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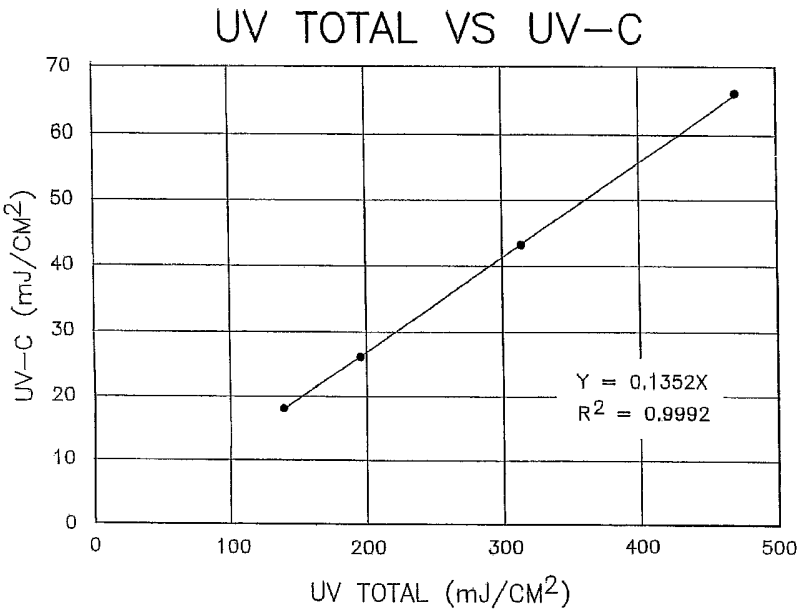
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(54) Title: AROMATIC/ACRYLATE TACKIFIER RESIN AND ACRYLIC POLYMER BLENDS



(57) Abstract: An adhesive composition comprising at least one tackifier resin and at least one acrylic polymer is provided wherein the tackifier resin comprises monomer repeating units from at least one aromatic monomer and at least one acrylate monomer; and wherein the tackifier resin has a low residual monomer concentration. Processes to produce the adhesive composition is also provided.

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Aromatic/Acrylate Tackifier Resin and Acrylic Polymer Blends

FIELD OF THE INVENTION

This invention is related to the field of tackifier resin and acrylic polymer blends. More specifically, this invention is related to the field of tackifier resin and acrylic polymer blends wherein said tackifier resin comprises repeating units from at least one aromatic monomer and at least one acrylic monomer; and wherein the tackifier resin has a low residual monomer concentration. The invention is also related to the field of processes to produce these tackifier resin and acrylic polymer blends.

BACKGROUND OF THE INVENTION

Tackifying resins are often used to modify various acrylic polymers to produce adhesive compositions. Traditional tackifier resins include, for example, rosins, rosin esters, colophonium-based resins, C_5 and C_9 based hydrocarbon resins, terpene-based resins, coumarone and indene-based resins, and phenolic resins. These tackifiers are used to produce, for example, pressure-sensitive adhesives and hot-melt adhesives.

Many of these commercial tackifiers cannot be used in certain applications. For example, in medical applications, some tackifiers cannot be utilized due to skin sensitivity concerns. The medical adhesive industry has a perception that rosins and rosin esters can cause skin sensitivity, therefore, rosins and rosins esters may not be used in this application.

In addition, tackifier resins used in many adhesive applications need to be clear and to not cause fogging. Also, tackifier resins may also need to not inhibit the breathability of an adhesive composition as indicated by the moisture vapor transport rate of the adhesive composition after the tackifier resin is added.

Therefore, there is a need in the adhesive industry for new tackifier resins that can modify acrylic polymers and provide these properties.

SUMMARY OF THE INVENTION

In accordance with one embodiment of this invention, an adhesive composition is provided comprising at least one tackifier resin and at least one acrylic polymer wherein the tackifier resin comprises monomer units from at least one aromatic monomer and at least one acrylate monomer; and wherein the tackifier resin has a low residual monomer concentration.

In accordance with another embodiment of this invention, a process is provided to produce the adhesive composition. The process comprises providing the tackifier resin and at least one acrylic polymer to produce the adhesive composition.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the relationship between Total UV and UV-C dose.

DETAILED DESCRIPTION

In an embodiment of this invention, an adhesive composition is provided comprising at least one tackifier resin and at least one acrylic polymer; wherein the tackifier resin comprises monomer repeating units from at least one aromatic monomer and at least one acrylate monomer; and wherein the tackifier resin has a low residual monomer concentration.

The aromatic monomer can be any aromatic monomer known in the art capable of polymerizing with at least one acrylate monomer to produce the tackifier resin. The term "aromatic monomer" means a monomer containing at least one group of unsaturated cyclic hydrocarbons containing one or more rings. Examples of aromatic monomers include, but are not limited to, olefinic substituted aromatics,

such as, styrene, alpha-methyl styrene, vinyl toluene, indene, methylindenes, divinylbenzene, dicyclopentadiene, and methyl-dicyclopentadiene. Most preferably, the aromatic monomer is styrene. The aromatic monomer can be added to a reactor zone in the polymerization process as a single type of monomer or a mixture and can be added in varying amounts and at varying addition times during the polymerization.

The acrylate monomer is any acrylate monomer known in the art capable of polymerizing with the aromatic monomer. The acrylate monomer can be added to a reactor zone in the polymerization process as a single type of monomer or as a mixture and can be added in varying amounts and at varying addition times during the polymerization.

In one embodiment, the acrylate monomer has the general formula:

$$R_1\text{-}CH=CR_2\text{-}COOR_3$$

wherein R_1 is selected from the group consisting of hydrogen, aliphatic groups, and aromatic groups; wherein R_2 is selected from the group consisting of hydrogen, aliphatic groups, and aromatic groups; and wherein R_3 is selected from the group consisting of hydrogen, aliphatic groups, aromatic groups. The term "aliphatic" is defined as a straight or branched chain arrangement of constituent carbon atoms and includes, but is not limited to, alkanes, alkenes, alkadienes, and alkynes. The aliphatic groups can contain functional groups, such as, but not limited to, hydroxyl, cycloaliphatic, acid, epoxide, amide, acrylonitril and acrylate. Preferably, the aliphatic group has 1 to about 20 carbon atoms, more preferably, from 1 to 12. The term "aromatic group" means at least one group of unsaturated cyclic hydrocarbons containing one or more rings. Aromatic groups can be selected from the group consisting of both unsubstituted and substituted aromatic groups having

constituents with up to about 6 carbon atoms. Preferably, the aromatic group has about 6 to about 20 carbon atoms.

The aromatic groups can contain functional groups, such as, but not limited to, hydroxyl, cycloaliphatic, acid, epoxide, amide, acrylonitril and acrylate. In some cases, these functional groups can lead to an acrylate monomer that has more than one reactive site for polymerization or other reactions.

In one embodiment, both R_1 and R_2 of the acrylate monomer are hydrogen. When the acrylate monomer is a methacrylic compound, R_2 is a CH_3 group.

For acid functionality monomers, R_3 is often hydrogen, such as, acrylic acid and methacrylic acid. The acid functionality monomers can also be difunctional components such as, for example, maleic acid, fumaric acid or can be the anhydride forms of these components.

In another embodiment, the functional group is often found in the R_3 group. Suitable examples are hydroxyethylacrylate, glycidylmethacrylate, and 1,3-butanediol dimethylacrylate.

Examples of acrylate monomers include, but are not limited to, methyl acrylate, acrylic acid, methacrylic acid, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, n-hexyl acrylate, n-hexyl methacrylate, ethylhexyl acrylate, ethylhexyl methacrylate, n-heptyl acrylate, n-heptyl methacrylate, 2-methylheptyl (meth)acrylate, octyl acrylate, octyl methacrylate, isooctyl (meth)acrylate, n-nonyl(meth)acrylate, iso-nonyl(meth)acrylate, decyl(meth)acrylate, isodecyl acrylate, isodecyl methacrylate, dodecyl(meth)acrylate, isobornyl(meth)acrylate, lauryl methacrylate, lauryl acrylate, tridecyl acrylate, tridecyl methacrylate, stearyl acrylate, stearyl methacrylate, glycidyl methacrylate, alkyl crotonates, vinyl acetate, di-n-butyl maleate, di-octylmaleate, acetoacetoxyethyl methacrylate, acetoacetoxyethyl acrylate, acetoacetoxypropyl methacrylate, acetoacetoxypropyl acrylate, diacetone acrylamide, acrylamide, methacrylamide, hydroxyethyl

methacrylate, hydroxyethyl acrylate, allyl methacrylate, tetrahydrofurfuryl methacrylate, tetrahydrofurfuryl acrylate, cyclohexyl methacrylate, cyclohexyl acrylate, n-hexyl acrylate, n-hexyl methacrylate, 2-ethoxyethyl acrylate, 2-ethoxyethyl methacrylate, isodecyl methacrylate, isodecyl acrylate, 2-methoxy acrylate, 2-methoxy methacrylate, 2-(2-ethoxyethoxy) ethylacrylate , 2-phenoxyethyl acrylate, 2-phenoxyethyl methacrylate, isobornyl acrylate, isobornyl methacrylate, caprolactone acrylate, caprolactone methacrylate, polypropyleneglycol monoacrylate, polypropyleneglycol monomethacrylate, poyethyleneglycol(400) acrylate, polypropyleneglycol(400) methacrylate, benzyl acrylate, benzyl methacrylate, sodium 1-allyloxy-2-hydroylpropyl sulfonate, acrylonitrile, and the like.

Acrylate monomers are described in "The Brandon Worldwide Monomer Reference Guide and Sourcebook" Second Edition, 1992, Brandon Associates, Merrimack, New Hampshire; and in "Polymers and Monomers", the 1996-1997 Catalog from Polyscience, Inc., Warrington, PA.

Two or more of the acrylate monomers may be used in combination. Preferably, the acrylate monomer has up to about 20 carbon atoms, such as, but not limited to, acrylic acid, 2-ethylhexyl acrylate, methyl methacrylate, methyl acrylate, acrylic acid, methacrylic acid, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, n-hexyl acrylate, n-hexyl methacrylate, ethylhexyl acrylate, ethylhexyl methacrylate, n-heptyl acrylate, n-heptyl methacrylate, 2-methylheptyl (meth)acrylate, octyl acrylate, octyl methacrylate, isooctyl (meth)acrylate, n-nonyl(meth)acrylate, iso-nonyl(meth)acrylate, decyl(meth)acrylate, isodecyl acrylate, isodecyl methacrylate, dodecyl(meth)acrylate, isobornyl(meth)acrylate, hydroxyethyl methacrylate, hydroxyethyl acrylate, allyl methacrylate, cyclohexyl methacrylate, cyclohexyl acrylate, n-hexyl acrylate, n-hexyl methacrylate, isobornyl acrylate, isobornyl methacrylate, and the like.

