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REMOVABLE, LOW MELT VISCOSITY ACRYLIC PRESSURE SENSITIVE ADHESIVES

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(57) Claim

1. An acrylic pressure-sensitive adhesive comprising:
   a) from 10 to 50% by weight of at least one higher alkyl acrylate having an alkyl group from 12 to 26 carbon atoms;
   b) from 50 to 90% by weight of at least one lower alkyl acrylate having an alkyl group from 4 to 12 atoms wherein said alkyl groups of said lower and higher alkyl acrylates do not simultaneously have 12 carbon atoms; and
   c) sufficient crosslinker to substantially prevent adhesive transfer, wherein said adhesive composition has high peel strength while maintaining good removability.

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(54) Title: REMOVABLE, LOW MELT VISCOSITY ACRYLIC PRESSURE SENSITIVE ADHESIVES

(57) Abstract

The present invention relates to a permanently removable, low melt viscosity acrylic pressure-sensitive adhesive comprising a lower alkylacrylate, a higher alkylacrylate and a crosslinker.

REMOVABLE, LOW MELT VISCOSITY
ACRYLIC PRESSURE SENSITIVE ADHESIVES

Field of Invention

The present invention relates to a permanently removable, low melt viscosity acrylic pressure-sensitive adhesive. In particular, the present invention relates to an adhesive comprising a lower alkyl acrylate, a higher alkyl acrylate and a crosslinker.

Background of the Invention

Removable pressure sensitive adhesives (PSA) adhered to a backing, which predictably adhere, yet remain repeatedly peelable from a variety of substrates over a long period of time without damaging or marring the substrate, have many commercial uses. For example, masking tapes, removable labels or office notes, protective films and medical tapes all must quickly adhere to metal, paper, plastics and skin, respectively, but must also peel smoothly away from these varied substrates without leaving behind any adhesive residue on or damaging the surface of a particular substrate.

Ideally, depending on the substrate, the removable adhesive must provide sufficient tack (or quick stick) to quickly fix the adhesive to the desired substrate, adequate peel strength to prevent damage of the surface when the adhesive is removed, and have the appropriate cohesive strength to control the transfer of adhesive to the substrate. Cohesive strength must also be controlled so to limit the cold flow of the adhesive on a surface, a process which leads to an undesirable building of peel strength over time. Balancing these pressure sensitive adhesive properties, particularly in a removable adhesive, poses difficulties to the formulator.

U.S. Patent No. 3,691,140 (Silver) discloses the use of solid, inherently tacky, pressure-sensitive adhesive microspheres which, when adhered to a first substrate, may when contacted to a second substrate be easily removed from the second substrate without delaminating the first substrate or the second substrate. While exhibiting a high degree of removability, microsphere adhesives tend to transfer to contact surfaces such the second substrate.

U.S. Patent No. 5,045,569 (Delgado) discloses hollow, inherently tacky pressure-sensitive adhesive acrylate microspheres which, due to their unique morphology, provide enhanced peel and shear strength and less adhesive transfer to substrates than "repositionable" adhesives based on solid acrylate-based microspheres. Although hollow microsphere adhesives show less adhesive transfer to substrates, they still have less than an optimum degree of adhesive transfer.

In contrast, U.S. Patent No. 4,599,265 (Esmay) discloses an adhesive having a high degree of cohesive strength. The adhesive disclosed is an acrylate, has low tack and maintains peelability from a variety of ordinary substrates. Esmay teaches that through the crosslinking of the tape's adhesive layer and the use of low levels of polar monomer (up to mole 3% of a strongly polar monomer, such as acrylic acid) along with alkyl acrylates having side chains 8-12 carbons in length in the copolymeric adhesive, the required balance of low tack and high cohesive strength can be imparted to the removable adhesive. One drawback associated with the Esmay adhesive is excessive adhesive bleeding of monomers through a substrate such as paper prior to curing. Such bleeding is undesirable because of the damage done to the substrate.

U.S. Patent No. 4,737,559 (Kellen et al.) describes another method of crosslinking an adhesive. Kellen et al. teaches the use of a PSA formulation in which the viscous flow, and resultant adhesion buildup, is controlled through the addition of small amount of a free radically polymerizable photocrosslinker (a monoethylenically unsaturated aromatic ketone, most preferably 4-acryloyl-oxy-benzophenone) to at least one alkyl acrylate or methacrylate. The Kellen et al. adhesive is formulated for adhesion to skin.

U.S. Patent No. 3,635,754 (Beede) discloses the use of a heat-activated, multi-phase pressure-sensitive adhesive copolymer whose melting point is greater than 35°C and whose glass transition temperature (T_g) is below 5°C. At room temperature, the adhesive is non-tacky. At that temperature, a crystalline or ordered phase and an amorphous or disordered phase co-exist. At skin temperature (approximately 35°C), the copolymer becomes amorphous and the adhesive is tacky. This phenomenon may be reversed by cooling the adhesive for removal from a substrate, with the crystallization of the side chains providing sufficient cohesive strength to prevent any transfer of adhesive to the substrate.

European Patent Application Serial Number 90/13420 (Stewart et al.) discloses a temperature activated, pressure-sensitive adhesive which is rapidly converted from non-tacky to tacky over a predetermined temperature range. Similar to the multi-phase adhesive of Beede, this temperature dependent adhesive relies on the careful selection of side chain crystallizable monomers, particularly those monomers which have linear aliphatic side chains of at least 10 carbon atoms, including C_{12}-C_{22} alkyl acrylates or methacrylates. Stewart et al. specify that these compositions, when a mixture of copolymerizable monomers are used, must contain at least 50% by weight monomers with crystallizable side chains. However, at room temperature, these adhesives are substantially non-tacky.

