about 1.4 (meth)acrylate groups on the resin molecule. In a further embodiment, the diglycidyl ether of bisphenol A is reacted with acrylic acid in an equivalent ratio to give an average of about 1 to about 1.6, or about 1.05 to about 1.6, or about 1.1 to about 1.5, or about 1.2 to about 1.4, or about 1.3 acrylate groups per resin molecule. In one embodiment of the invention, the epoxy (meth)acrylate resin is prepared by reacting a hydroxy-containing (meth)acrylic reagent and an epoxide intermediate to give a reaction product containing some unreacted epoxide groups, which is further reacted with a nucleophilic reagent to the epoxy (meth)acrylate resin containing essentially no epoxy group as described herein above. The nucleophilic reagent can comprise water, an alcohol, an amine, a carboxylic acid, or a mixture of any of the foregoing nucleophilic reagents. In one embodiment, the nucleophilic reagent can comprise an alcohol which can be monohydric or polyhydric or a mixture thereof, and can be aliphatic or aromatic or a mixture thereof. Useful alcohols comprise aliphatic monools
having 1 or more carbon atoms such as for example methanol, aliphatic diols having 2 or more carbon atoms to include ether-containing and polyether-containing diols such as, for example, ethylene glycol and di(ethylene glycol) and poly(ethylene glycol)s, and mixtures thereof. In one embodiment, the reaction product of the epoxide intermediate and hydroxy-containing (meth)acrylate reagent contains some unreacted epoxy groups and is further reacted with an alcohol. In embodiments of the invention, the alcohol is an aliphatic diol. In a further embodiment, the reaction product of the diglycidyl ether of bisphenol A and acrylic acid, having an average of about 1 to about 1.6, or about 1.05 to about 1.6 acrylate groups per resin molecule, is reacted with a glycol in an equivalent ratio of 1 epoxide:1 OH to give essentially no epoxy group in the epoxy (meth)acrylate resin molecule. The epoxy (meth)acrylate resin can range in molecular weight from about 300 to about 10,000, or about 350 to about 7,000, or about 400 to about 4,000, or about 300 to about 3,000, or about 350 to about 2,000, or about 400 to about 1,500. In several embodiments of the invention, the epoxy (meth)acrylate resin can have a Brookfield viscosity at ambient temperature near 25°C of 100-5,000, 200-4,000, 300-2,500, 100-700, 200-600, or 300-500 cP (centipoise) or mPa-s (millipascal-second). Useful epoxy (meth)acrylate resins include the acrylated epoxy resins EBECRYL™ 600, 629, 860 and 3780 and RXO™ 2034 available from UCB Radcure Inc. and PHOTOMER™ 3016, 3038 and 3071 available from Henkel Corp.

**Alkoxylated Monool (Meth)acrylate Resin**

Alkoxylated monool (meth)acrylate resins comprise resins which can be formed by reacting a monool with an alkylene oxide to form an alkoxylated monool, followed by reaction of the alkoxylated monool with a (meth)acrylate-esterifying reagent to form the alkoxylated monool (meth)acrylate resin.

The monool can be a hydrocarbon or hetero-atom-containing hydrocarbon having one hydroxy group. The monool can comprise an aliphatic monohydric alcohol having 1 or more carbon atoms such as, for example, 1-hexadecanol and 2-methoxyethanol, a nonaromatic cyclic or polycyclic monohydric alcohol having generally 4 or more carbon atoms such as, for example, cyclohexanol, a monohydroxy-containing aromatic compound.
generally containing 6 or more carbon atoms such as, for example, phenol and 4-nonylphenol, or a mixture of any one of the foregoing monools.

The alkylene oxide can be an epoxide having 2 or more carbon atoms such as, for example, ethylene oxide or propylene oxide or can be a mixture of 2 or more epoxides wherein the epoxides differ in the number of carbon atoms such as, for example, a mixture of ethylene oxide and propylene oxide.

In one embodiment of the invention, the monool is reacted with an alkylene oxide to give a monoalkoxylated product having on average a monool to alkylene oxide mole ratio of 1:0.5-1.4. In another embodiment, the monool is reacted with an alkylene oxide to give a polyalkoxylated product having on average a monool to alkylene oxide mole ratio of 1:1.5 or greater. In several embodiments, the monool is reacted with the alkylene oxide in respectively a mole ratio of 1:0.1-20, or 1:1-15, or 1:1-10, or 1:2-10, or 1:1.5-50, or 1:1.5-25, or 1:1.5-15. In another embodiment, alkylphenol is reacted with an alkylene oxide in respectively a mole ratio of 1:1.5-6 or 1:2-6 where the alkyl group of the alkylphenol has 1-20, or 3-18 or 4-14 carbon atoms.