Most preferably, the acrylate monomers are acrylic acid and 2-ethylhexyl acrylate.

Functionality can be built in to the tackifier resin by choosing an acrylate monomer containing at least one functional group. The functional group can be selected from hydroxy, cycloaliphatic, acid, epoxide, amide, acrylonitril and acrylate groups. Most preferable, the acrylate monomer contains acid groups or hydroxyl groups. This functionality can lead to even better cohesion in the adhesive composition as determined by the Shear Adhesion Failure Test (SAFT), however, the tackifier resin can be less heat stable due to trans-esterfication reactions. Other specific functional groups can be chosen to improve MVTR, fogging, and adhesion.

The tackifier resin can be produced by any process known in the art. In one embodiment, the tackifier resin can be produced by a radical catalyzed polymerization mechanism:

Decomposition: $I \text{ ------- } 2^* R\bullet$

Initiation: $R\bullet + M \text{ -------- } M_1\bullet$

Propagation: $M_i\bullet + M \text{ ------- } M_{i+1}\bullet$

Termination: $M_i\bullet + M_j\bullet \text{ ----- } M_i + M_j$

wherein I represents an initiator; R• represents a radical; and M represents a monomer.

Any polymerization initiator known in the art for radical catalyzed polymerization can be utilized. Initiators are typically chosen based on the desired molecular weight of the tackifier resin and the polymerization temperature. The effect of decomposition products of the initiator on the odor of the tackifier resin can also be a factor. Suitable initiators can be chosen from all kinds of commercially available organic peroxides, such

as, but not limited to, diacyl peroxides, dialkylperoxidicarbonates, tert-alkyl peroxyesters, di-tert-alkyl peroxides, tert-alkyl hydroperoxides, ketone peroxides, and mixtures thereof. Preferably, the initiator is selected from the group consisting of di-tert-butyl peroxide, dicumyl peroxide, and di-amyl peroxide.

The radical catalyzed polymerization can occur in a reactor zone in the presence of at least one solvent. Processes can be utilized without the use of solvent. Generally, the reactor zone comprises at least one reactor. The solvent can be any solvent that is known in the art to be utilized in radical catalyzed polymerizations. Examples of solvents include, but are not limited to, xylene, toluene, ethylbenzene, trimethylbenzene, and mixtures thereof. Preferably, the solvent is xylene or a mixture of the isomers of methyethylbenzene, trimethylbenzene, ethyl-dimethylbenzene, propylmethylbenzene and tetramethylbenzene. Most preferably, the solvent is xylene.

Radical catalyzed polymerization to produce the tackifier resins can be batch, fed batch or continuous. Reaction temperatures for the radical catalyzed polymerization can be from 0 to about 250°C, preferably from about 100°C to about 200°C, and most preferably from 150°C to 160°C. Initiator levels can be from about 0.1% by weight to about 6% by weight based on the weight of the monomer feed, preferably the amount of initiator can range from 0.1% to 3%.

In one embodiment, a process to produce a tackifier resin is provided comprising contacting a tackifier resin product stream with at least one carrier at a temperature sufficient to remove a portion of at least one residual monomer to produce the tackifier resin. Residual monomer is defined as unreacted monomer or monomers contained in the tackifier resin. The tackifier resin product stream comprises tackifier resin and optionally, at least one solvent. A portion of the residual solvent can also be removed from the tackifier resin product stream. The tackifier resin and solvent were previously discussed in this disclosure.

The tackifier resin concentration is particularly useful in adhesives for medical applications since it can have a clear color. The low residual monomer concentration in the inventive tackifier resin can also reduce or eliminate skin sensitivity properties. It can also give much better fogging behavior of the adhesive composition over adhesive compositions containing tackifier resins without low residual monomer concentrations.

The amount of the residual monomer in the tackifier resin depends on the use of the adhesive composition. In one embodiment, the inventive tackifier resin can have a low residual monomer concentration such that the tackifier resin does not significantly decrease the MVTR of the adhesive composition. A tackifier resin does not significantly decrease the MVTR of the adhesive composition if the MVTR is not decreased by more than 25%, preferably 10% over the adhesive composition without the tackifier resin. Preferably, the MVTR of the adhesive composition is the same or increased over the adhesive composition without the tackifier resin. For example, the MVTR of the adhesive composition can range from about 200 to about 3000, preferably from 500 to 1500.

The contacting of the tackifier resin product stream with the carrier to remove a portion of the residual monomers can be conducted by any means known in the art. Examples of carriers include, but are not limited to, steam, nitrogen and ethane. Preferably, the carrier is stream. The temperature and pressure of the carrier is that which is sufficient to remove a portion of the residual monomers to obtain the desired residual monomer concentration of the tackifier resin or desired MVTR of the adhesive composition. Depending on the application, it may also be desirous that the residual monomer concentration of the tackifier resin is such that it does not increase fogging of the adhesive composition or cause any significant level of skin sensitivity. Preferably, the residual monomer concentration of the tackifier resin is less than about 600 ppm by weight based on the weight of the tackifier resin, more

preferably less than about 300 ppm by weight, and most preferably, less than 250 ppm by weight.

In another embodiment, the residual monomer level of the tackifier resin is less than about 200 ppm aromatic monomer based on the weight of the tackifier resin and less than about 400 ppm acrylic monomer, preferably less than about 100 ppm by weight aromatic monomer and less than about 200 ppm by weight acrylic monomer, and most preferably, less than 100 pm by weight aromatic monomer and less than 150 ppm by weight acrylic monomer.

In yet another embodiment of this invention, the residual solvent level in the tackifier resin is less than about 500 ppm by weight based on the weight of the tackifier resin, preferably less than about 200 ppm by weight, and most preferably, less than 50 ppm by weight.

The contacting of the tackifier resin product stream with the carrier can occur at any temperature and pressure sufficient to obtain the desired residual monomer concentration in the tackifier resin. Preferably, the contacting can occur at a temperature in the range of about 150°C to about 250°C, more preferably, from 160°C to 220°C. Preferably, the contacting of the tackifier resin product stream with the carrier occurs at a pressure in the range of about 10 mbar to about 1000 mbar, preferably from 20 mbar to 200 mbar.

In another embodiment of this invention, a process to produce the tackifier resin is provided. The process comprises:

a) providing at least one aromatic monomer, at least one acrylate monomer, and optionally, at least one solvent to a reactor zone to produce a reaction mixture;

b) polymerizing the reaction mixture in the presence of at least one initiator to produce a tackifier resin product stream; and

c) contacting the tackifier resin product stream with a carrier to remove a portion of at least one residual monomer from the tackifier resin product stream to yield the tackifier resin. The process of

contacting the tackifier resin product stream with the carrier has been previously discussed in this disclosure.

In another embodiment of this invention, a process to produce the tackifier resin is provided. The process comprises:

a) providing at least one aromatic monomer, at least one acrylate monomer, and optionally at least one solvent to a reactor zone to produce a reaction mixture;

b) polymerizing the reaction mixture in the presence of at least one initiator to produce a tackifier resin product stream;

c) heating the tackifier resin product stream at a temperature sufficient to remove a portion of at least one residual monomer from the tackifier resin product stream; and

d) contacting the tackifier resin product stream with at least one carrier to further remove a portion of the residual monomers to produce the tackifier resin. Preferably, the residual monomer concentration of the tackifier resin is less than about 600 ppm by weight based on the weight of the tackifier resin. The residual monomer concentration and residual solvent concentration can vary and were discussed previously in this disclosure.

The heating of the tackifier resin product stream can be conducted by any method known in the art. For example, the tackifier resin product stream can be heated while in the reactor vessel or it can be removed to other processing equipment. The heating is conducted at a temperature and pressure sufficient to remove a portion of at least one residual monomer. The temperature however should not be too high to cause color deterioration of the tackifier resin. The residual monomer can be removed by heating the tackifier resin product stream to a temperature ranging from about 150°C to about 250°C, preferably 160°C to 220°C. The pressure can vary from about 10 mbar to about 1000 mbar, preferably from 20 mbar to 200 mbar. Generally, the portion removed can range from about 1% by weight to about 200% by weight based on the weight of the tackifier resin. Preferably, the portion

removed can range from 50% by weight to 150% by weight. The duration of the heating varies depending on the amount of tackifier resin product stream to be handled. For example, the duration can range from about 0.5 hours to about 8 hours.

The contacting of the tackifier resin product stream with a carrier was previously described in this disclosure.

In another embodiment, a tackifier resin is produced by a process comprising:

a) providing at least one aromatic monomer, at least one acrylate monomer, and optionally at least one solvent to a reactor zone to produce a reaction mixture;

b) polymerizing the reaction mixture in the presence of at least one initiator to produce a tackifier resin product stream;

c) heating the tackifier resin product stream at a temperature in a range of about 150°C to about 250°C to remove a portion of the residual monomers from the tackifier resin product stream; and

d) contacting the tackifier resin product stream with a carrier to further remove a portion of the residual monomers to yield the tackifier resin having residual monomer concentrations of less than about 200 ppm of aromatic monomer and 400 ppm of acrylate monomer. The residual monomer level and residual solvent level can vary as discussed previously in this disclosure.

In yet another embodiment of the invention, the tackifer resin is produced by a processs comprising:

a) contacting at least one aromatic monomer, at least one acrylate monomer, and at least one initiator to produce a monomer-initiator stream;

b) routing the monomer-initiator stream to a reaction zone containing solvent at a temperature in the range of about 100°C to about 250°C;

c) polymerizing the monomer-initiator feed stream at polymerization conditions to produce a tackifier resin product stream;

d) optionally, providing an additional amount of initiator to the reaction zone;

e) heating the tackifier resin product stream at a temperature in a range of about 150°C to about 250°C and at a pressure of about 10 mbar to about 1000 mbar to remove a portion of the residual monomer from the tackifier resin product stream; and

f) contacting the tackifier resin product stream with steam at a temperature of about 150°C to about 250°C and at a pressure of about 10 bar to about 1000 mbar to further remove residual monomers from the tackifier resin product stream to yield the tackifier resin having residual monomer concentrations of less than 200 ppm by weight of aromatic monomer based on the weight of the tackifier resin and 400 ppm of acrylate monomer based on the weight of the tackifier resin. The tackifier resin can also have a residual solvent concentration of less than about 500 ppm.

By careful choice of the type of aromatic monomer and acrylic monomer, it is possible to control and fine-tune the properties of the adhesive composition for specific applications. Possible variations in the tackifier resin polymerization process are aromatic monomer type, acrylate monomer type, functionality in the form of acid or hydroxyl groups in the acrylate monomer, different process conditions, which all result in different softening points and molecular weights of the tackifier resin.