In using PSAs, it is also desirable to combine these removable qualities with the procedural, economical and environmental advantages of a hot melt processible adhesive. To date, most attempts to prepare acrylic hot melt PSAs have been limited because such materials have poor cohesive strength at room temperature or are too viscous even for use at high temperatures found in current melt processing equipment and practices. Maintaining sufficient cohesive strength, as noted above, is one critical factor in the formulation of permanently removable PSAs.

Typically, the cohesive strength of acrylic polymeric PSAs, which are not microspheres, may be improved in a variety of ways, but each way has its disadvantages, especially when the formulator wishes to maintain a low melt viscosity for the PSA. The molecular weight of the acrylic polymer may be raised to improve cohesive strength, but an unavoidable and unacceptable rise in melt viscosity also results. Polar monomer content, such as acrylic acid, may also be increased to improve cohesive strength, a property which is useful in many adhesive applications. However, increased polar monomer content also causes greater adhesion buildup, as described by U.S. Patent No. 3,008,850 (Ulrich). Finally, cohesive strength may be enhanced through the covalent crosslinking of the adhesive. Covalent crosslinking, though providing the needed increase in cohesive strength, eliminates the potential for melt processing.

Physical crosslinking is described in U.S. Patent No. 4,554,324 (Husman et al.). Husman et al. disclose a hot melt processible acrylate PSA which gains the needed balance of cohesive strength, high tack, and low melt viscosity through the chemical modification of the soft acrylate backbone by grafting reinforcing high T_g polymeric moieties to the acrylate chain. These high T_g moieties provide glassy domains which enhance the cohesive strength of the adhesive at lower temperatures without dramatically increasing the melt viscosity of the composition. The peel adhesion strengths of the exemplified compounds, however, tend to exceed those values which are required for removability from most substrates.

Thus, there currently exists a need for a permanently removable acrylic pressure sensitive adhesive which displays a superior balance of tack, peel strength and cohesive strength which may be formulated for removal from a variety of substrates without damaging or depositing adhesive residue on the substate and without building excessively in adhesion over time.

Summary of the Invention

Unless otherwise noted, the term "acrylate" is intended to refer to methacrylates in addition to acrylates.

The permanently removable, acrylic pressure-sensitive adhesive of the invention comprises:

a) from about 10 to about 50 % by weight of at least one higher alkyl acrylate having an alkyl group from 12 to 26 carbon atoms;

b) from about 50 to about 90 % by weight of at least one lower alkyl acrylate having an alkyl group from 4 to 12 atoms wherein said upper and lower alkyl acrylates cannot simultaneously have alkyl chains of 12 carbon atoms; and

c) sufficient crosslinker to impart enough cohesive strength to the adhesive in order to prevent substantial adhesive transfer.

In one embodiment of the present invention, the lower alkyl acrylate has an alkyl group which is linear and has from 4 to 8 carbon atoms.

In another embodiment of the present invention, the lower alkyl acrylate has an alkyl group which is branched and has from 4 to 12 carbon atoms.

In a preferred embodiment of the present invention, the high alkyl acrylate has a carbon group which is branched and has from 13 to 26 carbon atoms.

This invention also provides for pressure-sensitive adhesive sheets coated with the permanently removable, acrylic adhesive composition.

Further, the present invention discloses methods of making adhesive coating sheets with the acrylic adhesive composition of the present invention.

Detailed Description of the Invention

The permanently removable, low melt viscosity acrylic pressure-sensitive adhesive of the invention comprises three components: (1) at least one lower alkyl acrylate having an alkyl group which comprises from about 4 to 12 carbon atoms, (2) at least one higher alkyl acrylate having an alkyl group which comprises from about 12 to 26 carbon atoms and (3) sufficient crosslinker to impart cohesive strength to the adhesive.

The linear or branched lower alkyl acrylate or methacrylate esters useful in preparing the removable, low melt viscosity pressure sensitive adhesives of this invention are linear or branched monofunctional unsaturated acrylate or methacrylate esters of non-tertiary alkyl alcohols, the alkyl groups of which have from about 4 to about 12 carbon atoms. These lower linear and branched acrylates, as is well known in the pressure sensitive adhesive art, provide the properties of low glass transition temperature and viscoelastic characteristics that result in materials which are tacky in nature. Examples of the shorter chain, lower alkyl acrylates and methacrylates used in the invention include, but are not limited to, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, isooctyl acrylate, n-octyl acrylate, n-octyl methacrylate, 2-methylbutyl acrylate, isononyl acrylate, isoamyl acrylate, isodecyl acrylate, isodecyl methacrylate, 4-methyl-2-pentyl acrylate, and mixtures thereof. Preferred lower acrylate and methacrylate esters of the invention include isooctyl acrylate, n-butyl acrylate, and 2-ethylhexyl acrylate.

The higher alkyl acrylate or methacrylate monomers useful in preparing the pressure sensitive adhesives of this invention are monofunctional unsaturated acrylate or methacrylate esters of non-tertiary alkyl alcohols, the alkyl groups of which have from about 12 to about 26 carbon atoms. Preferably, the alkyl groups have from about 13 to about 26 carbon atoms. The long side chains of these acrylate and methacrylate esters increase the entanglement molecular weight of the polymer and facilitate the melt processing of the polymer. At the concentrations used in this invention, no crystallization of the side chains occurs and the resulting polymers are amorphous. If substantial crystallization were present, the modulus of the material would increase and this increased modulus would cause a loss of pressure sensitive adhesive tack. The long alkyl chains of these acrylate and methacrylate esters also increase the non-polar character of the adhesive, thus reducing the specific inter-molecular interactions, such as hydrogen bonding, acid-base interaction, and the like, which lead to excessive adhesion build-up between the adhesives and substrates susceptible to such interactions.