The (meth)acrylate-esterifying reagent can comprise methacrylic acid, acrylic acid, an alkyl methacrylate, an alkyl acrylate, or a mixture thereof, wherein the alkyl group of the alkyl methacrylate or acrylate generally can have 1-10 carbon atoms.

The alkoxylated monool and (meth)acrylate-esterifying reagent can be reacted respectively in a mole ratio of 1:0.1 to greater than 1 to esterify the alkoxylated monool and form the alkoxylated monool (meth)acrylate resin. In embodiments of the invention, a nonylphenol is reacted ethylene oxide to form an ethoxylated nonylphenol containing on average 2-6 oxyethylene units, and the ethoxylated nonylphenol is then esterified with an acrylate-esterifying reagent to give equal to or greater than 80%, or 85%, or 90% of an ethoxylated nonylphenol acrylate resin. The alkoxylated monool (meth)acrylate resin can have a molecular weight of 190-1500, or 200-1250, or 300-1000. In several embodiments of the invention, the alkoxylated monool (meth)acrylate resin can have a Brookfield viscosity at ambient temperature near 25°C of 40-400, 60-300, or 80-200 cP or mPa-s. Useful alkoxylated monool (meth)acrylate resins are the ethoxylated nonylphenol acrylate SR-504 which is available from Sartomer Company, Inc. and has an
acrylate functionality of 1, a molecular weight of 450 corresponding to an average of 4 ethoxy units, and a viscosity at 25°C of 100 cP or mPa-s and the polypropoxylated nonylphenol acrylate NK-Ester NPA-5P which is available from Kowa American Corp.

The other curable resin component (D) is optionally present in the adhesive depending on the requirements of the intended area of use and service conditions. Useful other curable resins include the low viscosity mixture of (meth)acrylate resins CN3100 available from the Sartomer Company. The at least one other curable resin component (D) can be present in the inventive adhesive based on weight from about 0.5% to about 85%, or about 1% to about 70% or about 1.5% to about 60%.

(E) Additive(s)

Component (E) of the invention comprises at least one or more additives. The (meth)acrylate resin curable adhesive of the present invention can comprise one or more additives depending on the intended area of use and service conditions. Component (E) can comprise diluents, surfactants comprising materials that function to defoam, wet, emulsify, disperse, level, or any combination of the foregoing functions, antioxidants, surface lubricants, polymerization inhibitors to include quinone based free radical scavengers such as for example MEHQ (hydroquinone methyl ether), antistatic agents, fillers, rheology control agents including materials known as thickeners, coloring agents to include pigments and dyes, plasticizers, chain transfer agents, materials containing an amino group to improve free radical reactivity and cure response, photosensitizers to extend spectral response to higher wavelengths to improve speed and depth of cure, and mixtures of any of the foregoing additives. The diluent can comprise a nonreactive or noncurable diluent to include for example a polyolefinic petroleum derived oil, a reactive or curable diluent to include vinyl-containing and (meth)acrylate-containing monofunctional and polyfunctional diluents such as, for example, isooclyl acrylate and 1,4-butanediol diacrylate, or a mixture of any of the foregoing diluents. The antioxidant can comprise a hindered phenol such as, for example, the cinnamate ester hindered phenol Irganox 1076 available from Ciba Specialty Chemicals, an organometallic compound, an aromatic amine,
a phosphite, an organic sulfide, or a mixture of any of the foregoing antioxidants. Component (E) is optionally present in the inventive adhesive depending on intended use and service conditions. Each of the component (E) additives can be present in the inventive adhesive on a weight basis up to 85% or from about 0.005% to about 85%, or about 0.005% to about 50%, or about 0.01% to about 15%.

Precured Adhesive

The (meth)acrylate resin curable adhesive of the invention can be prepared by admixing, usually with a stirring or mixing device, the components in generally any order of addition at ambient temperature near 15°C or at an elevated temperature up to generally 4°C, or 8°C, or 9°C or 11°C until the admixed components are homogeneous.

