Title: REACTIVE HOT MELT ADHESIVE WITH VISIBEL DYE

Abstract: High green strength reactive hot melt adhesives are prepared including an effective amount of a visible dye that will not alter the open time, green strength, viscosity, adhesion properties or stability of the adhesive.
REACTIVE HOT MELT ADHESIVE WITH VISIBLE DYE

FIELD OF THE INVENTION

The invention relates to hot melt adhesives, in particular reactive hot melt adhesives having a dye that does not negatively affect the properties of the adhesive.

BACKGROUND OF THE INVENTION

Hot melt adhesives are solid at room temperature but, upon application of heat, melt to a liquid or fluid state in which form they are applied to a substrate. On cooling, the adhesive regains its solid form. The hard phase(s) formed upon cooling the adhesive imparts all of the cohesion (strength, toughness, creep and heat resistance) to the final adhesive. Curable hot melt adhesives, which are also applied in molten form, cool to solidify and subsequently cure by a chemical crosslinking reaction. An advantage of hot melt curable adhesives over traditional liquid curing adhesives is their ability to provide "green strength" upon cooling prior to cure.

The majority of reactive hot melts are moisture-curing urethane adhesives. These adhesives consist primarily of isocyanate terminated polyurethane prepolymer that react with surface or ambient moisture in order to chain-extend, forming a new polyurethane polymer. Polyurethane prepolymer are conventionally obtained by reacting diols with diisocyanates. Pure diols are favored for use, instead of polyols with higher functionality, to avoid excessive branching that can lead to poor pot stability. Methylene bisphenyl diisocyanate (MDI) is favored over lower molecular weight isocyanates to minimize volatility. Cure is obtained through the diffusion of moisture from the atmosphere or the substrates into the adhesive, and subsequent reaction. The reaction of moisture with residual isocyanate forms carbamic acid. This acid is unstable, decomposing into an amine and carbon dioxide. The amine reacts rapidly with isocyanate to form a urea. The final adhesive product is a crosslinked material held together primarily through urea groups and urethane groups.

The prior art discloses that that the performance of reactive hot melt adhesives for most applications may be substantially improved by the incorporation of acrylic polymers into
conventional polyurethane adhesives, in particular reactive hydroxy-containing and non-reactive acrylic copolymers. Improvement in green strength may be obtained by adding higher molecular weight polymers (reactive or not) and/or incorporating crystalline diols, most commonly polyester diols.

These prior art adhesives are generally yellowish in color. Upon application, the reactive hot melts are usually applied in a thin layer that is visually transparent, thus causing problems for users visually attempting to determine whether or not a layer of reactive hot melt adhesive has any defects. Attempts to incorporate visible dye into reactive hot melts have failed in that the visible dyes have altered the properties, including the color quality, viscosity, green strength, open time and stability, of the adhesive. Consequently, dye that is detected via application of ultraviolet light has been utilized to allow users to check the quality of the application of the adhesive. UV dye, however, requires the extra step of passing the coated object under a black light and does not provide for unaided visual inspection. It would be advantageous to provide a reactive hot melt adhesive with a visible dye so that an object could be coated, visually inspected for the quality of the coating, and then immediately laminated. Thus, there remains a need for improvement in reactive hot melt technology to allow for the use of visible dyes. The present invention addresses this need.

SUMMARY OF THE INVENTION

The invention provides moisture curable reactive hot melt adhesive compositions that contain visible dyes that do not negatively impact the quality of the adhesive.

One aspect of the invention is directed to a polyurethane hot melt adhesive composition comprising an isocyanate, a polyol, an effective amount of a visual dye, and, optionally one or more plastics or thermoplastic polymers. Another embodiment of the invention is directed to a method of improving the color of a polyurethane hot melt adhesive comprising adding an effective amount of a visible dye to a reactive hot melt adhesive formulation.

Yet another embodiment of the invention is directed to a method for bonding materials together which comprises applying the reactive hot melt adhesive composition of the
invention in a liquid form to a first substrate, bringing a second substrate in contact with the composition applied to the first substrate, and subjecting the applied composition to conditions which will allow the composition to cool and cure to an irreversible solid form, said conditions comprising moisture.