Examples of the long side chain acrylate and methacrylate esters used in the present invention include, but are not limited to, lauryl acrylate, lauryl methacrylate, isotridecyl acrylate, n-tetradecyl acrylate, n-tetradecyl methacrylate, n-hexadecyl acrylate, n-hexadecyl methacrylate, n-octadecyl acrylate, n-octadecyl methacrylate, eicosanyl acrylate, hexacosanyl acrylate and mixtures thereof. Preferred long side chain alkyl acrylates and methacrylates include lauryl acrylate, lauryl methacrylate, octadecyl acrylate, octadecyl methacrylate, hexacosanyl acrylate, eicosanyl acrylate and isotridecyl acrylate.

Crosslinkers which enhance the cohesive strength of the removable pressure sensitive adhesive composition, include, but are not limited to: multifunctional acrylates and methacrylates; triazine-, benzophenone- and acetophenone- derived photocrosslinking compounds; and silanes.

Preferred crosslinkers are selected according to the processing method used in preparing the adhesives of this invention. For compositions which require no further melt processing following the initial polymerization, multifunctional acrylates and methacrylates, such as 1,4butanediol diacrylate and 1,6-hexanediol diacrylate can be used as crosslinkers. Additional polyfunctional acrylic monomers which can be used as crosslinkers in the present invention are disclosed in U.S. Patent No. 4,379,201 (Heilmann et al.), which is incorporated herein by reference.

Chromophore-substituted halomethyl-s-triazines, such as those described by U.S. Patent Nos. 4,329,384 (Vesley et al.); 4,330,590 (Vesley); and 4,379,201 (Vesley), all of which are incorporated herein by reference, are also preferred crosslinking agents for compositions or applications which require no further melt processing or solvent casting.

Silanes can also be used as crosslinkers. Suitable silanes include trialkoxy silanes having mono-ethylenically unsaturated functionality. Other suitable silanes include silanes having dialkoxy or monoalkoxy substituted silane groups having mono-ethylenically unsaturated functionality.

Compositions of the invention which require further processing and undergo crosslinking by exposure to ultraviolet radiation following the initial polymerization may employ several preferred classes of crosslinkers including: chromophore-substituted halomethyl-s-triazines, such as those in the Vesley Patents described above, all of which are incorporated herein by reference; mono-ethylenically unsaturated aromatic ketones, particularly 4-acryloyl-oxy-benzophenone, as described by Kellen et al. in U.S patent No. 4,737,559, which is incorporated herein by reference.

The pressure sensitive adhesive of this invention should comprise from about 10 to about 50 % by weight of at least one linear or branched alkyl acrylate or methacrylate having from 12 to 26 carbon atoms; from about 50 to about 90 % by weight of at least one linear lower alkyl acrylate (C_4-C_8) or branched lower alkyl acrylate (C_4-C_{12}); and sufficient crosslinker to impart cohesive strength to the adhesive. More preferably, the novel and unobvious pressure sensitive adhesive should comprise from about 30 to 50% by weight higher linear or branched alkyl acrylate or methacrylate esters having alkyl groups from 12 to 26 carbon atoms; from about 50 to about 70% by weight linear or branched lower acrylate or methacrylate having alkyl groups from about 4 to 12 carbon atoms and from about 0.05 to 1.0% and preferably, from about 0.1 to about 0.5% by weight crosslinker. The adhesive should have enough tack to adhere to a contact surface and have sufficient peel adhesion to allow a substrate coated with the adhesive to be easily removed from a contact surface.

The photoprocessible adhesives can be polymerized using any solution polymerization method. In the preferred method, the monomers along with the solvent and crosslinker are charged into a four-neck reaction vessel which is equipped with a stirrer, a thermometer, a condenser, addition funnel and a thermowatch. After the monomer is charged into the reaction vessel, a concentrated thermal initiator solution is added to the addition funnel. The whole reaction vessel and addition funnel with their contents are then purged with nitrogen to create an inert atmosphere. Once purged, the solution within the vessel is heated to about 55 °C and the initiator is added. A 98 to 99% percent conversion should be obtained after about 20 hours.

If the solution is then coated onto a substrate and no further processing is desired, the coating can be cured by exposure to ultraviolet light.

If the solution is not cast, but instead a hot melt coating is desired, the solvent is stripped. The solvent is stripped by applying the mixture onto a siliconized release liner which is then heated resulting in solvent evaporation. Thus, an adhesive product is left in solid form. The adhesive is then heated from about 145 °C to about 170 °C to reduce melt viscosity, coated onto a suitable substrate and then cured by exposure to an ultraviolet light source.

Another method of applying the adhesive of the present invention comprises UV prepolymerization of the monomer mixture to a syrup-like consistency, followed by the addition of a crosslinker. A suitable crosslinker is then added to a syrup-like mixture. Next, this syrup-like mixture is knife-coated onto a substrate and UV polymerized in an inert atmosphere to yield the finished adhesive coating.

The adhesive of the present invention can also be polymerized by charging the monomers with solvent, initiator and a silane crosslinker into a three-neck reaction vessel equipped with a stirrer, a thermometer, a thermowatch and condenser. After the monomer is charged into the reaction vessel, the whole reaction vessel with its contents is purged with nitrogen and heated to 55 °C. After about 20 hours, a 97 to 98% percent conversion should be obtained. The material is then coated on a substrate and dried in an oven. Typically, a catalyst can be added to the solution prior to coating and oven drying. In the presence of moisture, a crosslinked adhesive is obtained and no further processing is required.