The curable adhesive of this invention prior to curing can have a viscosity at the temperature of application of about 100 to about 70,000, or about 100 to about 65,000, or about 600 to about 45,000, or about 600 to about 10,000, or about 600 to about 8,000, or about 1,000 to about 7,000, or about 1,000 to about 6,000, or about 1,000 to about 5,000, or about 1,000 to about 4,000, or about 1,000 to about 3,000 cP or mPa-s. The inventive curable adhesive prior to curing can have a viscosity in cP or mPa-s at the temperature of application of 6,000 or less, or 4,000 or less, or 3,000 or less. The temperature of application can range from ambient to an elevated temperature including from 15°-107°, 15°-80°, 20°-80°, 25°-107°, 25°-93°, 25°-82°, 25°-71°, or 25°-66°C. The temperature of application can be 107°C or less, or 93°C or less, or 82°C or less, or 71°C or less, or 66°C or less. The curable adhesive has a sufficient precure tack to effectively bond adherents before the adhesive is cured. In one embodiment of the invention, the adhesive has sufficient precure tack to effectively bond a plastic label and plastic container before the adhesive is cured in a high speed bottling process. The precure tack is considered to be sufficient when the adherents remain attached or bonded to each other during processing prior to curing of the adhesive such as, for example, when the adhesive prior to curing holds together a thermoplastic based label and a plastic or glass bottle without flagging in a high speed labeling operation. Flagging is an industry term.
indicating that the label has come at least partially loose from the bottle and generally results in a defectively labeled container.

In several embodiments of the invention, the uncured adhesive has a precure tack as measured by a minimal pressure adhesive loop tack test procedure of 3.3-26, or 4.3-20, or 7.1-17 g/cm². The uncured inventive adhesive can have a loop tack of at least 4.3, at least 5.7, at least 7.1, or at least 10.6 g/cm².

a Minimal Pressure Adhesive Loop Tack Test

I. PURPOSE

To measure the tack of a coated adhesive with minimal pressure.

II. EQUIPMENT

Machine with reversing capability and a vertical jaw separation rate of 12 inch per minute. Stainless steel test panel, 1" width, made of 304 Bright Annealed Stainless Steel

III. PROCEDURE

1. Bend the specimen back onto itself, being careful not to crease it, forming a teardrop shaped loop with the adhesive surface towards the outside.

2. Fasten the ends together using a strip of 1" wide tape, (If needed).

3. Insert the specimen into the upper grip so that the tape is completely within the jaws and exposed adhesive surface will contact the test surface perfectly flat.

4. Start the machine, bringing the specimen in contact with the test panel and immediately reversing direction.

5. The force gauge will record the maximum force required to break the bond between the specimen and the test panel. The force required to break the bond between the specimen and test panel shall be reported in force per square inch.

Cured Adhesive

The uncured (meth)acrylate resin adhesive of the invention can be cured by initiating polymerization of the polymerizable resin or resins present in the adhesive. In an embodiment of the invention, the uncured adhesive is
cured by initiating a free radical polymerization of the (meth)acrylate resin or resins present in the adhesive by any suitable initiation method to include the initiation methods described hereinabove. In one embodiment, the uncured adhesive comprising a UV-activated free radical photoinitiator is cured by exposure to a UV source as described hereinabove.

In several embodiments of the invention the cured adhesive has an average peel adhesion as measured by test procedure ASTM D1876 of 70-1,400, or 80-1,000, or 90-850 gf (grams force).

Examples

The following nonlimiting examples further describe and illustrate the (meth)acrylate resin curable adhesive of this invention.

Example 1

A UV curable adhesive is prepared by blending on a wt. basis 30 parts of a urethane acrylate resin BR-3641AA from Bomar Specialties, 30 parts of an aromatic hydrocarbon resin tackifier Piccolastic® A75 from Eastman, and 36 parts of another curable resin CN3100 from Sartomer near 90°C until the tackifier is dissolved. During the cool down phase of the preparation, 4 parts by wt. of a UV photoinitiator 1-hydroxycyclohexyl phenyl ketone Esacure® KS300 from Sartomer is added to the blend and dissolved to complete the preparation of the adhesive, which prior to curing has a viscosity of 1,900 mPa-s at 66°C and a minimal pressure adhesive loop tack of 4.3 g/cm². After curing the adhesive has an ASTM D1876 average peel adhesion of 138 gf.