Still another aspect of the invention is directed to an article of manufacture comprising the adhesive of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The disclosures of all documents cited herein are incorporated in their entireties by reference.

All percents are percent by weight of the adhesive composition, unless otherwise stated.

It has now been discovered that reactive hot melt adhesives may be prepared using dyes that are visible without the application of UV light. The adhesives of the invention have green strength, open time, viscosity, adhesion properties and stability commensurate with known reactive hot melt adhesives that do not contain a visible dye. Such adhesives provide a contrast between the substrate and the adhesive that is detectable via human and/or machine vision. These adhesives may be printed in any desired pattern.

The moisture curable, hot melt polyurethane adhesives of the invention may be prepared through the reaction of a mixture of an isocyanate-containing compound, a polyol, at least one visible dye component and, preferably, a thermoplastic polymer, at a temperature of from about 120°F to about 275°F. MDI is a preferred isocyanate for use with the present invention.

The visible dye component of the invention is chosen so that it does not negatively alter the properties of the adhesive. Commercially available dyes for use with polyurethane, such as Sudan Blue commercialized by BASF and others, negatively alter the color quality, viscosity, green strength, stability and open time of reactive hot melt adhesives. It has surprisingly been found that visible dyes that do not contain an active hydrogen group, or in
which the \((n-1)\) valences of the heteroatoms of the active hydrogen group have aromatic substituents, do not negatively alter the quality of the adhesive. Regarding the change in color, while not wishing to be bound to any theory, it is thought that most active hydrogen containing visible dyes react with the isocyanate group to form urea. Adding more conjugation to the dye structure results in a greater energy of absorption and thus a color change occurs as the light goes to a longer wavelength, i.e., blue to green. It is thought that the use of the visible dye that does not contain an active hydrogen group or in which the \((n-1)\) valences of the heteroatoms of the active hydrogen group have aromatic substituents reverse the reaction with the isocyanate or do not produce the reaction, thus eliminating the color change.

For example, acceptable visible dyes that do not contain an active hydrogen group, or in which the \((n-1)\) valences of the heteroatoms of the active hydrogen group have aromatic substituents include dyes having the following structure:

![Chemical Structures]

One commercial example of such a dye is THERMOPLAST BLUE 684, commercialized by BASF.

The reactive hot melt compositions of the invention are useful for bonding articles composed of a wide variety of substrates (materials), including but not limited to wood, metal, polymeric plastics, glass and textiles. As such, these adhesives find particular use in applications such as use in water towers, for bonding to exterior surfaces, bonding to wood with high levels of pitch and e.g., in marine and automotive applications. Other non-limiting
uses include textile bonding applications (carpet and clothing), use in the manufacture of
footwear (shoes), use as a glazing/backbedding compound in the manufacture of windows,
use in the manufacture of doors including entry doors, garage doors and the like, use in the
manufacture of architectural panels, use in bonding components on the exterior of vehicles,
and the like.

The urethane prepolymer that can be used to prepare the adhesives of the invention
are those conventionally used in the production of polyurethane hot melt adhesive
compositions. Any suitable compound, which contains two or more isocyanate groups, may
be used for preparing the urethane prepolymer. Typically from about 2 to about 25 parts by
weight of an isocyanate is used.