The amount of aromatic monomer repeating units in the tackifier resin can range from about 0.1% to 99.9% based on the total amount of monomer repeating units in the tackifier resin, preferably from about 20% to about 70%, and most preferably from 25% to 65%. The amount of acrylate monomer repeating units in the tackifier resin can range from 0.1% to 99.9%, preferably from about 30% to about 80%, and most preferably, from 35% to 75% based on the total amount of monomer repeating units in the tackifier resin.

The tackifier resin can have a R&B softening point ranging from being a liquid at room temperature to about 180°C , preferably from about 50°C to about 150°C, and most preferably, from 75°C to 120°C. The acid number of the tackifier resin can range from about 0 to about 300 mg KOH/g resin, preferably from about 0 mg KOH/g resin to about 200 mg KOH/g resin, and most preferably from 5 to 150 mg KOH/g resin. The hydroxyl number can vary from about 0 to about 300, preferably from 0 to 200. The MMAP cloud point of the tackifier resin is typically less than 50°C, preferably the MMAP ranges from about -20°C to about 30°C, and most preferably from -10°C to 20°C.

The number average molecular weight (Mn) of the tackifier resin can range from about 1,500 to about 7,000 daltons, preferably from about 1,600 to about 4,500, and most preferably from 2,000 to 4,000. The weight average molecular weight (Mw) of the tackifier resin can range from about 2,000 to about 25,000 daltons, preferably from about 2,500 to about 12,000 and most preferably from 3,000 to 10,000. The z-average molecular weight (Mz) of the tackifier resin can range from about 3,000 to about 75,000 daltons, preferably from about 4,500 to about 30,000, and most preferably 5,000 to 20,000.

In one embodiment of this invention, the Gardner color of the tackifier resin generally is lower than 5, preferably is lower than 2, and most preferably is lower than 1. When the tackifier resin is used in medical applications, the Gardner color of the tackifier resin is generally lower than 2, and preferably is lower than 1. Light colored tackifier resins are often required for certain applications, especially in the medical adhesive field.

When the adhesive composition is used in medical applications, the residual monomer concentrations in the tackifier resin is typically less than about 200 ppm by weight aromatic monomer based on the weight of the tackifier resin and less than about 400 ppm by weight acrylic monomer based on the weight of the tackifier resin. Preferably,

the amount of residual aromatic monomer is less than about 100 ppm by weight, and the amount of residual acrylic monomer is less than about 200 ppm by weight based on the weight of the tackifier resin. Most preferably, the amount of residual aromatic monomer is less than 100 ppm by weight based on the weight of the tackifier resin, and the amount of residual acrylic monomer is less than 150 ppm based on the weight of the tackifier resin.

Also, especially for use in medical applications, the residual solvent in the tackifier resin is less than about 500 ppm based on the weight of the tackifier resin, preferably less than about 200 ppm, and most preferably, less than 50 ppm.

In another embodiment of this invention, the tackifier resin comprises monomer repeating units from at least one aromatic monomer and monomer repeating units from at least one acrylate monomer, wherein the monomer repeating units is at least one selected from styrene, acrylic acid, and 2-ethylhexyl acrylate. The amount of styrene repeating units can range from 0.1 to 99.9% based on the total amount of monomer repeating units in the tackifier resin. The amount of acrylic acid and 2-ethylhexyl acrylate can range from 0.1% to 99.9% based on the total amount of monomer repeating units in the tackifier resin. Preferably, the amount of styrene repeating units can range from about 20% to about 70%, and the combined amount of acrylic acid repeating units and 2-ethylhexyl acrylate repeating units can range from about 30% to about 80%. Most preferably, the amount of styrene repeating units can range from 25% to 65%, and the combined amount of acrylic acid repeating units and 2-ethylhexyl acrylate repeating units can range from 35% to 75%.

When polymerization occurs at a temperature lower than about 160°C, the amount of acrylic acid in the tackifier resin can be less than about 30% in order to help prevent gelling of the tackifier resin. However, at polymerization temperatures in the range of about 160°C to

about 250°C, the amount of acrylic acid in the tackifier resin can range from 0.1% to 99.9%.

Any acrylic polymer can be utilized that is compatible with the tackifier resin. Acrylic polymers include both homopolymers, copolymers, and terpolymers. The copolymers can be random, block or graft. The acrylic polymers can comprise repeating units from at least one acrylic monomer listed previously in this specification for tackifier resins.

Acrylic polymers can be produced by copolymerizing acrylic monomers with polar copolymerizable monomers. Examples of such polar copolymerizable monomers include, but are not limited to, cyanoalkyl acrylates, acrylamides, or substituted acrylamides, N-vinyl pyrrolidone, N-vinyl caprolactam, acrylonitrile, vinyl chloride, vinylidene chloride, diallyl phthalate, and the like. When polar copolymerizable monomers are utilized, the amount of the polar copolymerizable monomer ranges from 0 to about 50% by weight based on the weight of the acrylic polymer, preferably from 0 to 30% by weight.

Examples of acrylic polymers include, but are not limited to, acrylic copolymers, acrylated polyethers, acrylated polyester-based polyurethanes, methacrylated polyesters, and acrylated epoxies.

Examples of commercially available acrylic polymers include, but are not limited to Solucryl 300 and Solucryl 303 solvent-based acrylic polymers produced by UCB in Brussels, Belgium and Acronal® V215 water-based acrylic polymer produced by BASF.

In one embodiment of this invention, the acrylic polymer can be produced during the polymerization process of the tackifier resin. For example, acrylic monomers and oligomers can be added during a radical catalyzed polymerization to produce the tackifier resin. The acrylic monomers and oligomers can be added in the reactor zone of a radical catalyzed polymerization process as a single type of monomer or

oligomer or as a mixture and can be added in varying amounts and at varying addition times during the polymerization.

Any acrylic monomers known in the art can be utilized that produce acrylic polymers that are compatible with the tackifier resin. In one embodiment, the acrylic monomers utilized can be at least one from the acrylic monomers listed previously in this specification for tackifier resins. Preferably, the acrylic monomer is at least one selected from the group consisting of acrylic acid, 2-ethylhexyl acrylate, methyl methacrylate, methyl acrylate, acrylic acid, methacrylic acid, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, n-hexyl acrylate, n-hexyl methacrylate, ethylhexyl acrylate, ethylhexyl methacrylate, n-heptyl acrylate, n-heptyl methacrylate, 2-methylheptyl (meth)acrylate, octyl acrylate, octyl methacrylate, isooctyl (meth)acrylate, n-nonyl(meth)acrylate, iso-nonyl(meth)acrylate, decyl(meth)acrylate, isodecyl acrylate, isodecyl methacrylate, dodecyl(meth)acrylate, isobornyl(meth)acrylate, hydroxyethyl methacrylate, hydroxyethyl acrylate, allyl methacrylate, cyclohexyl methacrylate, cyclohexyl acrylate, n-hexyl acrylate, n-hexyl methacrylate, isobornyl acrylate, isobornyl methacrylate, and the like.

Any acrylic oligomers known in the art can be utilized that produced acrylic polymers that are compatible with the tackifier resin. In one embodiment, the acrylic oligomers can comprise repeating units from at least one acrylic monomer listed previously in this specification for tackifier resins. Preferably, the acrylic oligomers comprise at least one repeating unit selected from the group consisting of acrylic acid, 2-ethylhexyl acrylate, methyl methacrylate, methyl acrylate, acrylic acid, methacrylic acid, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, n-hexyl acrylate, n-hexyl methacrylate, ethylhexyl acrylate, ethylhexyl methacrylate, n-heptyl acrylate, n-heptyl methacrylate, 2-methylheptyl (meth)acrylate, octyl acrylate, octyl methacrylate, isooctyl

(meth)acrylate, n-nonyl(meth)acrylate, iso-nonyl(meth)acrylate, decyl(meth)acrylate, isodecyl acrylate, isodecyl methacrylate, dodecyl(meth)acrylate, isobornyl(meth)acrylate, hydroxyethyl methacrylate, hydroxyethyl acrylate, allyl methacrylate, cyclohexyl methacrylate, cyclohexyl acrylate, n-hexyl acrylate, n-hexyl methacrylate, isobornyl acrylate, isobornyl methacrylate, and the like.

The amounts of tackifier resin and acrylic polymer in the adhesive composition various depending on the properties of the adhesive composition desired. In one embodiment of this invention, the amount of tackifier resin ranges from about 0% to about 50% based on the weight of the adhesive composition, preferably 0% to 25%.

The composition of the adhesive composition may be adjusted by adding a surfactant or by diluting with water or an aqueous medium. In addition, various additives can be added to the adhesive composition to give the adhesive composition desired properties or for preventing degradation, or for any other purpose. Such additives include, but are not limited to, reinforcing agents, fire retardants, foaming agents, conventional tackifiers, plasticizers, oils, antioxidants, polymers, curable/reactive monomers, crosslinking agents, fillers, and pigments. Because of the number of possible compounding ingredients, the properties of the adhesive composition prepared according to this invention can be varied to satisfy most foreseeable requirements for tack, peel, strength, shear strength, and solvent media resistant, on whatever combination of substrate utilized.

In another embodiment of this invention, a process is provided to produce the adhesive composition. The process comprises contacting at least one tackifier resin and at least one acrylic polymer to produce the adhesive composition. The tackifier resin and acrylic polymer were previously described in this disclosure.

In another embodiment of this invention, a process is provided to produce an adhesive film. The process comprises: 1) providing at least one tackifier resin and at least one acrylic polymer to produce an

adhesive composition, and 2) contacting the adhesive composition with at least one substrate.

Variations of properties of a given adhesive composition can be obtained by varying the process conditions. For example, properties can be changed by the selection of substrate, by curing in air or an inert atmosphere, and by varying the intensity of the radiation.

The adhesive composition can be coated on a substrate by any method known in the art. For example, the coating can be accomplished by knife coating, roll coating, gravure coating, and curtain coating. Coating thickness varies depending on the application. Suitable coating thicknesses are in the range of about 0 g/m^2 to about 200 g/m^2, preferably, from 10 g/m^2 to 100 g/m^2.

The adhesive composition can be coated on a wide array of substrates. Suitable examples include, but are not limited to, polymer films such as polyethylene terephthalate (PET) and biaxially oriented polypropylene (BOPP); woven and non-woven fabrics; metals and metal foils, such as aluminum copper lead, gold and the like; paper; glass; ceramics; and composite materials comprising laminates of one or more of these materials.