Example 2

A UV curable adhesive is prepared by blending on a wt. basis 12 parts of a urethane acrylate resin BR-3741AB from Bomar Specialties, 25.5 parts of a urethane acrylate resin BR-3641AA from Bomar Specialties, 25.5 parts of a urea-aldehyde condensate resin tackifier Laropal® A81 from BASF, 30.6 parts of another curable resin CN3100 from Sartomer, and 2.4 parts of another curable resin SR-504 from Sartomer near 90°C until the tackifier is dissolved. After cooling the blend to 55°C, 4 parts by wt. of a UV photoinitiator 1-hydroxycyclohexyl phenyl ketone Esacure® KS300 is added to the blend and dissolved to complete the preparation of the adhesive which is not homogeneous. Prior to curing the adhesive has a viscosity of 3,600 mPa-s at
66°C and a minimal pressure adhesive loop tack of 7.1 g/cm². After curing, the adhesive has an ASTM D18763330 average peel adhesion of 7.1 gf.

Example 3

A UV curable adhesive is prepared by blending on a wt. basis 20 parts of a urethane acrylate resin BR-3741AB from Bomar Specialties, 22.5 parts of a urethane acrylate resin BR-3641AA from Bomar Specialties, 22.5 parts of a urea-aldehyde condensate resin tackifier Laropal® A81 from BASF, 27 parts of another curable resin CN3100 from Sartomer, and 4 parts of another curable resin SR-504 from Sartomer near 90°C until the tackifier is dissolved. After cooling the blend to 55°C, 4 parts by wt. of a UV photoinitiator 1-hydroxycyclohexyl phenyl ketone Esacure® KS300 is added to the blend and dissolved to complete the preparation of the adhesive which is not homogeneous. Prior to curing, the adhesive has a viscosity of 2,800 mPa-s at 72°C and a minimal pressure adhesive loop tack of 10.6 g/cm². After curing, the adhesive has an ASTM D1876 average peel adhesion of 496 gf.

Example 4

A UV Curable adhesive is prepared by blending on a wt. basis 45 parts of a urethane acrylate resin BR-3641AA from Bomar Specialties, 36 parts of a urethane acrylate resin BR-3741AB from Bomar Specialties, and 15 parts of an aromatic hydrocarbon resin tackifier Piccolastic® A75 from Eastman near 90°C until the tackifier is dissolved. During the cool down phase of the preparation, 4 parts by wt. of a UV photoinitiator 1-hydroxycyclohexyl phenyl ketone Esacure® KS300 from Sartomer is added to the blend and dissolved to complete the preparation of the adhesive. Prior to curing, the adhesive has a viscosity of 4,000 mPa-s at 92°C and a minimal pressure adhesive loop tack of 13 g/cm². After curing, the adhesive has an ASTM D1876 average peel adhesion of 107 gf.

Each of the documents referred to in this application is incorporated herein by reference. All numerical quantities in this application used to describe or claim the invention are understood to be modified by the word "about" except where explicitly indicated otherwise. All component quantities throughout the application are understood to be as undiluted actives unless indicated otherwise even though diluents may normally be present. Range and ratio limits used to define the invention throughout this application are
understood to be combinable. Combinations of components to form the
inventive adhesive are understood to total to 100% unless indicated otherwise.

While the invention has been explained in relation to specific
5 embodiments, various modifications thereof will become apparent to those
skilled in the art upon reading this application. It is understood that these
various modifications, which fall within the scope of this detailed description
and the appended claims, form a part of this invention.
What is claimed is:

1. A curable adhesive, comprising:
   (A) at least one urethane (meth)acrylate resin; and
   (B) at least one tackifier;

   wherein the urethane (meth)acrylate resin has an average of about 1 to about 1.6 (meth)acrylate groups per resin molecule, the adhesive having sufficient precure tack, wherein the loop tack of the uncured adhesive is at least 4.3 g/cm².

2. The adhesive of claim 1 wherein the adhesive has a viscosity of 6,000 mPa-s or less at the temperature of application, wherein the temperature of application is 107°C or less.

3. The adhesive of claim 1 or 2 further comprising (C) at least one initiator.

4. The adhesive according to any one of the preceding claims further comprising (D) at least one other curable resin.

5. The adhesive according to any one of the preceding claims further comprising (E) at least one additive.

6. The adhesive of claim 3 wherein the initiator comprises a photoinitiator.

7. The adhesive according to any one of the preceding claims wherein the urethane (meth)acrylate resin is prepared from a polyol and an organic polyisocyanate.