Organic polyisocyanates, which may be used to practice the invention, include
alkylene diisocyanates, cycloalkylene diisocyanates, aromatic diisocyanates and aliphatic-
aromatic diisocyanates. Specific examples of suitable isocyanate-containing compounds
include, but are not limited to, ethylene diisocyanate, ethylidene diisocyanate, propylene
diisocyanate, butylene diisocyanate, trimethylene diisocyanate, hexamethylene diisocyanate,
toluene diisocyanate, cyclopentylene-1, 3-diisocyanate, cyclo-hexylene-1,4-diisocyanate,
cyclohexylene-1,2-diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,2-diphenylpropane-
4,4'-diisocyanate, xylylene diisocyanate, 1,4-naphthylene diisocyanate, 1,5-naphthylene
diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, diphenyl-4,4'-
diisocyanate, azobenzene-4,4'-diisocyanate, diphenylsulphone-4,4'-diisocyanate, 2,4-tolylene
diisocyanate, dichlorohexa-methylene diisocyanate, furfurylidene diisocyanate, 1-
chlorobenzene-2,4-diisocyanate, 4,4',4''-trisocyanatotriphenylmethane, 1,3,5-trisocyanatobenzene, 2,4,6-trisocyanato-toluene, 4,4'-dimethylphenyl-methane-2,2',5,5-
tetrationalsisocyanate, and the like. While such compounds are commercially available,
methods for synthesizing such compounds are well known in the art. Preferred isocyanate-
containing compounds are methylenebisphenyldiisocyanate (MDI), isophoronediisocyanate
(IPDI), hydrogenated methylenebisphenyldiisocyanate (HMDI) and toluene diisocyanate
(TDI).
Preferably the adhesive is prepared by including a thermoplastic polymer. The thermoplastic polymer may be either a functional or a non-functional thermoplastic. Suitable thermoplastic polymers include acrylic polymers, functional acrylic polymers, non-functional acrylic polymers, hydroxy functional acrylic polymers, polyvinyl acetate, polyvinyl chloride, methylene polyvinyl ether, cellulose acetate, styrene acrylonitrile, amorphous polyolefin, thermoplastic urethane, polyacrylonitrile, functional EVA, block copolymers, ethylene/acylate copolymers, ethyl methacrylate, ethyl hexyl acrylate, ethylene-n-butyl acrylate, polybutadiene diol, ethylene butadiene, isobutylene diol and mixtures thereof.

Most commonly, the prepolymer is prepared by the polymerization of a polyisocyanate with a polyol, most preferably the polymerization of a diisocyanate with a diol. The polyols used include polyhydroxy ethers (substituted or unsubstituted polyalkylene ether glycols or polyhydroxy polyalkylene ethers), polyhydroxy polyesters, the ethylene or propylene oxide adducts of polyols and the monosubstituted esters of glycerol, as well as mixtures thereof. The polyol is typically used in an amount of between about 10 to about 70 parts by weight.

Examples of polyether polyols include a linear and/or branched polyether having plural numbers of ether bondings and at least two hydroxyl groups, and contain substantially no functional group other than the hydroxyl groups. Examples of the polyether polyol may include polyoxyalkylene polyol such as polyethylene glycol, polypropylene glycol, polybutylene glycol and the like. Further, a homopolymer and a copolymer of the polyoxyalkylene polyols may also be employed. Particularly preferable copolymers of the polyoxyalkylene polyols may include an adduct at least one compound selected from the group consisting of ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, 2-ethylhexanediol-1,3, glycerin, 1,2,6-hexane triol, trimethylol propane, trimethylol ethane, tris(hydroxyphenyl)propane, triethanolamine, trispropanolamine, ethylenediamine and ethanolamine; with at least one compound selected from the group consisting of ethylene oxide, propylene oxide and butylene oxide.
A number of suitable polyols are commercially available. Non-limiting examples include CP4701 (Dow Chemicals), Niax 11-34 (Union Carbide Corp), Desmophen 3900 (Bayer), Propylan M12 (Lankro Chemicals), Highflex 303 (Dalichi Kogyo Seiyaku K.K.) and Daitocel T 32-75 (ICI). "Polymer polyols" are also suitable, i.e., graft polyols containing a proportion of a vinyl monomer, polymerized in situ, e.g., Niax 34-28.