The removable PSA of the present invention depending upon its viscosity, can be coated via any of a variety of conventional coating methods, such as roll coating, knife coating, hot melt coating, or extrusion. The composition can be applied to at least a portion of at least one surface of suitable flexible or inflexible backing or sheet and cured to produce PSA-coated sheet materials. For example, it can be placed on a backing to form a tape. Or it can be applied to a sheet to form pressure sensitive sheets. For many purposes, it is preferred that the adhesive can be coated on both sides of a sheet. Those skilled in the art will recognize that novel adhesive can be applied to a variety of sheets and backings and can be simultaneously coated on both sides of the sheet or backing. Useful flexible backing materials include paper, plastic films such as poly(propylene), poly(ethylene), poly(vinyl chloride), poly(tetrafluoroethylene), polyester [e.g., poly(ethylene) terephthalate)], polyimide film such as DuPont's Kapton®, cellulose acetate and ethyl cellulose. Backings can also be of woven fabric formed of threads of synthetic or natural materials such as cotton, nylon, rayon, glass, or ceramic material, or they can be of nonwoven fabric such as air-laid webs of natural or synthetic fibers or blends of these. In addition, suitable backings can be formed of metal, metallized polymeric film or ceramic sheet material. PSA-coated sheet materials can take the form of any article conventionally known to be utilized with PSA compositions, such as labels, tapes, transfer tapes (comprising a film of the PSA borne on at least one release liner), signs, covers, marking indices, and the like. Primers can be utilized, but they are not always necessary.

Test Methods

Removability

Adhesives of the present invention are considered removable if they are removed cleanly from a test substrate without causing any damage to the test substrate over a range of peel rates and varied periods of dwell at room temperature.

A strip 0.127 dm in width of the sheet coated with the adhesive to be tested is applied to the horizontal surface of a polyester, treated polyester or paper test substrate with at least 1.27 lineal dm in firm contact. Three passes in each direction with a 2 kg hard rubber roller are used to apply the strip. If air bubbles are entrapped between the test substrate and the test strip, the sample is discarded. After one day or one week dwell, the free end of the coated strip is doubled back nearly touching itself so the angle of removal will be about 135°. The free end is then pulled by hand at a variety of peel rates. The removability and peel force are judged according to the following ratings and recorded:

good - samples that are removed from the test substrate without damaging or leaving residue on the test substrate and which also exhibit high peel force and yet does not damage the paper backing over a range of peel rates;

aggressive - samples that are removed from the test substrate without damaging or leaving residue on the test substrate, but which can only be removed from the test substrate at a slow peel rate without damaging the paper backing;

raspy - samples that are removed from the test substrate without damaging or leaving residue on the test substrate, but which are too stiff to be removed smoothly;

tear - samples that display too high a peel adhesion to the test substrate, causing test substrate and/or paper backing to tear or delaminate at any peel rate;

ghost - samples that leave a very thin, non-tacky adhesive residue on the test substrate when removed from the polyester and treated polyester samples; and

weak - samples that have low tack and low peel.

cohesive failure - samples that leave adhesive residue on both the paper backing and the test substrate.

Peel Adhesion

Peel adhesion is the force required to remove a coated flexible sheet material from a test substrate measured at a specific angle and rate of removal. In the examples, this force is expressed in Newtons per decimeter (dm) width of coated sheet. The procedure followed is:

A strip 0.127 dm in width of the sheet coated with the adhesive to be tested is applied to the horizontal surface of a polyester, treated polyester or paper test substrate with at least 1.27 lineal dm in firm contact. Three passes in each direction with a 2 kg hard rubber roller are used to apply the strip. If air bubbles are entrapped between the test substrate and the test strip, the sample is discarded. The free end of the coated strip is doubled back nearly touching itself so the angle of removal will be 180°. The free end is attached to an adhesion tester scale. The polyester or paper test substrate is clamped in the jaws of a tensile testing machine which is capable of moving the substrate away from the scale at a constant rate of 2.3 meters per minute. The dwell time after roll down is 30 seconds. The scale reading in Newtons is recorded as the tape is peeled from the glass surface.

<u>Abbreviations and Tradenames</u>

AA - acrylic acid
ABP - 4-acryloyl-oxybenzophenone
BA - n-butyl acrylate
ECA - eicosanyl acrylate
HCA - hexacosanyl acrylate
HDDA - 1,6-hexanediol diacrylate
IOA - isooctyl acrylate
ITDA - isotridecyl acrylate
LA - lauryl acrylate
LMA - lauryl methacrylate
ODA - octadecyl acrylate
OAcM - n-octyl acrylate
ODMA - octadecyl methacrylate
SIL - methacryloxypropyltrimethoxysilane sold under trade name Silane A-174 by Union Carbide
VAZO™ 64 - 2,2'-azobis(isobutyronitrile), available from DuPont

The percentages in this specification and appended claims are all percentages by weight unless otherwise noted.