8. The adhesive according to any one of the preceding claims wherein the tackifier comprises a hydrocarbon resin, a urea-aldehyde condensate resin, or a mixture of any of the foregoing resins.

9. A curable adhesive, comprising:
(A) at least one urethane (meth)acrylate resin;
(B) at least one tackifier; and
(C) at least one initiator;
wherein the urethane (meth)acrylate resin has an average of about 1 to about 1.6 (meth)acrylate groups per resin molecule and is prepared from a polyol and an organic polyisocyanate, the adhesive having sufficient precure tack, wherein the loop tack of the uncured adhesive is at least 5.7 g/cm².

10. The adhesive of claim 9 wherein the polyol comprises a polyether polyol, a polyester polyol, or a mixture of any of the foregoing polyols.

11. The adhesive of claim 9 or 10 wherein the polyol comprises a diol.

12. The adhesive according to any one of claims 9 to 11 wherein the polyisocyanate comprises an aliphatic polyisocyanate, an aromatic polyisocyanate, or a mixture of any of the foregoing polyisocyanates.

13. The adhesive according to any one of claims 9 to 12 wherein the polyisocyanate comprises a diisocyanate.

14. The adhesive according to any one of claims 9 to 13 wherein the tackifier comprises a hydrocarbon resin, a urea-aldehyde condensate resin, or a mixture of any of the foregoing resins.

15. A curable adhesive, comprising:
   (A) at least one urethane (meth)acrylate resin;
   (B) at least one tackifier; and
   (C) at least one photoinitiator;
wherein the urethane (meth)acrylate resin has an average of about 1 to about 1.6 (meth)acrylate groups per resin molecule and is prepared from a polyol and an organic polyisocyanate, the adhesive having sufficient precure tack, wherein the loop tack of the uncured adhesive is at least 5.7 g/cm².
16. The adhesive of claim 15 wherein the polyol comprises a polyether polyol, a polyester polyol, or a mixture of any of the foregoing polyols.

17. The adhesive of claim 15 or 16 wherein the polyol comprises a diol.

18. The adhesive according to any one of claims 15 to 17 wherein the polyisocyanate comprises an aliphatic polyisocyanate, an aromatic polyisocyanate, or a mixture of any of the foregoing polyisocyanates.

19. The adhesive according to any one of claims 15 to 18 wherein the polyisocyanate comprises a diisocyanate.

20. The adhesive according to any one of claims 15 to 19 wherein the tackifier comprises a hydrocarbon resin, a urea-aldehyde condensate resin, or a mixture of any of the foregoing resins.

21. The adhesive according to any one of claims 15 to 20 wherein the urethane (meth)acrylate resin is prepared from a diol and an organic diisocyanate.

22. The adhesive according to any one of claims 15 to 21 wherein the urethane (meth)acrylate is prepared from a polyether diol and an aliphatic diisocyanate, the tackifier comprises an aliphatic hydrocarbon resin or an aromatic hydrocarbon resin or a mixture of any of the foregoing hydrocarbon resins, and the photoinitiator comprises an ultraviolet photoinitiator.
AMENDED CLAIMS

Received by the International Bureau on 23 January 2007 (23.01.2007)

1. A curable adhesive, comprising:
   (A) at least one urethane (meth)acrylate resin prepared from at least a polyether polyol, an organic polyisocyanate, a hydroxylalkyl (meth)acrylate and an alcohol; wherein the urethane (meth)acrylate resin has an average of about 1 to about 1.6 (meth)acrylate groups per resin molecule; and
   (B) at least one tackifier;

2. The adhesive according to any one of the preceding claims wherein the polyether polyol is a polyether diol and the organic polyisocyanate is a diisocyanate.

3. The adhesive of any one of the preceding claims further comprising (D) at least one other curable resin.

4. The adhesive of any one of the preceding claims further comprising (P) at least one additive.

5. The adhesive of claim 2 wherein the tackifier comprises a hydrocarbon resin, a urea-aldehyde condensate resin, or a mixture of any of the foregoing resins.

6. The adhesive according to any one of the preceding claims wherein the polyether polyol is a polyether diol and the organic polyisocyanate is a diisocyanate.