Polyester polyols are formed from the condensation of one or more polyhydric alcohols having from 2 to 15 carbon atoms with one or more polycarboxylic acids having from 2 to 14 carbon atoms. Examples of suitable polyhydric alcohols include ethylene glycol, propylene glycol such as 1,2-propylene glycol and 1,3-propylene glycol, glycerol, pentaerythritol, trimethylolpropane, 1,4,6-octanetriol, butanediol, pentanediol, hexanediol, dodecanediol, octanediol, chloropentanediol, glycerol monallyl ether, glycerol monoethyl ether, diethylene glycol, 2-ethylhexanediol-1,4, cyclohexanediol-1,4, 1,2,6-hexanetriol, 1,3,5-hexanetriol, 1,3-bis-(2-hydroxyethoxy)propane and the like. Examples of polycarboxylic acids include phthalic acid, isophthalic acid, terephthalic acid, tetrachlorophthalic acid, maleic acid, dodecylmaleic acid, octadecenylmaleic acid, fumaric acid, aconitic acid, trimeellitic acid, tricarballylic acid, 3,3'-thiodiropionic acid, succinic acid, adipic acid, malonic acid, glutaric acid, pimelic acid, sebacic acid, cyclohexane-1,2-dicarboxylic acid, 1,4-cyclohexadiene-1,2-dicarboxylic acid, 3-methyl-5,cyclohexadiene-1,2-dicarboxylic acid and the corresponding acid anhydrides, acid chlorides and acid esters such as phthalic anhydride, phthaloyl chloride and the dimethyl ester of phthalic acid. Preferred polycarboxylic acids are the aliphatic and cycloaliphatic dicarboxylic acids containing no more than 14 carbon atoms and the aromatic dicarboxylic acids containing no more than 14 atoms.

Commercially available polyols which may be used in the practice of the invention include polyethers such as ARCOL PPG 2025 (Bayer), PolyG 20-56 (Arch) and Pluracol P-2010 (BASF), polyesters such as Dynacoll 7360 (Creanova), Formrez 66-32 (Crompton) and Rucoflex S-105-30 (Bayer) and polybutadiene such as PolyBD R-45HTLO (Elf Atochem).

In addition, the urethane prepolymers may be prepared by the reaction of a polyisocyanate with a polyamino or a polymercapto-containing compound such as diamin
polypropylene glycol or diamino polyethylene glycol or polythioethers such as the condensation products of thiodiglycol either alone or in combination with other glycols such as ethylene glycol, 1,2-propylene glycol or with other polyhydroxy compounds disclosed above. In accordance with one embodiment of the invention, the hydroxyl containing acrylic polymer may function as the polyol component, in which case, no additional polyol need be added to the reaction.

Further, small amounts of low molecular weight dihydroxy, diamino, or amino hydroxy compounds may be used such as saturated and unsaturated glycols, e.g., ethylene glycol or condensates thereof such as diethylene glycol, triethylene glycol, and the like; ethylene diamine, hexamethylene diamine and the like; ethanolamine, propanolamine, N-methylidithanolamine and the like.

Virtually any ethylenically unsaturated monomer containing a functionality greater than one may be utilized in the compositions of the present invention. Functional monomers include, without limitation, acid, hydroxy, amine, isocyanate, and thiol functional monomers. Hydroxyl functionality is preferred and is described in detail herein.

Most commonly employed are hydroxyl substituted C₄ to C₁₂ esters of acrylic and methacrylic acids including, but not limited to hydroxyl substituted methyl acrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, isobutyl acrylate, n-propyl or iso-propyl acrylate or the corresponding methacrylates. Mixtures of compatible (meth)acrylate monomers may also be used. Additional monomers that may be used include the hydroxyl substituted vinyl esters (vinyl acetate and vinyl propionate), vinyl ethers, fumarates, maleates, styrene, acrylonitrile, etc. as well as comonomers thereof.

These monomers may be blended with other copolymerizable comonomers as formulated so as to have a wide range of Tₐ values, as between about -48°C and 105°C, preferably 15°C to 85°C. Suitable comonomers include the C₄ to C₁₂ esters of acrylic and methacrylic acids including, but not limited to methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, n-propyl or iso-propyl acrylate or the corresponding methacrylates. Mixtures of compatible (meth)acrylate monomers may also be used.
Additional monomers that may be used include the vinyl esters (vinyl acetate and vinyl propionate), vinyl ethers, fumarates, maleates, styrene, acrylonitrile, ethylene, etc. as well as comonomers thereof. The hydroxyl containing monomers may be the same or different from the monomers used in the remainder of the acrylic polymerization. The particular monomers selected will depend, in large part, upon the end use for which the adhesives are intended. Thus, adhesives to be used in pressure sensitive applications or in applications wherein adhesion to metal is required will be selected to obtain a lower Tg polymer than may be desired in non-pressure sensitive applications or those involving more easily bonded substrates.