Example 1

In a 500 ml four-necked reaction vessel, equipped with a stirrer, thermometer, condenser, addition funnel and thermowatch, 84.0 grams of IOA, 75 grams of ODA (@ 48% solids in ethyl acetate), 121 grams of ethyl acetate, and 0.92 gram of ABP (@ 26% solids in ethyl acetate) were charged. A solution of 0.36

gram VAZO™ 64 in 20 grams of ethyl acetate was added to the addition funnel. Both the solution in the reaction vessel and the materials in the addition funnel were then purged with argon (or nitrogen). The solution in the reaction vessel was then heated to 55°C and initiator was added. After about 20 hours, a 98-99% conversion was obtained. The mixture was then coated from solution onto light weight, unprimed paper. No bleeding of the adhesive solution through the paper was observed. An oven dried coating thickness of 0.5 to 1.0 mil of the adhesive solution was obtained. The coating was passed three times under UV light (PPG UV processor equipped with medium pressure mercury lamps at 30 Watts/2.5 cm) at 25 meters/min.

The coated paper was then adhered, as specified in the above removability test, to two different test substrates: one being an 100 mm thick untreated poly(ethylene terephthalate) sheet ("PET", commercially available as PP2410 from Minnesota Mining and Manufacturing Company) the second being a 100 mm thick sheet of poly(ethylene terephthalate) film surface treated with hydrolyzed cellulose acetate ("treated PET", commercially available as G3120 from Minnesota Mining and Manufacturing Company). Removability was then measured for samples from both test substrates after dwell of one day and one week.

The test results were reported in Table 1.

Table 1

REMOVABILITY

Composition	Wt. % ratio	PET 1 day	 1 week	treated PET 1 day	 1-week
IOA/ODA/ABP	70/30/0.2	good	good	good	good

Comparative Examples C-1, C-2 and C-3

Examples C-1, C-2 and C-3 were prepared according to the procedure of Example 1. However, the examples were not prepared with a linear or branched higher alkyl acrylate or methacrylate. The removabilities of these compositions are reported in Table 2.

Table 2

REMOVABILITY

Ex.	Com-position	Wt. % ratio	PET		treated PET	
			1 day	1 week	1 day	1 week
C-1	IOA/OA /ABP	70/30/ 0.2	aggress	aggress	aggress	aggress
C-2	IOA/OA cM/ABP	70/30/ 0.2	raspy	tear	tear	tear
C-3	IOA/EA /ABP	70/30/ 0.2	aggress	aggress	aggress	aggress

The examples illustrate the need for the inclusion of at least one linear or branched higher alkyl acrylate or methacrylate in the romovable adhesive composition of the present invention.

Examples 2-5

Examples 2-5 were prepared according to the procedure outlined in Example 1. Their removabilities are recorded in Table 3.

Table 3

REMOVABILITY

Ex.	Com-position	Wt. % ratio	PET		treated PET	
			1 day	1 week	1 day	1 week
2	IOA/ODA/ ABP	90/10/ 0.2	good	good	good	good
3	IOA/ODA/ ABP	80/20/ 0.2	good	good	good	good
4	IOA/ODA/ ABP	60/40/ 0.2	good	good	good	good
5	IOA/ODA/ ABP	50/50/ 0.2	good	good	good	good

Examples 2-5 illustrate the compositional range at which IOA/ODA adhesives retain their removability from both test substrates.

Comparative Examples C-4 AND C-5

Comparative Examples C-4 and C-5 were prepared in accordance with Example 1. These two comparative examples were prepared with higher alkyl acrylate compositions in excess of the ranges of the adhesive of the present invention.

Table 4

REMOVABILITY

Ex.	Com-position	Wt. % ratio	PET		treated PET	
			1 day	1 week	1 day	1 week
C-4	IOA/ODA/ ABP	40/60/ 0.2	tear	tear	tear	tear
C-5	IOA/LA/ ABP	30/70/ 0.2	weak	weak	weak	weak

As can be seen, Comparative Examples C-4 had too much adhesion causing substrate tear and C-5 exhibited virtually no adhesion.

Examples 6-15

Examples 6-15 were prepared in accordance with the procedure of Example 1. However, different higher alkyl acrylates and methacrylates were used. The results of the tests are reported in Table 5.

Table 5

REMOVABILITY

Ex.	Com-position	Wt. % ratio	PET		treated PET	
			1 day	1 week	1 day	1 week
6	IOA/LMA/ ABP	90/10/ 0.2	good	good	good	good
7	IOA/LMA/ ABP	80/20/ 0.2	good	good	good	good
8	IOA/LMA/ ABP	50/50/ 0.2	good	good	good	good
9	IOA/ODMA/ ABP	90/10/ 0.2	good	good	good	good
10	IOA/ODMA/ ABP	70/30/ 0.2	good	good	good	good
11	IOA/ODMA/ ABP	90/10/ 0.2	good	good	good	good
12	IOA/ITDA/ ABP	70/30/ 0.2	good	good	good	good
13	IOA/ECA/ ABP	70/30/ 0.3	good	good	good	good
14	IOA/HCA/ ABP	70/30/ 0.3	good	good	good	good
15	IOA/ITDA/ ABP	60/40/ 0.2	good	good	good	good

Examples 6-15 illustrate that compositional range varying higher alkyl acrylates and methacrylates at which the adhesives retain their removability from both test substrates.

Examples 16-20

Examples 16-20 were prepared in accordance with the procedure of Example 1. However, butyl acrylate was used instead of isooctyl acrylate. In addition, a number of different weight ratios of butyl acrylate were used. Test results are shown in Table 6.

Table 6

REMOVABILITY

Ex.	Composition	Wt. % ratio	PET		treated PET	
			1 day	1 week	1 day	1 week
16	BA/ODA/ ABP	90/10/ 0.2	good	good	good	good
17	BA/ODA/ ABP	80/20/ 0.2	good	good	good	good
18	BA/ODA/ ABP	70/30/ 0.2	good	good	good	good
19	BA/ODA/ ABP	60/40/ 0.2	good	good	good	good
20	BA/ODA/ ABP	50/50/ 0.2	good	good	good	good

Examples 16-20 illustrate that compositional range of butyl acrylates at which the adhesives retain their removability from both test substrates.