7. The adhesive of any one of the preceding claims wherein the tackifier comprises a hydrocarbon resin, a urea-aldehyde condensate resin, or a mixture of any of the foregoing resins.

8. A curable adhesive, comprising:
   (A) at least one urethane (meth)acrylate resin prepared from at least a polyether polyol, an organic polyisocyanate, a hydroxylalkyl (meth)acrylate and an alcohol; wherein the urethane (meth)acrylate resin has an average of about 1 to about 1.6 (meth)acrylate groups per resin molecule; and
   (B) at least one tackifier;
polyol, an organic polyisocyanate, a hydroxyalkyl (meth)acrylate and an alcohol; wherein the urethane (meth)acrylate resin has an average of about 1 to about 1.6 (meth)acrylate groups per resin molecule;

(B) at least one tackifier and

(C) at least one initiator;

wherein the adhesive having sufficient precure tack, wherein the loop tack of the uncured adhesive is at least 5.7 g/cm², and the adhesive having a viscosity of 6,000 mPa-s or less at a temperature of application of not greater than 107°.

9. The adhesive of claim 8 wherein the polyether polyol comprises a diol.

10. The adhesive of any one of claims 8 or 9 wherein the polyisocyanate comprises an aliphatic polyisocyanate, an aromatic polyisocyanate, or a mixture of any of the foregoing polyisocyanates.

11. The adhesive of any one of claims 8 to 10 wherein the polyisocyanate comprises a diisocyanate.

12. The adhesive of any one of claims 8 to 11 wherein the tackifier comprises a hydrocarbon resin, a urea-aldehyde condensate resin, or a mixture of any of the foregoing resins.

13. A curable adhesive, comprising:

(A) at least one urethane (meth)acrylate resin prepared from at least one polyether polyol, an organic polyisocyanate, a hydroxyalkyl (meth)acrylate and an alcohol; wherein the urethane (meth)acrylate resin has an average of about 1 to about 1.6 (meth)acrylate groups per resin molecule;

(B) at least one tackifier; and

(C) at least one photoinitiator;

wherein the adhesive having sufficient precure tack, wherein the loop tack of the uncured adhesive is at least 5.7 g/cm², and the adhesive having a viscosity of 6,000 mPa-s or less at a temperature of application of not greater than 107°.
14. The adhesive of claim 13 wherein the polyether polyol comprises a diol.

15. The adhesive of claim 13 or 14 wherein the polyisocyanate comprises an aliphatic polyisocyanate, an aromatic polyisocyanate, or a mixture of any of the foregoing polyisocyanates.

16. The adhesive of any one of claims 13 to 15 wherein the polyisocyanate comprises a diisocyanate.

17. The adhesive of any one of claims 13 to 16 wherein the tackifier comprises a hydrocarbon resin, a urea-aldehyde condensate resin, or a mixture of any of the foregoing resins.

18. The adhesive of any one of claims 13 to 17 wherein the urethane (meth)acrylate is prepared from a polyether diol and an aliphatic diisocyanate, the tackifier comprises an aliphatic hydrocarbon resin or an aromatic hydrocarbon resin or a mixture of any of the foregoing hydrocarbon resins, and the photoinitiator comprises an ultraviolet photoinitiator.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09J175/16

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09J

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category*</th>
<th>Citation of document with indication where appropriate, of the relevant passages</th>
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<td>page 1, lines 8-13</td>
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<td>page 2, line 12 - page 13, line 12; claims, examples</td>
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<td>X</td>
<td>WO 01/16244 A (COGNIS CORP [US]) 8 March 2001 (2001-03-08) page 2, line 16 - page 12, line 13; claims; examples</td>
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<td>paragraphs [0001], [0007] - [0119]; claims; examples 8-11</td>
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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

'B' earlier document but published on or after the international filing date

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Date of the actual completion of the international search

15 November 2006

Date of mailing of the international search report

24/11/2006

Name and mailing address of the ISA/
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Authorized officer

Otegui Rebol l o, Juan
**INTERNATIONAL SEARCH REPORT**

International application No
PCT/US2006/034800

**DOCUMENTS CONSIDERED TO BE RELEVANT**

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<td>US 4 820 745 A (MUELLER HARTMUT [DE] ET AL) 11 April 1989 (1989-04-11) column 1, lines 7-25 column 2, lines 28-67 column 3, line 67 - column 12, line 20; claims; example F26</td>
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