When the adhesive is to be prepared utilizing monomeric materials, the respective monomers may be added to the polyols and polymerized therein prior to formation of the prepolymer or may be added to the already formed prepolymer and the acrylic polymerization subsequently performed. In the case of polyamino or polymercapto containing prepolymer, in-situ vinylic polymerization must be performed only in the pre-formed prepolymer.

The hydroxyl containing ethylenically unsaturated monomer is polymerized using conventional free radical polymerization procedures to a relatively low molecular weight. For purposes of clarification, use of the term "low molecular weight" means number average molecular weights in the range of approximately 1,000 to 50,000, preferred for use are monomers having an average molecular weight in the range of from about 5,000 to about 30,000. Molecular weight distribution is characterized by Gel Permeation Chromatography using a PL Gel, Mixed 10 micron column, a Shimadzu Model RID 6A Detector with a tetrahydrofuran carrier solvent at a flow rate of 1 milliliter per minute. The low molecular weight is obtained by carefully monitoring and controlling the reaction conditions and, generally, by carrying out the reaction in the presence of a chain transfer agent such as dodecyl mercaptan. Subsequent to the polymerization of the ethylenically unsaturated monomer(s), the polyisocyanate and any additional ingredients required for the urethane prepolymer forming reaction are added and that reaction is carried out using conventional condensation polymerization procedures. In this manner, the resultant isocyanate terminated
urethane prepolymer forms the reactive curing hot melt adhesive described above which contains about 2 to about 90% of the low molecular weight hydroxyl containing polymer.

It is also possible to polymerize the low molecular weight polymer in the presence of the already formed isocyanate terminated urethane prepolymer. This method has the drawback of subjecting the prepolymer to unnecessary heating during the acrylic polymerization, heating that might result in branching, viscosity increase, depletion of needed isocyanate groups and possible gellation. Although these disadvantages are subject to control, more stringent control of conditions are required as compared to polymerization in the non-isocyanate functional urethane components. When the reaction is run in the polyl or other non-isocyanate containing component, there is also the advantage of lower reaction viscosities and reduced exposure to isocyanate vapors because of the lesser amount of heating required.

Optionally, the hydroxyl containing functionality may be introduced into the adhesive in the form of pre-polymerized low molecular weight hydroxyl containing polymers. In the latter case, typical polymers include hydroxyl substituted butyl acrylate, hydroxylated butyl acrylate/methyl methacrylate copolymers, hydroxylated ethyl acrylate/methyl methacrylate copolymers, and the like. Preferred polymers have a number average molecular weight of 5,000 to 30,000 and a hydroxyl number of 4 to 30. If used in the form of low molecular weight polymers, the polymers may be blended with the polyl prior to reaction thereof with the isocyanate or they may be added directly to the isocyanate terminated prepolymer.

While the adhesives may be used directly as described above, if desired the adhesives of the present invention may also be formulated with conventional additives which are compatible with the composition. Such additives include plasticizers, compatible tackifiers, curing catalysts, dissociation catalysts, fillers, anti-oxidants, pigments, DMDEE, adhesion promoters, stabilizers, aliphatic C6-C10 terpene oligomers and the like. Conventional additives that are compatible with a composition according to this invention may simply be determined by combining a potential additive with the composition and determining if they are compatible. An additive is compatible if it is homogenous within the product.
limited examples of suitable additives include, without limitation, rosin, rosin derivatives, rosin ester, aliphatic hydrocarbons, aromatic hydrocarbons aromatically modified aliphatic hydrocarbons, terpenes, terpene phenol, modified terpene, high molecular weight hindered phenols and multifunctional phenols such as sulfur and phosphorous-containing phenol, terpene oligomers, DMDEE, paraffin waxes, microcrystalline waxes and hydrogenated castor oil.