Comparative Examples C-7 and C-8

Comparative Examples C-7 and C-8 were made in accordance with the procedure of Example 16. These two comparative examples were prepared with higher alkyl acrylate compositions in excess of the ranges of the adhesive of the present invention. Test results are reported in Table 7.

Table 7

REMOVABILITY

Ex.	Composition	Wt. % ratio	PET		treated PET	
			1 day	1 week	1 day	1 week
C-6	BA/ODA /ABP	40/60/ 0.2	shocky	tear	tear	tear
C-7	BA/ODA /ABP	30/70/ 0.2	weak	weak	weak	weak

As can be seen, Comparative Examples C-6 had too much adhesion and C-7 exhibited virtually no adhesion at all.

Example 21

This example demonstrates the preparation and removability of a hot melt processible adhesive of this invention.

In a 500 ml four-necked reaction vessel, equipped with a stirrer, thermometer, condensor and thermowatch, 84.0 grams of IOA, 75 grams of ODA (@ 48% solids in ethyl acetate), 121 grams of ethyl acetate, and 0.92 gram of ABP (@ 26% solids in ethyl acetate), and solution of 0.36 gram VAZO™ 64 in 20 grams of ethyl acetate were charged. The solution in the reaction vessel was then purged with nitrogen to create an inert atmosphere. The solution in the reaction vessel was then heated to 55°C for 20 hours. A 98-99% conversion was obtained. The mixture was then coated from solution onto a siliconized release liner and oven dried at 65°C for 15 minutes. The solid polymer was then removed from the liner and placed into a small piston coater. The solid polymer was then heated to 145-170°C and coated onto a roll of 30 pound machine-glazed bond paper stock. The coating was passed three times under UV light (PPG UV processor equipped with medium pressure mercury lamps at 30 Watts/2.5 cm) at 25 meters/min. A coating thickness of 0.4 to 1.0 mil of the hot melt adhesive was obtained.

The coated paper was then adhered, as specified in the above removability test, to two different test substrates: one being an 100 mm thick untreated poly(ethylene terephthalate) sheet ("PET", commercially available as PP2410 from Minnesota Mining and Manufacturing Company) the second being a 100 mm thick sheet of poly(ethylene terephthalate) film surface treated with hydrolyzed cellulose acetate ("treated PET", commercially available as G3120 from Minnesota Mining and Manufacturing Company). Removability was then measured for samples from both test substrates after dwell of one day and one week.

Table 8

REMOVABILITY

Ex.	Composition	Wt. % ratio	PET		treated PET	
			1 day	1 week	1 day	1 week
21	IOA/ODA/ABP	70/30/0.2	good	good	good	good

Examples 22-27

Examples 22-27 were made in accordance with Example 21. Compositions and weight ratios of the compositions are reported in Table 9.

Table 9

REMOVABILITY

Ex.	Composition	Wt. % ratio	PET		treated PET	
			1 day	1 week	1 day	1 week
22	IOA/ODA/ABP	90/10/0.2	good	good	good	good
23	IOA/ODA/ABP	80/20/0.2	good	good	good	good
24	IOA/ODA/ABP	60/40/0.2	good	good	tear	good
25	BA/ODA/ABP	70/30/0.2	good	good	good	good
26	BA/ODA/ABP	60/40/0.2	good	good	good	good
27	BA/ODA/ABP	50/50/0.2	good	good	good	good

As can be seen, Examples 20-25 all exhibited good removability.

Examples 28-31

Examples 28-31 were prepared in accordance with the procedure of Example 21 with varying compositions and weight ranges. Examples 28-31 were tested for peel adhesion on a variety of substrates. Three different test substrates were used: one being a 100 mm thick untreated poly(ethylene terephthalate) sheet ("PET"), the second being a 100 mm thick sheet of poly(ethylene terephthalate) film surface treated with hydrolyzed cellulose acetate ("treated PET") and the third being copy paper. Peel adhesion was then measured for samples for all three test substrates. The test results are shown in Table 10.

TABLE 10

Peel Adhesion (N/dm)

Ex.	Composition	Wt. %	PET	PET TREATED	PAPER
28	IOA/ODA/ABP	60/40/0.2	1.8	0.7	1.3
29	BA/ODA/ABP	70/30/0.2	9.2	9.2	10.5
30	BA/ODA/ABP	60/40/0.2	15.1	13.6	25.8
31	BA/ODA/ABP	50/50/0.2	7.4	8.3	6.8

As can be seen, Examples 28-31 exhibited suitable peel adhesion.

EXAMPLE 32

Example 32 was prepared in the same manner as Examples 28-31. However, two higher alkyl acrylates were used instead of one. The test results are shown in Table 11.

TABLE 11

Ex.	Composition	Wt. % ratio	PET		treated PET	
			1 day	1 week	1 day	1 week
32	IOA/ODA/LMA/ABP	70/20/10/0.2	good	good	good	good

As can be seen, Example 32 exhibited good removability.

EXAMPLES 33-34

Examples 33-34 were prepared in same manner as Example 1. However, the ratios of the crosslinker ABP were varied. Test results are recorded in Table 12.

TABLE 12

EX.	COMPOSITION	WT. % RATIO	PEEL ADHESION		
			PET	TREATED PET	PAPER
33	IOA/ODA/ ABP	70/30/0.3	6.6	3.1	1.5
34	IOA/ODA/ ABP	70/30/0.4	0.7	1.3	0.7

COMPARATIVE EXAMPLE 8-C

Comparative Example 8-C was made in the same manner as Example 1 without any crosslinker. The results are reported in Table 13.