Possible adhesive applications in which the adhesive composition may be used are numerous. Examples include, but are not limited to, skin-contact medical applications, surgical tapes, bandages, wound care, operation tapes and drapes, hygiene applications including feminine care products, box sealing tapes, masking applications, low fogging, automotive interior applications including foam gaskets, instrument displays, sound deadening, trim bonding, sealants, chaulks, general pressure sensitive adhesives, semi-pressure sensitive adhesives, building & hydroxyl ion adhesives, assembly adhesives, adhesive films and membranes, bottle labeling, water soluble adhesives, laminating adhesives, adhesives for flexible packaging, concrete curing compounds, mounting tapes, double sided tapes, electrical tapes, permanent and removable labels, filmic labels, pressure sensitive

adhesives for the graphic industry, labels for laser printers, insulation tapes, primer compounds, tie layers, road marking adhesives, inks, mounting tapes, labels for chemicals (sea water resistance), and labeling for pharmaceuticals and cosmetics, etc.

Another embodiment of this invention comprises a laminated structure of at least a first and a second substrate, the substrates being joined by a layer of the adhesive composition.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

EXAMPLES

This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

Test Methods

Acid number was determined by ASTM D974-02.

Compatibility of the tackifier resin was determined by mixing the tackifier resin with an adhesive component in the desired ratio at about 150°C to produce a tackifier resin/adhesive component mixture. The tackifier resin/adhesive component mixture was then poured on a heat bank. The heat bank consisted of a metal plate with a temperature gradient from 50°C to 200°C. On the left side, the heat bank was cool, on the right side, the heat bank was warm, and in between these two points, a temperature gradient was calibrated. A clear tackifier resin/adhesive component mixture indicated a compatible system. Hazy tackifier resin/adhesive component mixtures were incompatible. When the tackifier resin/adhesive component mixture stayed clear over the entire heat bank, the cloud point or compatibility temperature was < 50°C. When the tackifier resin/adhesive component mixture was cloudy

over the entire bank, the cloud point was >200°C. When the tackifier resin/adhesive component mixture was clear above a certain temperature and cloudy below a certain temperature, the temperature at which it was cloudy was the cloud point. Table 1 below summarizes the results of this test:

Table 1. Compatibility Test

Compatibility Temperature	Results
Compatibility temperature < 50°C	Completely compatible system
100°C > compatibility temperature > 50°C	Reasonable compatible system
150°C > compatibility temperature > 100°C	Partly compatible system
Compatibility temperature > 150°C	Incompatible system

Fogging was determined by ASTM D5393-97.

Gardner Color was measured using ASTM D1544-98.

Hydroxy number was measured using ASTM D464.

Loop tack was determined according to the European Association For Self Adhesive Tape Industry (AFERA) method 4015.

Lymph Node Assay was conducted accorded to the Organisation for Economic Co-operation and Development (OECD) draft new guideline 429: Skin Sensitization: Local Lymph Node Assay (LLNA) and according to the OECD Principles of Good Laboratory Practice (as revised in 1997), Paris, ENV/MC/CHEM(98)17.

Three deviations were made in the LLNA. First, the mice were marked for identification differently. Secondly, the protocol calls for CO_2/NO_2 anesthesia at autopsy, however, due to practical reasons, the mice were sacrificed by using euthasate. Thirdly, instead of analysis of (co)variance followed by Dunnett's multiple comparison tests, statistical analyses were performed by means of the Welch-ANOVA (for ^3H-thymidine incorporation in the auricular lymph nodes (ARN)) because

Levene's test for variances showed that variances occurred between the different groups.

Mettler Drop Softening Point (MDSP) was determined by a modified ASTM D6090-99 method. The method was modified in that the measurement was performed without a ball and using a cup with a 4.5 mm hole.

MMAP Cloud Point (methylcyclohexane and aniline) was determined by ASTM D-611.

Molecular weight distribution parameters, Mn, Mw, Mz and Mp (weight at the top of the peak) were determined by Gel Permeation Chromatography (GPC) on a Waters GPC 2690 system equipped with Waters Styragel HR2 (7.8X300mm) columns and a Waters 410 RI detector. Polystyrene standards were used for calibration.

Moisture Vapor Transport Rate (MVTR) was measured by ASTM 3-96.

Peel was determined by AFERA 4001. The following definitions are utilized to interpret the data from this test. Cohesive failure and slip-stick are defined in the Handbook of Pressure Sensitive Adhesive Technology, 2nd Edition, edited by Don Satas and Van Nostrand Reinhold. Cohesive failure is a failure mode leaving adhesive residue on the test panel. Slip-stick is a failure mode in which the peel force is not smooth but starts to fluctuate periodically from low to high force.

Residual monomer levels were determined by a gas chromatograph (GC) for the styrene, 2-ethylhexyl acrylate and xylene and with a high performance liquid chromatograph (HPLC) for acrylic acid.

The procedure followed when using the gas chromatograph is described below. About 5 grams of the sample and 50 mg anisole were placed in a flask, and 10 ml of acetronitrile were added. Then, the sample was dissolved in an ultrasound bath. A Trace 2000 GC Thermo Quest was utilized having a CP-WAX 57 CB (Chrompack) column having a length of 25 meters, an inner diameter of 0.25 mm, and a film

thickness of 0.2 um. The temperature was 50°C for 20 minutes with a change of temperature of 4°C per minute, and a maximum of 200°C was achieved for 5 minutes. The detector was a FID at 230°C. A split injector was utilized, and the carrier was hydrogen. The internal standard utilized was 250 mg anisole, and 50 mg of the substance to be analyzed (e.g. xylene, acrylate) were dissolved in 10 ml of acetonitrite.

The procedure followed when using HPLC is described below. This method was used for the analysis of styrene-acrylate tackifier resins to determine the residual acrylic acid content. The samples were dissolved in tetrahydrofuran or carbon disulfide and then filtered prior to analysis by reverse phase HPLC. An external standard of acrylic acid was used for calibration. The acrylic acid standard and the styrene-acrylate tackifier resin samples were analyzed on a Zorbax® RX-C18 column (5μm), using a two-part gradient. This two-part gradient consisted of part (1) 2% methanol in 0.05 M phosphoric acid for the elution of the acrylic acid and part (2) 100% tetrahydrofuran for purging the column during the actual sample analysis. The purge helped to minimize chromatographic problems for repetitive analysis. Peak detection was accomplished by monitoring the eluent with a UV detector. The primary UV wavelength monitored was 200 nm. The average response factor for acrylic acid was determined by several injections. The calibration curve of the acrylic acid standard was linear over the range of 0-1000 ppm with a lower limit of detection of about 5 ppm.

The following is a summary of the apparatus and chromatographic conditions utilized for the HPLC.

Apparatus:

(1) Liquid chromatograph, Hewlett-Packard Model 1090, or equivalent.

(2) Ultraviolet (UV) detector, Hewlett-Packard Model 1100, or equivalent.

(3) Data system or integrator capable of measuring peak area.

(4) Column, Zorbax® RX-C18 (5μm), 150 mm x 4.6 mm – available from Agilent located in Palo Alto, California.

(5) Guard column cartridge, Zorbax® RX-C18 (5µm), 12.5 mm x 4.6 mm – available from Agilent, or equivalent.

(6) Sample loop injection valve, 5 µL, Rheodyne Model 7125 – available from Supelco located in Bellefonte, PA.

(7) Vortex mixer- available from VWR Scientific located in West Chester, PA.

Chromatographic Conditions

Flow rate:	1.0 ml/min
Injection volume:	5 µL
Column oven temperature:	40°C
Detector:	UV
Wavelengths:	200 nm, 210 nm
Mobile Phase:	A = Methanol/5 mmol H_3PO_4 in water (2/98)
	B = Tetrahydrofuran (100)
Gradient:	Part 1) 0-10.10 min 100% A
	Part 2) 10.10–25.0 min 100% B (column purge)

Ring and Ball Softening Point was determined by ASTM E-28 with Walter Herzog MC-753 equipment.

Shear Adhesion Failure Test (SAFT) was determined when tape was placed on a metal plate weighing 1 kg. The tape on this plate was heated from 30°C with the heat increasing by 0.37°C/minute until the tape released from the plate.

Shear was determined by AFERA 4012.

UV absorbance was measured spectrophotometrically using a DR/4000 U Spectrophotometer supplied by Lange Group in Tiel, The Netherlands.

UV-C is the effective wavelength for curing a UV-curable adhesive composition. UV-C was measured with a calibrated UVICURE PLUS 8788, a self-contained electro-optic radiometer obtained from Electronic Instrumentation and Technology, Inc, Sterling, VA.

In some experiments, the total UV dose was measured. In others, the UV-C dose was measured. A relation between total UV dose and UV-C dose was determined for the equipment utilized in these examples. Testing was conducted by varying the UV dose for some

UV-curable adhesive compositions. The results are given in Figure 1 and Table 2

Table 2. Relation Between Total UV Dose and UV-C Dose for the Equipment Used

UV total	UV-C
139	18
195	26
311	42
470	64

Table 2 and Figure 1 can be used to compare the results when measuring total UV rather than UV-C.

Inventive Example 1: Synthesis of the Inventive Styrene-Acrylate Tackifier Resins

Styrene-acrylate tackifier resins were produced in a high-pressure reactor using a fed batch method. Xylene was used as a solvent and was pumped into the reactor and heated with stirring under nitrogen atmosphere to 150°C. The monomers (styrene, acrylic acid, and 2-ethyl hexyl acrylate) and 2% by weight initiator based on the weight of the monomers were mixed to produce a monomer-initiator feed stream. The monomer-initiator feed stream was added gradually to the hot solvent over two hours to produce a reaction mixture. During the addition of the monomer-initiator feed, the reaction temperature was maintained at 150°C.

After the monomer-initiator feed stream addition was completed, the reaction mixture was stirred for another 30 minutes at this temperature and at a pressure of about 3 bar. Subsequently, a small amount of initiator was post-added, and the process was maintained for another 30 minutes at 150°C to produce a tackifier resin product stream. The styrene-acrylate tackifier resin was isolated from the tackifier resin product stream by distilling off the solvent. The temperature was slowly increased to 170°C, and vacuum was applied up to 25 mbar. After about

30 minutes, 90% of the solvent was evaporated. After 2.5 hours, the temperature reached 170°C and vacuum reached 25 mbar, and about 99% of the solvent was removed. At this point, steam from the bottom of the reactor was injected resulting in about 0.5 liter of condensate per minute. Vacuum was slightly increased to 40 mbars as a result of the steam stripping. Steam stripping of the styrene-acrylic tackifier resin occurred for about 9 hours for Formulation I and 7 hours for Formulation II. The properties of the styrene-acrylate tackifier resin produced in this process are given in Table 3.