The reactive hot melt adhesives of the invention may also contain flame retardant components. Fire retardant additives known in the art for imparting flame resistance to polyurethane compositions may be added. Such compounds include inorganic compounds such as a boron compound, aluminum hydroxide, antimony trioxide and the like, and other halogen compounds including halogen-containing phosphate compounds such as tris(chloroethyl)phosphate, tris(2,3-dichloropropyl)-phosphate, and the like. These and other flame retarding compositions are described in U.S. Patent Nos. 3,773,695, 4,266,042, 4,585,806, 4,587,273 and 4,849,467, and European Patent No. 0 587 942. In a preferred embodiment, ethylenebistetramethylphthalimide and/or tris(2,3-dibromopropyl)-isocyanurate is added as a prime flame retardant component. The ethylenebistetramethylphthalimide and/or tris(2,3-dibromopropyl)isocyanurate may be used with or without other flame retardants. The composition may further comprise a chlorinated paraffin and/or an aryl phosphate ester as a further flame retardant component. The optional chlorinated paraffin imparts flame retardancy as well as performing as a viscosity modifier. The aryl phosphate ester further imparts improved adhesion to the substrates. The flame retardant polyurethane-based reactive hot melt adhesives when used in the practice of the invention gives excellent flame retardancy while maintaining the targeted properties of the base polymer, such as good green strength, controlled setting speed and good thermal stability at elevated temperatures.

The invention also provides a method for bonding articles together which comprises applying the reactive hot melt adhesive composition of the invention in a liquid melt form to a first article, bringing a second article in contact with the composition applied to the first article, and subjecting the applied composition to conditions which will allow the composition to cool.
and cure to a composition having an irreversible solid form, said conditions comprising moisture. The quality of the coating of the adhesive can be visually inspected before the second article is brought into contact with the first article. The composition is typically distributed and stored in its solid form, and is stored in the absence of moisture. When the composition is ready for use, the solid is heated and melted prior to application. Thus, this invention includes reactive polyurethane hot melt adhesive compositions in both its solid form, as it is typically to be stored and distributed, and its liquid form, after it has been melted, just prior to its application.

After application, to adhere articles together, the reactive hot melt adhesive composition is subjected to conditions that will allow it to solidify and cure to a composition that has an irreversible solid form. Solidification (setting) occurs when the liquid melt is subjected to room temperature. Curing, i.e. chain extending, to a composition that has an irreversible solid form, takes place in the presence of ambient moisture.

As used herein, "irreversible solid form" means a solid form comprising polyurethane polymers extended from the aforementioned polyurethane prepolymer. The composition having the irreversible solid form typically can withstand temperatures of up to 150⁰C. Using a flame retardant the thermal stability of the irreversible solid can be improved.

Many modifications and variations of this invention can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. The specific embodiments described herein are offered by way of example only, and the invention is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled.
CLAIMS

1. A polyurethane hot melt adhesive composition comprising an isocyanate, a polyol, a dye that is visible without the use of ultraviolet light and which does not substantially negatively alter the viscosity, green strength, open time, adhesion properties and/or stability of the adhesive, and optionally a thermoplastic polymer.

2. The adhesive of claim 1, wherein the thermoplastic polymer is selected from the group comprising functional thermoplastic polymers, non-functional thermoplastic polymers, and mixtures thereof.

3. The adhesive of claim 2, wherein the thermoplastic polymer is selected from the group comprising acrylic polymers, functional acrylic polymers, non-functional acrylic polymers, hydroxy functional acrylic polymers, polyvinyl acetate, polyvinyl chloride, methylene polyvinyl ether, cellulose acetate, styrene acrylonitrile, amorphous polyolefin, thermoplastic urethane, polyacrylonitrile, functional EVA, block copolymers, ethylene/acrylate copolymers, ethyl methacrylate, ethyl hexyl acrylate, ethylene-n-butyl acrylate, polybutadiene diol, ethylene butadiene, isobutylene diol, and mixtures thereof.

4. The adhesive of claim 1, wherein the polyol is a polyether polyol.

5. The adhesive of claim 1, wherein the polyol is a polyester polyol.

6. The adhesive of claim 1, wherein the polyol is a mixture of a polyester polyol and a polyether polyol.

7. The adhesive of claim 1, wherein the dye contains no active hydrogen groups.
8. The adhesive of claim 1, wherein the dye contains active hydrogen groups and wherein (n-1) valences of the heteroatoms of the active hydrogen groups have aromatic substituents.