TABLE 13

Ex.	COMPOSITION	WT. % RATIO	PEEL ADHESION		
			PET	TREATED PET	PAPER
8-C	IOA/ODA/ ABP	70/30/0	COHESIVE FAILURE		

EXAMPLES 35-38

Example 35 was prepared in the following manner: 0.1 gram of 2,2-dimethoxy-2-phenyl acetophenone sold under the tradename Escacure KB1 by Sartomer Company was dissolved in 100 grams of a 70/30 monomer mixture of isooctyl acrylate and octadecylacrylate. The mixture was purged with nitrogen and prepolymerized under a set of 40 Watt fluorescent UV lights resulting in a mixture having syrup-like consistency. Next, 0.18 grams of HDDA were added together with 0.1 grams of Escacure KB1 to the syrup-like mixture.

The mixture was then knife-coated onto a substrate and completely polymerized under a bank of fluorescent UV lights in an inert atmosphere. Three different test substrates were used: one being a 100 mm thick untreated poly(ethylene terephthalate) sheet ("PET"), the second being a 100 mm thick sheet of poly(ethylene terephthalate) film surface treated with hydrolyzed cellulose acetate ("treated PET") and the third being copy paper. Peel adhesion was then measured for samples for all three test substrates.

Examples 36-38 were prepared in the same manner as Example 35 except that the amount of HDDA and/or ODA was changed.

The compositions and weight ratios of Examples 34-37 are reported in Table 14 as are the results of the testing.

TABLE 14

EX.	COMPOSITION	WT. % RATIO	PEEL ADHESION		
			PET	TREATED PET	PAPER
35	IOA/ODA/HDDA	70/30/0.1	22.5	30.4	48.4
36	IOA/ODA/HDDA	70/30/0.2	17.5	20.4	24.7
37	IOA/ODA/HDDA	80/20/0.1	34.8	31.7	52.1
38	IOA/ODA/HDDA	80/20/0.2	20.6	24.3	30.2

EXAMPLES 39-41

Example 39 was prepared in the following manner: A 500 ml. three-necked reaction vessel, equipped with a stirrer, thermometer, thermowatch and condensor was charged with 84 grams of IOA, 75 grams of ODA (@48 % solids in ethyl acetate), 121 grams of ethyl acetate and 0.2 grams of silane crosslinker sold under the tradename Silane A-174 by Union Carbide. Next, a solution of 0.36 grams of VAZO™ dissolved in 20 grams of ethyl acetate was added to the charge. Then the vessel was purged with nitrogen and heated to 55°C for about 20 hours.

Prior to coating, about 0.04 grams of dibutyl tin dilaurate catalyst was mixed into the solution. The material was coated onto the substrate and dried in the oven. Three different test substrates were used: one being a 100 mm thick untreated poly(ethylene terephthalate) sheet ("PET"), the second being a 100 mm thick sheet of poly(ethylene terephthalate) film surface treated with hydrolyzed cellulose acetate ("treated PET") and the third being copy paper. Peel adhesion was then measured on all three test substrates.

Examples 40 and 41 were made in the same manner except the amount of SIL was varied as indicated in Table 15. The results of the testing are reported in Table 15.

TABLE 15

EX.	COMPOSITION	WT. % RATIO	PEEL ADHESION (N/dm)		
			PET	TREATED PET	PAPER
39	IOA/ODA/SIL	70/30/0.2	2.4	3.5	5.3
40	IOA/ODA/SIL	70/30/0.3	1.8	1.8	1.8
41	IOA/ODA/SIL	70/30/0.4	1.5	1.5	1.6

In summary, a novel and unobvious adhesive has been described having a low melt viscosity. Although specific embodiments and examples of the present invention have been described herein, it should be borne in mind that these are by way of explanation and illustration and the present invention is not limited thereby. Certainly modifications which are within the ordinary skill in the art are considered to lie within the scope of this invention as defined by the following claims including all equivalents.

The claims defining the invention are as follows:

1. An acrylic pressure-sensitive adhesive comprising:
   a) from 10 to 50% by weight of at least one higher alkyl acrylate having an alkyl group from 12 to 26 carbon atoms;
   b) from 50 to 90% by weight of at least one lower alkyl acrylate having an alkyl group from 4 to 12 atoms wherein said alkyl groups of said lower and higher alkyl acrylates do not simultaneously have 12 carbon atoms; and
   c) sufficient crosslinker to substantially prevent adhesive transfer, wherein said adhesive composition has high peel strength while maintaining good removability.

2. The adhesive of Claim 1 wherein said alkyl group of said lower alkyl acrylate is linear and has 4 to 8 carbon atoms.

3. The adhesive of Claim 1 wherein said alkyl group of said higher alkyl acrylate has from 13 to 26 carbon atoms.

4. The adhesive of Claim 1 wherein said crosslinker is selected from the group consisting of a multifunctional acrylates, multifunctional methacrylates, chromophore-substituted halomethyl-s-triazines, benzophenones, acetophenones, silanes and mono-ethylenically unsaturated aromatic ketones.

5. The adhesive of Claim 1 wherein said crosslinker comprises from about 0.05 to about 1.0% by weight of said adhesive.

6. The adhesive of Claim 1 wherein said adhesive comprises from about 30 to 50 percent by weigh of said higher alkyl acrylate; from about 50 to 70% by weight of said lower alkyl acrylate and from about 0.1 to about 0.5% by weight of said crosslinker.