Table 3. Tackifier Resin Formulations and Properties

	Styrene-Acrylic Tackifier Formulation I	Data before steaming	Styrene-Acrylic Tackifier Formulation II	Data before steaming
Styrene (wt%)	61.2		24.9	
2-Ethylhexyl acrylate (wt%)	30.7		44.2	
Acrylic acid (wt%)	8.0		13.7	
DTBP[1] (wt% based on total monomer weight)	1.7		1.5	
Temperature (°C)	153		150	
R&B Softening Point (°C)	99.7	98.3	82.1	
Color, Gardner	0.1	0.1	0.5	
Acid Number, mg KOH/g	60.1	59.1	112	
Mz, Daltons	15060		13400	
Residuals :				
Styrene, ppm	29	34	<10	20
2-ethylhexyl acrylate, ppm	12	476	40	990
Acrylic Acid, ppm	110	218	134	
Solvent, ppm	24	1092	<10	640

[1] DTBP – di-tert butyl peroxide

Residual styrene levels were less than 29 ppm, and residual 2-ethylhexyl acrylate levels were less than 40 ppm. Residual acrylic acid was less than 134 ppm, and residual solvent was less than 24 ppm. These levels were significantly less than the residual monomer and solvent levels of the styrene-acrylate tackifier resins prior to steaming and to other commercial tackifiers as shown in Comparative Example 2. It should also be noted that the other properties of the styrene-acrylate

tackifier resins were hardly effected by removing a substantial portion of the residual monomers. Low levels of residual monomers are extremely important for the end application, since the residual monomers can cause skin sensitivity. Low residual monomer and solvent levels in the tackifier resins can also positively influence the fogging behavior of an UV-curable adhesive composition.

Comparative Example 2 – Residual Monomer Levels in Other Tackifiers

Tackifier resins were obtained from SC Johnson and evaluated to determine the amount of residual monomers. The data are shown in Table 4.

Table 4. Residual Monomer Levels in Comparative Tackifiers

Product Name	Joncryl 586	Joncryl 678	Joncryl SX815
R&B (°C)	121.8	165	115.3
Acid Number (mg KOH/g)	104	216	39
Gardner Color	0	0	0
MMAP (°C)	35	57	42
Mp (Daltons)	4161	8064	10285
Mn (Daltons)	2692	4621	5455
Mw (Daltons)	4921	9663	11275
Mz (Daltons)	8432	17755	19550
Residual Monomer			
Acrylic Acid (ppm)	585	2200	580
Styrene (ppm)	1200	200	60
Alpha-methyl styrene (ppm)	1000	800-900	600

As can be observed from the data in Table 4, the residual monomer concentration for the tackifier resins from SC Johnson are significantly above the inventive tackifier resins.

Example 3 – Variation of Monomer Repeating Unit Amounts in Styrene-Acrylate Tackifier Resins –Effect on Properties

The amount of the monomer repeating units in the styrene-acrylate tackifier resins were varied using the same process as described in Example 1, and the resulting properties of the styrene-acrylate tackifier resins were monitored. The results of these experiments are given in Table 5.

Table 5. Variation of Monomer Amounts in Styrene-Acrylate Tackifier Resins –Effect on Properties

Exp. No	styrene wt%	acrylic acid wt%	2-ethyl hexyl acrylate wt%	MDSP °C	Colour Gardner	Acid number mg KOH/g	MMAP °C	Mp Dalton	Mn Dalton	Mw Dalton	Mz Dalton
3.1	25	5	70	44.9	0.1	39	6	7123	3519	8358	15921
3.2	25	15	60	84.4	0.4	112	7	8462	3729	10139	21198
3.3	25	25	50	114.9	0.6	187	15	7725	3390	9382	18976
3.4	38.3	11.7	50	95.9	0.2	88	4	10100	4099	11752	23766
3.5	38.3	18.3	43.3	112.9	0.3	130	16	10916	3859	12729	27459
3.6	45	5	50	76.2	0.3	35	-2	11030	4434	12299	23896
3.7	45	25	30	141.2	0.7	172	32	12128	4087	18170	52090
3.8	51.7	11.7	36.7	116.4	0.2	87	15	12560	4712	14004	27649
3.9	55	20	25	142.7	0.5	141	31	12418	3953	14815	32181
3.10	65	5	30	108.5	0.2	37	11	12712	5138	13953	25842
3.11	65	15	20	141.4	0.2	110	27	12997	4405	14603	28915
3.12	65	25	10	171.2	1.5	149	44	13415	3831	20018	51019

When the amount of monomer was varied, styrene-acrylate tackifier resins were obtained with a MDSP from about 44.9°C to about 171.2°C, with acid numbers from 35 mg KOH/g to 187 mg KOH/g, a MMAP from 4°C to 32°C, and a Mz from 15921 to 51019 Dalton. More styrene instead of acrylic acid or 2-ethylhexylacrylate made the styrene-acrylate tackifier resin more aromatic resulting in a higher MDSP and a higher Mz. More acrylic acid increased the acid number and the functionality. It also increased the softening point and the MDSP.

Example 4: Skin Sensitivity of the Tackifier Resin

A local lymph node assay test (LLNA) in mice was performed to determine if the styrene-acrylate tackifier of Formulation II in Example 1 has skin sensitivity properties. Under the experimental conditions, there were no indications that the styrene-acrylate tackifier resin of Formulation II (see Example 1) had sensitizing properties.

The basic principle underlying the LLNA is that sensitizers induce a primary proliferation of lymphocytes in the lymph node draining the site of chemical application. This proliferation only occurs with allergens and is proportional to the dose applied. Therefore, the LLNA provides a simple means of obtaining an objective, quantitative measurement of sensitization.

Hexyl cinnamic aldehyde was used as a positive control. The hexyl cinnamic aldehyde was mixed in acetone/olive oil to a concentration of 25% by volume. A mixture of acetone and olive oil in a 4:1 ratio was used as a negative control. The tackifier resin was diluted in acetone/olive oil (4:1 v/v) to the desired concentration.

Twenty mice were divided into 5 groups of 4 animals each. Three groups of 4 mice each were treated with different doses of the tackifier resin (Group B: 10%; Group C: 25%; and Group D: 50%). Group E was treated with the positive control substance, and Group A was treated with the

negative control. On day 0, 1, and 2, the test substance was administered with 25 µl on each ear of the mouse.

The data collected showed that there were no indications that the tackifier resin had skin sensitizing properties.

Example 5 – Thermal Stability of Styrene-Acrylate Tackifier Resins

The thermal stability of the styrene-acrylate tackifier resins produced in Example 1 has been studied. The results are given in Table 6. The styrene-acrylate tackifier resins were heated as specified in Table 6.

Table 6. Thermal Stability of Styrene-Acrylate Tackifier Resins Produced In Example 1

		Styrene-Acrylic – Formula I	Styrene Acrylic – Formula II
R&B softening point (°C)	Initial	96.3	75.7
	3 hours at 160°C	99.1	82.9
	10 hours at 140°C	99.2	83.2
Acid number (mg KOH/g)	Initial	59	117
	3 hours at 160°C	59	119
	10 hours at 140°C	59	118
Gardner color	Initial	0.2	0.5
	3 hours at 160°C	0.2	0.7
	10 hours at 140°C	0.3	0.8
Molecular weight (Dalton)	initial Mn	3804	2970
	Mw	9320	7187
	Mz	17833	14688
	3 hours at 160°C Mn	3671	2928
	Mw	9300	7299
	Mz	17904	15348
	10 hours at 140°C Mn	3718	2979
	Mw	9300	7329
	Mz	17833	15321

The R&B softening point of the styrene-acrylate tackifier resin increased slightly upon heating. All other tackifier resin properties were not influenced by heating under the given circumstances. Therefore, it can be concluded that the styrene-acrylate tackifier resins do not only have good gelling stability but also a good heat stability, despite the fact that no antioxidants were used. The Reactol® AC 11 and AC 18 tackifier resins were also aged upon heating, and both products showed an unstable performance. Initially, Reactol® AC11 and AC18 tackifier resins were liquid, after 24 hours at 175°C, the products were gels. This can be due to trans-esterification reactions. However, at temperatures below about 175°C, Reactor® AC11 and AC 18 tackifier resins function well in UV-curable adhesive compositions and do not gel.

Example 6 – Moisture Vapor Transfer Rate and Fogging Tests

Two other advantages of the use of styrene-acrylate tackifier resins compared to conventional tackifiers, such as, Foral® 85-E rosin esters and Kristalex® F100 aromatic resin are that styrene-acrylate tackifiers can give better results in fogging tests and does not significantly reduce the MVTR of the adhesive composition. Films prepared with an 18:85 ratio of tackifier resin to UV-curable acrylic composition were evaluated. In case of MVTR, the films were transferred to a highly breathable kimwipe structure, and the values was corrected by assuming that the resistances (1/MVTR) were additive. Results are given in Table 7.

Table 7. MVTR Results and Fogging Results of Various Tackifier Resins in acResin® 258 Acrylic Copolymer (15:85) at a Coating Weight of 30g/m^2 and a UV-C Dose of 25 mJ/cm^2

	MVTR	Fogging
Curing dose	25	25
No resin	971	96.5
Foral 85-E	696	81
Kristalex F100	769	83
Styrene-acrylate Tackifier (Formulation I)	790	95.4
Styrene-acrylate Tackifier (Formulation II)	843	96.5
Reactol AC 11	1035	78.3
Reactol AC 18	698	88.5
Reactol OS 65	2478	90.7

Only insignificant decreases in the MVTR was observed for the styrene-acrylate tackifier resins compared to the acResin® acrylic copolymer alone. In case of Reactol® AC 11 acrylic resin and Reactol® OS 65 acrylic resin, even an increase was observed. In case of Reactol® OS 65 acrylic resin, the MVTR was even twice as high as for the other films so this indicates that the styrene-acrylate chemistry can be modified to effect MVTR in a controlled way.

The fogging data at 25 mL/cm^2 clearly showed that the results for styrene-acrylate tackifiers of Formulation I and II were much better than for conventional tackifiers such as Foral® 85-E rosin esters and Kristalex® aromatic resin. Foral® 85-E rosin esters and Kristalex® aromatic resins increased fogging while the use of the inventive styrene-acrylate tackifier resins produced in Example 1 hardly showed any differences in fogging compared to the acResin ® 258 acrylic copolymer alone. The Reactol® tackifier resins also tended to increase fogging, which again showed the effect of the residual monomer removal. In case of the styrene-acrylate tackifier resin of Formulation I, almost no increase was observed.