9. The adhesive of claim 1, wherein the dye does not change color during the manufacturing of the adhesive.

10. The adhesive of claim 1 further comprising one or more additives from the group comprising plasticizers, compatible tackifiers, curing catalysts, dissociation catalysts, fillers, anti-oxidants, pigments, adhesion promoters, stabilizers, aliphatic C₆-C₁₀ terpene oligomers, rosin, rosin derivatives, rosin ester, aliphatic hydrocarbons, aromatic hydrocarbons aromatically modified aliphatic hydrocarbons, terpenes, terpene phenol, modified terpene, high molecular weight hindered phenols and multifunctional phenols such as sulfur and phosphorous-containing phenol, terpene oligomers, DMDEE, paraffin waxes, microcrystalline waxes, hydrogenated castor oil, and mixtures thereof.

11. The adhesive of claim 1, wherein upon application the adhesive provides a contrast between the substrate and the adhesive that is detectable via human and/or machine vision.

12. A method of improving the color quality of a polyurethane adhesive comprising adding an effective amount of a visible dye to an adhesive formulation, wherein the adhesive comprises a thermoplastic polymer.

13. The method of claim 12, wherein the visible dye contains active hydrogen groups and wherein (n-1) valences of the heteroatoms of the active hydrogen groups have aromatic substituents.

14. The method of claim 11, wherein the thermoplastic polymer is selected from the group comprising functional thermoplastic polymers, non-functional thermoplastic polymers and mixtures thereof.
15. The method of claim 14, wherein the thermoplastic polymer is selected from the group comprising acrylic polymers, functional acrylic polymers, non-functional acrylic polymers, hydroxy functional acrylic polymers, polyvinyl acetate, polyvinyl chloride, methylene polyvinyl ether, cellulose acetate, styrene acrylonitrile, amorphous polyolefin, thermoplastic urethane, polyacrylonitrile, functional EVA, block copolymers, ethylene/acrylate copolymers, ethyl methacrylate, ethyl hexyl acrylate, ethylene-n-butyl acrylate, polybutadiene diol, ethylene butadiene, isobutylene diol, and mixtures thereof.

16. The method of claim 12, wherein the polyl is a polyether polyl.

17. The method of claim 12, wherein the polyl is a polyester polyl.

18. The method of claim 12, wherein the polyl is a mixture of a polyester polyl and a polyether polyl.

19. The method of claim 12, wherein the adhesive further comprises one or more additives from the group comprising plasticizers, compatible tackifiers, curing catalysts, dissociation catalysts, fillers, anti-oxidants, pigments, adhesion promoters, stabilizers, aliphatic C₆-C₁₀ terpene oligomers, rosin, rosin derivatives, rosin ester, aliphatic hydrocarbons, aromatic hydrocarbons, aromatically modified aliphatic hydrocarbons, terpenes, terpene phenol, modified terpene, high molecular weight hindered phenols and multifunctional phenols such as sulfur and phosphorous-containing phenol, terpene oligomers, DMDEE, paraffin waxes, microcrystalline waxes, hydrogenated castor oil, and mixtures thereof.

20. A method of bonding materials together which comprises applying the reactive hot melt adhesive composition of claim 1 in a molten form to a first substrate, bringing a second substrate in contact with the composition applied to the first substrate, and subjecting the
compositions to conditions which will allow the compositions to cool and cure to an irreversible solid form, the conditions comprising moisture.

21. The method of claim 12, further comprising the step of visually inspecting the composition after application to the first substrate and before the second substrate is brought into contact with the composition.

22. The method of claim 12 wherein the adhesive comprises a non-functional acrylic polymer.

23. The method of claim 12 wherein the adhesive comprises a functional acrylic polymer.

24. The method of claim 23 wherein the functional acrylic polymer is a hydroxy functional polymer.

25. An article of manufacture comprising the adhesive of claim 1.