Example 7: Solvent-Based Adhesive Compositions

Styrene acrylate tackifiers can be used to tackify solvent-based acrylic polymers. These styrene-acrylic tackifier can be used in radiation-curable, heat curable, and non-cured adhesive compositions. In this example, two styrene-acrylate tackifier resins, Formulation I and II from Example 1, were compared with two conventional tackifiers in two solvent-based acrylic polymers, Solucryl 300 and Solucryl 303, produced by UCB in Brussels, Belgium. The tackifier resins were mixed in a 5:85 ratio with the solvent-based acrylic polymer and coated at a coating weight of 30 g/m^2. The coatings were dried and cross linked for 10 minutes at 110°C.

The results were also compared with hot-melt adhesives produced from the styrene-acrylate tackifier resins of Formulation I and II and acResin® acrylic copolymer produced by BASF. The following procedure was used in the hotmelt coating method. The acResin® acrylic copolymer and tackifier resin were mixed together in an aluminium tray on a hot-plate at 150°C to produce a UV-curable acrylic adhesive composition. After the mixing, the UV-curable acrylic adhesive composition was poured in a LC 200 pilot-plant-scale Lab-coater and coated onto 200 mm wide bi-axially oriented polypropylene (BOPP) film at about an average 7 m/minute coating speed at 140°C. The coating speed depended on the viscosity of the UV-curable adhesive composition, therefore, 7m/minute was the average.

Table 8. Application Results of Various Tackifier Resins with acResin® 258 Acrylic Copolymer (15:85) at a Coating Weight of 30g/m^2 and a UV-C Dose of 50mJ/cm^2 Compared with Application Results of Several Tackifier Resins with Solvent-Based Acrylic Polymers in a Ratio 15:85 at a Coating Weight of 30 g/m^2

	Peel Adhesion to Steel 1 min (N/25mm)	Peel Adhesion to PE 10 min (N/25mm)	Loop tack to steel (N/25mm)	SAFT, 1kg 0.5°C/min (°C)
	Hotmelt, UV	Hotmelt, UV	Hotmelt, UV	Hotmelt, UV
acResin® 258, no resin	6.94	1.01	12.91	141
Styrene-acrylic resin (Formulation I) + acResin® 258	9.09	2.20	16.54	100
Styrene-acrylic resin (Formulation II) + acResin® 258	11.75	2.59	16.38	78
Solucryl 300, no resin	6.79	1.37	10.12	155
Styrene-acrylic resin (Formulation I) + Solucryl 300	8.55	1.82	11.28	114
Styrene-acrylic resin (Formulation II) + Solucryl 300	8.73	1.57	13.22	104
Reactol AC 11 + Solucryl 300	6.88	1.25	11.31	151
Reactol AC 18 + Solucryl 300	7.83	1.32	12.78	150
Foral 85-E + Solucryl 300	8.07	3.05	10.81	144
Kristalex F100 * + Solucryl 300	6.27	1.55	6.42	155
Solucryl 303, no resin	6.61	2.04	9.02	149
Styrene-acrylic resin (Formulation I) + Solucryl 303	9.22	1.95	15.15	148
Styrene-acrylic resin (Formulation II) + Solucryl 303	8.00	1.39	8.62	79
Reactol AC 11 + Solucryl 303	7.02	1.46	8.21	148
Reactol AC 18 + Solucryl 303	8.14	1.99	14.94	147
Foral 85-E + Solucryl 303	8.46	3.29	8.93	139
Kristalex F100 * + Solucryl 303	6.13	1.71	5.46	148

* - Kristalex F100 was incompatible in the Solucryl polymers

The results showed that Foral®85-E rosin ester was a very good tackifier for the Solucryl 300 type. Good peel to PE values were found for Foral® 85-E rosin ester, while the SAFT was hardly effected (decreased from 155°C to 144°C). The use of the styrene-acrylate tackifier resin also improved peel to steel, to PE and especially loop tack was improved, more than with Foral® 85-E rosin ester.

Styrene-acrylate tackifier (Formulation I) was found to be a very good tackifier for the Solucryl 303® acrylic polymer. Peel to steel and loop tack both increased while SAFT was hardly effected. Foral 85-E® rosin ester also showed an increase in peel to steel and PE, but the loop tack decreased, and there was a larger increase in SAFT.

Generally, it can be concluded that depending on the solvent-based acrylate polymer and the desired properties of the adhesive, styrene-acrylate tackifier resins, such as those of Formulation I and II in Example 1, can be used as a tackifier resin for solvent-based acrylic polymers.

When comparing the hotmelt UV-curable adhesive composition to the solvent-based adhesive compositions, it can be concluded that the use of the tackifier resin in hot-melt UV-curable adhesive compositions generally results in lower SAFT values, while SAFT values for the solvent-based adhesive compositions are higher when using tackifier resins.

Example 8 - Water-Based Adhesive Compositions

Styrene-acrylate tackifiers also can be used in water-based acrylic polymer systems. The tackifier resins were dispersed in water to a 50% dispersion, using a surfactant for stabilization. The final dispersion was mixed in a 1:3 ratio with Acronal® V215, a water based acrylic polymer from BASF. The adhesives were coated and dried to 21 gsm.

Table 9. Application Results of Various Tackifier Resins in a Water-Based Adhesive Compositions Containing Acronal® V 215 as an Adhesive Component

	Peel Adhesion to cardboard at 23°C	Peel Adhesion to PE at 23°C	Loop tack to PE at 23°C	Shear adhesion on steel at 23°C
	5 min (N/25mm)	5 min (N/25mm)	5 min (N/25mm)	(minutes)
Acronal + no resin	7	7	8	8000
Styrene-Acrylic Tackifier (Formulation I) + Acronal	4	15	6	2310
Styrene-Acrylic Tackifier (Formulation II) + Acronal	4	14	5	990
Reactol AC 11 + Acronal	10	18	8	195
Tacolyn[1] 3179H + Acronal	16	25	12	150

[1]Tacolyn® 3179H is a rosin ester dispersion produced by Eastman Chemical company.

The results in the Table 9 showed that the styrene-acrylate tackifiers can be used in water-based adhesive compositions and show clearly the effect of the various tackifier resins. The effects appear to be softening point related. With Reactol AC 11 having the lowest softening point, shear was decreased the most, but peel adhesion clearly increased compared to the Acronal® V 215 polymer alone. Using the two other tackifiers, Reactol® AC11 and Tacolyn® 3179H, the shear adhesion was clearly decreased, and especially peel adhesion to PE was improved. No large differences were found for the adhesion properties between styrene-acrylate tackifier resins of Formulation I and II of Example 1. Only the shear for the styrene-acrylate tackifier resin of Formulation I was higher, which was most likely

due to the higher softening point. The properties of the Reactol® AC 11 acrylic resin came close to the conventional tackifier dispersion (Tacolyn® 3179H), normally used for these water-based polymers. Adhesion was slightly decreased, but cohesion (shear) was increased.

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THAT WHICH IS CLAIMED IS:

1. An adhesive composition comprising at least one tackifier resin and at least one acrylic polymer wherein said tackifier resin comprises monomer repeating units from at least one aromatic monomer and at least one acrylate monomer; and wherein said tackifier resin has a low residual monomer concentration.

2. An adhesive composition according to Claim 1 wherein said aromatic monomer is at least one selected from the group consisting of olefinic substituted aromatics.

3. An adhesive composition according to Claim 2 wherein said aromatic monomer is selected from the group consisting of styrene, alpha-methyl styrene, vinyl toluene, indene, methylindenes, divinylbenzene, dicyclopentadiene, and methyl-dicyclopentadiene.

4. An adhesive composition according to Claim 1 wherein said acrylate monomer has the general formula:

$$R_1\text{-}CH=CR_2\text{-}COOR_3$$

wherein R_1 is selected from the group consisting of hydrogen, aliphatic groups, and aromatic groups; wherein R_2 is selected from the group consisting of hydrogen, aliphatic groups, and aromatic groups; and wherein R_3 is selected from the group consisting of hydrogen, aliphatic groups, aromatic groups.

5. An adhesive composition according to Claim 4 wherein said aliphatic group has 1 to about 20 carbon atoms.

6. An adhesive composition according to Claim 5 wherein said aliphatic group has 1 to 12 carbon atoms.

7. An adhesive composition according to Claim 4 wherein said aromatic group has about 6 to about 20 carbon atoms.

8. An adhesive composition according to Claim 4 wherein both R_1 and R_2 of said acrylate monomer are hydrogen.

9. An adhesive composition according to Claim 1 wherein said acrylate monomer is selected from the group consisting of methyl acrylate, acrylic acid, methacrylic acid, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, n-hexyl acrylate, n-hexyl methacrylate, ethylhexyl acrylate, ethylhexyl methacrylate, n-heptyl acrylate, n-heptyl methacrylate, 2-methylheptyl (meth)acrylate, octyl acrylate, octyl methacrylate, isooctyl (meth)acrylate, n-nonyl(meth)acrylate, iso-nonyl(meth)acrylate, decyl(meth)acrylate, isodecyl acrylate, isodecyl methacrylate, dodecyl(meth)acrylate, isobornyl(meth)acrylate, lauryl methacrylate, lauryl acrylate, tridecyl acrylate, tridecyl methacrylate, stearyl acrylate, stearyl methacrylate, glycidyl methacrylate, alkyl crotonates, vinyl acetate, di-n-butyl maleate, di-octylmaleate, acetoacetoxyethyl methacrylate, acetoacetoxyethyl acrylate, acetoacetoxypropyl methacrylate, acetoacetoxypropyl acrylate, diacetone acrylamide, acrylamide, methacrylamide, hydroxyethyl methacrylate, hydroxyethyl acrylate, allyl methacrylate, tetrahydrofurfuryl methacrylate, tetrahydrofurfuryl acrylate, cyclohexyl methacrylate, cyclohexyl acrylate, n-hexyl acrylate, n-hexyl

methacrylate, 2-ethoxyethyl acrylate, 2-ethoxyethyl methacrylate, isodecyl methacrylate, isodecyl acrylate, 2-methoxy acrylate, 2-methoxy methacrylate, 2-(2-ethoxyethoxy) ethylacrylate , 2-phenoxyethyl acrylate, 2-phenoxyethyl methacrylate, isobornyl acrylate, isobornyl methacrylate, caprolactone acrylate, caprolactone methacrylate, polypropyleneglycol monoacrylate, polypropyleneglycol monomethacrylate, poyethyleneglycol(400) acrylate, polypropyleneglycol(400) methacrylate, benzyl acrylate, benzyl methacrylate, sodium 1-allyloxy-2-hydroylpropyl sulfonate, acrylonitrile, and mixtures thereof.

10. An adhesive composition according to Claim 1 wherein said acrylate monomer has up to about 20 carbon atoms.

11. An adhesive composition according to Claim 10 wherein said acrylate monomer is selected from the group consisting of acrylic acid, 2-ethylhexyl acrylate, methyl methacrylate, methyl acrylate, acrylic acid, methacrylic acid, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, n-hexyl acrylate, n-hexyl methacrylate, ethylhexyl acrylate, ethylhexyl methacrylate, n-heptyl acrylate, n-heptyl methacrylate, 2-methylheptyl (meth)acrylate, octyl acrylate, octyl methacrylate, isooctyl (meth)acrylate, n-nonyl(meth)acrylate, iso-nonyl(meth)acrylate, decyl(meth)acrylate, isodecyl acrylate, isodecyl methacrylate, dodecyl(meth)acrylate, isobornyl(meth)acrylate, hydroxyethyl methacrylate, hydroxyethyl acrylate, allyl methacrylate, cyclohexyl methacrylate, cyclohexyl acrylate, n-hexyl acrylate, n-hexyl methacrylate, isobornyl acrylate, isobornyl methacrylate, and mixtures thereof.

12. An adhesive composition according to Claim 11 wherein said acrylate monomers are acrylic acid and 2-ethylhexyl acrylate.

13. An adhesive composition according to Claim 1 wherein said acrylate monomer contains at least one functional group selected from the group consisting of hydroxy, cycloaliphatic, acid, epoxide, amide, acrylonitril and acrylate groups.

14. An adhesive composition according to Claim 1 wherein said tackifier resin is produced by a radical catalyzed polymerization process utilizing at least one initiator.

15. An adhesive composition according to claim 14 wherein said initiator is selected from the group consisting of diacyl peroxides, dialkylperoxidicarbonates, tert-alkyl peroxyesters, di-tert-alkyl peroxides, tert-alkyl hydroperoxides, ketone peroxides, and mixtures thereof.

16. An adhesive composition according to Claim 1 wherein said tackifier resin is produced by a process comprising contacting a tackifier resin product stream with at least one carrier at a temperature sufficient to remove a portion of at least one residual monomer to produce said tackifier resin.

17. An adhesive composition according to Claim 1 wherein said tackifier resin does not significantly decrease the moisture vapor transport rate of said adhesive composition containing said tackifier resin.

18. An adhesive composition according to Claim 17 wherein said tackifier resin does not decrease said moisture vapor transport rate of said adhesive composition by more than 25% over said adhesive composition without said tackifier resin.

19. An adhesive composition according to Claim 17 wherein said moisture vapor transport rate of said adhesive composition is the same or increased over said adhesive composition without said tackifier resin.

20. An adhesive composition according to Claim 17 wherein said moisture vapor transport rate of said adhesive composition ranges from about 200 to about 3000.

21. An adhesive composition according to Claim 20 wherein said moisture vapor transport rate of said adhesive composition ranges from about 500 to 1500.

22. An adhesive composition according to Claim 1 wherein said residual monomer concentration of said tackifier resin is less than about 600 ppm by weight based on the weight of said tackifier resin.

23. An adhesive composition according to Claim 22 wherein said residual monomer concentration of said tackifier resin is less than about 300 ppm by weight based on the weight of said tackifier resin.

24. An adhesive composition according to Claim 23 wherein said residual monomer concentration of said tackifier resin is less than about 200 ppm aromatic monomer based on the weight of said tackifier resin and less than about 400 ppm acrylic monomer.

25. An adhesive composition according to Claim 24 wherein said residual monomer concentration of said tackifier resin is less than about 100 ppm by weight aromatic monomer and less than about 150 ppm by weight acrylic monomer.

26. An adhesive composition according to Claim 1 wherein said tackifier resin has a residual solvent concentration less than about 500 ppm by weight based on the weight of said tackifier resin.

27. An adhesive composition according to Claim 1 wherein the amount of aromatic monomer repeating units in said tackifier resin ranges from about 20% to about 70% based on the total amount of monomer repeating units in said tackifier resin.

28. An adhesive composition according to Claim 1 wherein the amount of acrylate monomer repeating units in said tackifier resin ranges from about 30% to about 80% based on the total amount of monomer repeating units in said tackifier resin.

29. An adhesive composition according to Claim 1 wherein said tackifier resin has a R&B softening point ranging from being a liquid at room temperature to about 180°C.

30. An adhesive composition according to Claim 1 wherein the acid number of said tackifier resin ranges from about 0 to about 300 mg KOH/g resin.

31. An adhesive composition according to Claim 1 wherein the hydroxyl number of said tackifier resin ranges from about 0 to about 300.

32. An adhesive composition according to Claim 1 wherein the MMAP cloud point of said tackifier resin is less than 50°C.

33. An adhesive composition according to Claim 1 wherein the number average molecular weight (Mn) of said tackifier resin ranges from about 1,500 to about 7,000 daltons.

34. An adhesive composition according to Claim 33 wherein said number average molecular weight (Mn) of said tackifier resin ranges from 2,000 to 4,000 daltons.

35. An adhesive composition according to Claim 1 wherein the weight average molecular weight (Mw) of said tackifier resin ranges from about 2,000 to about 25,000 daltons.

36. An adhesive composition according to Claim 35 wherein said weight average molecular weight (Mw) of said tackifier resin ranges from 3,000 to 10,000.

37. An adhesive composition according to Claim 1 wherein the z-average molecular weight (Mz) of said tackifier resin ranges from about 3,000 to about 75,000 daltons.

38. An adhesive composition according to Claim 37 wherein said z-average molecular weight (Mz) of said tackifier resin ranges from 5,000 to 20,000.

39. An adhesive composition according to Claim 1 wherein the Gardner color of said tackifier resin is less than 5.

40. An adhesive composition according to Claim 1 wherein said tackifier resin comprises monomer repeating units from styrene, acrylic acid, and 2-ethylhexyl acrylate.

41. An adhesive composition according to Claim 40 wherein the amount of styrene repeating units ranges from 0.1% to 99.9% based on the total amount of monomer repeating units in said tackifier resin.

42. An adhesive composition according to Claim 40 wherein the amount of acrylic acid and 2-ethylhexyl acrylate ranges from 0.1% to 99.9% based on the total amount of monomer repeating units in said tackifier resin.

43. An adhesive composition according to claim 41 wherein the amount of styrene repeating units ranges from about 20% to about 70% based on the total amount of monomer repeating units in said tackifier resin, and the combined amount of acrylic acid repeating units and 2-ethylhexyl acrylate repeating units ranges from about 30% to about 80%.

44. An adhesive composition according to Claim 1 wherein said tackifier resin does not significantly decrease the moisture vapor transport rate of said adhesive composition comprising said tackifier resin.

45. An adhesive composition according to Claim 1 wherein said tackifier resin does not significantly increase fogging of an adhesive composition comprising said tackifier resin.

46. An adhesive composition according to Claim 1 wherein said tackifier resin does not significantly exhibit skin sensitivity properties.

47. An adhesive composition according to Claim 1 wherein said tackifier resin does not significantly decrease the moisture vapor transport rate of said adhesive composition comprising said tackifier resin; and wherein said tackifier resin does not significantly increase fogging of said adhesive composition.

48. An adhesive composition according to Claim 47 wherein said tackifier resin does not significantly exhibit skin sensitivity properties.

49. An adhesive composition according to Claim 1 wherein said acrylic polymer are selected from homopolymers, copolymers, and terpolymers.

50. An adhesive composition according to Claim 49 wherein said acrylic polymer comprises at least one acrylate repeating unit selected from the group consisting of methyl acrylate, acrylic acid, methacrylic acid, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, n-hexyl acrylate, n-hexyl methacrylate, ethylhexyl acrylate, ethylhexyl methacrylate, n-heptyl acrylate, n-heptyl methacrylate, 2-methylheptyl (meth)acrylate, octyl acrylate, octyl methacrylate, isooctyl (meth)acrylate, n-nonyl(meth)acrylate, iso-nonyl(meth)acrylate, decyl(meth)acrylate, isodecyl acrylate, isodecyl methacrylate, dodecyl(meth)acrylate, isobornyl(meth)acrylate, lauryl methacrylate, lauryl acrylate, tridecyl acrylate, tridecyl methacrylate, stearyl acrylate, stearyl methacrylate, glycidyl methacrylate, alkyl crotonates, vinyl acetate, di-n-butyl maleate, di-octylmaleate, acetoacetoxyethyl methacrylate, acetoacetoxyethyl acrylate, acetoacetoxypropyl methacrylate, acetoacetoxypropyl acrylate, diacetone acrylamide, acrylamide, methacrylamide, hydroxyethyl methacrylate, hydroxyethyl acrylate, allyl methacrylate, tetrahydrofurfuryl methacrylate, tetrahydrofurfuryl acrylate, cyclohexyl methacrylate, cyclohexyl acrylate, n-hexyl acrylate, n-hexyl

methacrylate, 2-ethoxyethyl acrylate, 2-ethoxyethyl methacrylate, isodecyl methacrylate, isodecyl acrylate, 2-methoxy acrylate, 2-methoxy methacrylate, 2-(2-ethoxyethoxy) ethylacrylate , 2-phenoxyethyl acrylate, 2-phenoxyethyl methacrylate, isobornyl acrylate, isobornyl methacrylate, caprolactone acrylate, caprolactone methacrylate, polypropyleneglycol monoacrylate, polypropyleneglycol monomethacrylate, poyethyleneglycol(400) acrylate, polypropyleneglycol(400) methacrylate, benzyl acrylate, benzyl methacrylate, sodium 1-allyloxy-2-hydroylpropyl sulfonate, acrylonitrile, and mixtures thereof.

51. An adhesive composition according to Claim 49 wherein said acrylic polymer comprises monomer repeating units from polar copolymerizable monomers.

52. An adhesive composition according to Claim 51 wherein said polar copolymerizable monomers are selected from the group consisting of cyanoalkyl acrylates, acrylamides, or substituted acrylamides, N-vinyl pyrrolidone, N-vinyl caprolactam, acrylonitrile, vinyl chloride, vinylidene chloride, diallyl phthalate, and mixtures thereof.

53. An adhesive composition according to Claim 1 wherein said acrylic polymer is at least one selected from the group consisting of acrylic copolymers, acrylated polyethers, acrylated polyester-based polyurethanes, methacrylated polyesters, and acrylated epoxies.

54. An adhesive composition according to Claim 1 wherein said acrylic polymer is produced during the polymerization process of the tackifier resin by the addition of at least one acrylic monomer or at least one acrylic

oligomer to a reactor zone in the presence of an initiator to produce said tackifier resin and said acrylic monomer.

55. An adhesive composition according to Claim 54 wherein said acrylic monomer is at least one selected from the group consisting of methyl acrylate, acrylic acid, methacrylic acid, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, n-hexyl acrylate, n-hexyl methacrylate, ethylhexyl acrylate, ethylhexyl methacrylate, n-heptyl acrylate, n-heptyl methacrylate, 2-methylheptyl (meth)acrylate, octyl acrylate, octyl methacrylate, isooctyl (meth)acrylate, n-nonyl(meth)acrylate, iso-nonyl(meth)acrylate, decyl(meth)acrylate, isodecyl acrylate, isodecyl methacrylate, dodecyl(meth)acrylate, isobornyl(meth)acrylate, lauryl methacrylate, lauryl acrylate, tridecyl acrylate, tridecyl methacrylate, stearyl acrylate, stearyl methacrylate, glycidyl methacrylate, alkyl crotonates, vinyl acetate, di-n-butyl maleate, di-octylmaleate, acetoacetoxyethyl methacrylate, acetoacetoxyethyl acrylate, acetoacetoxypropyl methacrylate, acetoacetoxypropyl acrylate, diacetone acrylamide, acrylamide, methacrylamide, hydroxyethyl methacrylate, hydroxyethyl acrylate, allyl methacrylate, tetrahydrofurfuryl methacrylate, tetrahydrofurfuryl acrylate, cyclohexyl methacrylate, cyclohexyl acrylate, n-hexyl acrylate, n-hexyl methacrylate, 2-ethoxyethyl acrylate, 2-ethoxyethyl methacrylate, isodecyl methacrylate, isodecyl acrylate, 2-methoxy acrylate, 2-methoxy methacrylate, 2-(2-ethoxyethoxy) ethylacrylate , 2-phenoxyethyl acrylate, 2-phenoxyethyl methacrylate, isobornyl acrylate, isobornyl methacrylate, caprolactone acrylate, caprolactone methacrylate, polypropyleneglycol monoacrylate, polypropyleneglycol monomethacrylate, poyethyleneglycol(400) acrylate, polypropyleneglycol(400) methacrylate, benzyl acrylate, benzyl methacrylate, sodium 1-allyloxy-2-hydroylpropyl sulfonate, acrylonitrile, and mixtures thereof.

56. An adhesive composition according to Claim 54 wherein said acrylic oligomers comprise repeating units from at least one acrylic monomer selected from the group consisting of methyl acrylate, acrylic acid, methacrylic acid, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, n-hexyl acrylate, n-hexyl methacrylate, ethylhexyl acrylate, ethylhexyl methacrylate, n-heptyl acrylate, n-heptyl methacrylate, 2-methylheptyl (meth)acrylate, octyl acrylate, octyl methacrylate, isooctyl (meth)acrylate, n-nonyl(meth)acrylate, iso-nonyl(meth)acrylate, decyl(meth)acrylate, isodecyl acrylate, isodecyl methacrylate, dodecyl(meth)acrylate, isobornyl(meth)acrylate, lauryl methacrylate, lauryl acrylate, tridecyl acrylate, tridecyl methacrylate, stearyl acrylate, stearyl methacrylate, glycidyl methacrylate, alkyl crotonates, vinyl acetate, di-n-butyl maleate, di-octylmaleate, acetoacetoxyethyl methacrylate, acetoacetoxyethyl acrylate, acetoacetoxypropyl methacrylate, acetoacetoxypropyl acrylate, diacetone acrylamide, acrylamide, methacrylamide, hydroxyethyl methacrylate, hydroxyethyl acrylate, allyl methacrylate, tetrahydrofurfuryl methacrylate, tetrahydrofurfuryl acrylate, cyclohexyl methacrylate, cyclohexyl acrylate, n-hexyl acrylate, n-hexyl methacrylate, 2-ethoxyethyl acrylate, 2-ethoxyethyl methacrylate, isodecyl methacrylate, isodecyl acrylate, 2-methoxy acrylate, 2-methoxy methacrylate, 2-(2-ethoxyethoxy) ethylacrylate , 2-phenoxyethyl acrylate, 2-phenoxyethyl methacrylate, isobornyl acrylate, isobornyl methacrylate, caprolactone acrylate, caprolactone methacrylate, polypropyleneglycol monoacrylate, polypropyleneglycol monomethacrylate, poyethyleneglycol(400) acrylate, polypropyleneglycol(400) methacrylate, benzyl acrylate, benzyl methacrylate, sodium 1-allyloxy-2-hydroylpropyl sulfonate, acrylonitrile, and mixtures thereof.

57. An adhesive composition according to Claim 1 wherein the amount of said tackifier resin ranges from about 0.1% by weight to about 50% by weight based on the weight of the adhesive composition.

58. An adhesive composition according to Claim 1 wherein the amount of said tackifier resin ranges from 0.1% by weight to 25% by weight based on the weight of the adhesive composition.

59. A process of making an adhesive composition, said process comprising providing at least one tackifier resin and at least one acrylic polymer; wherein said tackifier resin comprises monomer repeating units from at least one aromatic monomer and at least one acrylate monomer; and wherein said tackifier resin has a low residual monomer concentration.

60. A process according to Claim 59 further comprising contacting said adhesive composition with at least one substrate to produce an article.

61. A process according to Claim 60 wherein said substrate is selected from the group consisting of polyethylene terephthalate, biaxially oriented polypropylene, woven fabrics, non-woven fabrics, metals, metal foils, paper, glass, ceramics, and composite materials comprising laminates of one or more of these materials.

62. An adhesive composition produced by the process of Claim 59.

63. An adhesive composition consisting essentially of at least one tackifier resin and at least one acrylic polymer; wherein said tackifier resin consists essentially of monomer repeating units from at least one aromatic

monomer and at least one acrylic monomer; and wherein said tackifier resin has a low residual monomer concentration.

64. An adhesive composition according to Claim 63 wherein said aromatic monomer is styrene.

65. An adhesive composition according to Claim 64 wherein said acrylic monomers are 2-ethyl hexyl acrylate and acrylic acid.

66. An article comprising said adhesive composition of Claim 1.

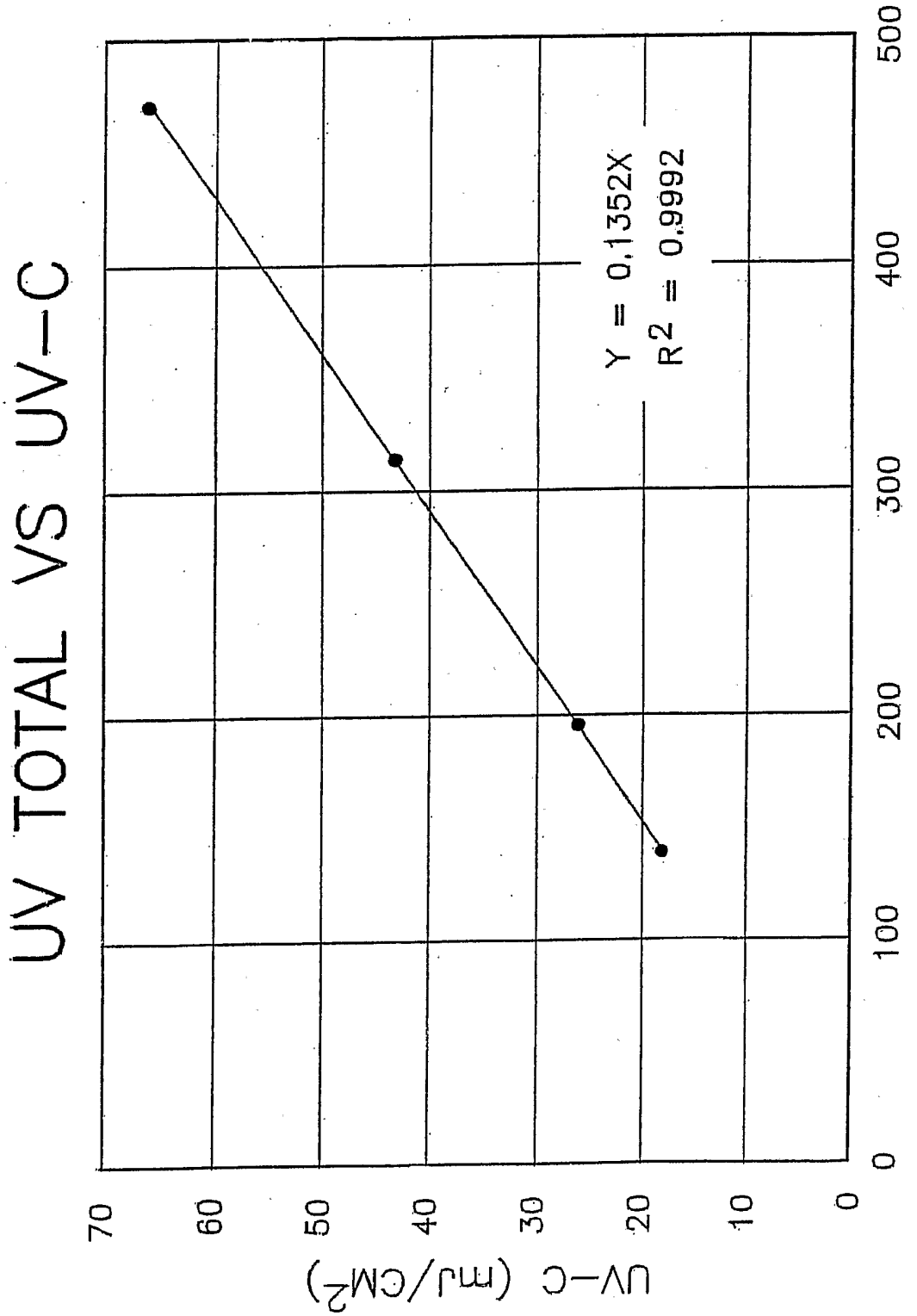

UV TOTAL VS UV-C
Y = 0,1352X
R2 = 0,9992
UV-C (mJ/CM2)
UV TOTAL (mJ/CM2)
0
10
20
30
40
50
60
70
0
100
200
300
400
500

Figure 1

INTERNATIONAL SEARCH REPORT

Interna[redacted]al Application No
PCT/US2005/004467

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09J133/00 C09J125/14 B01D3/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F C09J

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
PAJ, WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	DATABASE WPI Section Ch, Week 197907 Derwent Publications Ltd., London, GB; Class A13, AN 1979-13138B XP002330429 & JP 54 003136 A (ARAKAWA KAGAKU KOGYO KK) , 11 January 1979 (1979-01-11) abstract	1-66

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 June 2005	30/06/2005

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Simmerl, R

Form PCT/ISA/210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US2005/004467

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