7. An adhesive coated sheet material having a bearing on at least one major surface thereof an adhesive composition comprising:
   a) from 10 to 50% by weight of at least one higher alkyl acrylate having an alkyl group from 12 to 26 carbon atoms;
   b) from 50 to 90% by weight of a lower alkyl acrylate having an alkyl group from 4 to 12 atoms wherein said alkyl groups of said lower and higher alkyl acrylates do not simultaneously have 12 carbon atoms; and
   c) sufficient crosslinker to substantially prevent adhesive transfer, wherein said adhesive composition has high peel strength while maintaining good removability.

8. The sheet of Claim 7 wherein said adhesive comprises from about 30 to 50 percent by weight of said higher alkyl acrylate; from about 50 to 70% by weight of said lower alkyl acrylate and from about 0.05 to about 1.0% by weight of said crosslinker.

9. The sheet of Claim 8 wherein said crosslinker comprises from about 0.1 to about 0.5% by weight of said adhesive.

10. The sheet of Claim 7 wherein said alkyl group of said higher alkyl acrylate has from 13 to 26 carbon atoms.

11. The sheet of Claim 7 wherein said crosslinker is selected from the group consisting of a multifunctional acrylates, multifunctional methacrylates, benzophenones, acetophenones, chromophore-substituted halomethyl-s-triazines, silanes and mono-ethylenically unsaturated aromatic ketones.

12. A method of making a pressure-sensitive adhesive coating sheet material comprising the following steps:
   a) polymerizing an adhesive mixture comprising a) from 10 to 50% by weight of at least one higher alkyl acrylate having an alkyl group from 12 to 26 carbon atoms; b) from 50 to 90% by weight of at least one lower alkyl acrylate having an alkyl group from 4 to 12 atoms wherein said alkyl

groups of said lower and higher alkyl acrylates do not simultaneously have 12 carbon atoms; and c) sufficient crosslinker to substantially prevent adhesive transfer, wherein said adhesive has high peel strength while maintaining good removability;

b) coating and drying said adhesive onto said sheet; and

c) curing said adhesive by exposing said adhesive to ultraviolet light.

13. The method of Claim 12 further including the steps of:

a) solidifying said polymerizable adhesive;

b) heating and coating said adhesive prior to curing said adhesive on said sheet.

14. The method of Claim 12 wherein said adhesive comprises from about 30 to 50 percent by weight of said higher alkyl acrylate; from about 50 to 70% by weight of said lower alkyl acrylate and from about 0.1 to about 0.5% by weight of said crosslike.

15. The method of Claim 13 wherein said adhesive comprises from about 30 to 50 percent by weight of said higher alkyl acrylate; from about 50 to 70% by weight of said lower alkyl acrylate and from about 0.1 to about 0.5% by weight of said crosslinker.

16. The method Claim 14 wherein said crosslinker is selected from the group consisting of selected from the group consisting of multifunctional acrylates and methacrylates, benzophenones, acetophenones and chromophore-substituted halomethyl-s-triazines.

17. The method of Claim 15 wherein said crosslinker is selected from the group consisting of selected from the group consisting of chromophore-substituted halomethyl-s-triazines, benzophenones, acetophenones and mono-ethylenically unsaturated aromatic ketones and further wherein the amount of crosslinker is sufficient to substantially prevent adhesive transfer.

18. A method of making a pressure-sensitive adhesive coating sheet material comprising the following steps:
    a) UV prepolymerizing an adhesive mixture to a syrup-like consistency wherein said mixture comprises: a) from 10 to 50% by weight of at least one higher alkyl acrylate having an alkyl group from 12 to 26 carbon atoms; b) from 50 to 90% by weight of at least one lower alkyl acrylate having an alkyl group from 4 to 12 atoms wherein said alkyl groups of said lower and higher alkyl acrylates do not simultaneously have 12 carbon atoms;
    b) adding crosslinker to said mixture;
    c) coating said mixture with said crosslinker to said sheet; and
    d) UV polymerizing said mixture.

19. The method of Claim 18 wherein said adhesive comprises from about 30 to 50 percent by weight of said higher alkyl acrylate; from about 50 to 70% by weight of said lower alkyl acrylate and from about 0.1 to about 0.5% by weight of said crosslinker.

20. A method of making a pressure-sensitive adhesive coating sheet material comprising the following steps:
    a) polymerizing an adhesive mixture comprising a) from 10 to 50% by weight of at least one higher alkyl acrylate having an alkyl group from 12 to 26 carbon atoms; b) from 50 to 90% by weight of at least one lower alkyl acrylate having an alkyl group from 4 to 13 atoms wherein said alkyl groups of said lower and higher alkyl acrylates do not simultaneously have 12 carbon atoms; and c) sufficient silane crosslinker to substantially prevent adhesive transfer, wherein said adhesive has high peel strength while maintaining good removability;
    b) coating said adhesive onto said sheet; and
    c) drying said adhesive; and
    d) curing said adhesive in the present of moisture.

21. The method Claim 20 wherein said adhesive comprises from about 30 to 50 percent by weight of said higher alkyl acrylate; from about 50 to 70% by weight of said lower alkyl acrylate and from about 0.1 to about 0.5% by weight of said crosslinker.

DATED this 16th day of October 1995.

MINNESOTA MINING AND MANUFACTURING COMPANY
By their Patent Attorneys
DAVIES COLLISON CAVE

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/10776

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08F220/18; C09J7/02

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C08F ; C09J

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category°	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
Y	US,A,3 900 674 (COFFMAN) 19 August 1975 see claim 1 see column 4, line 56 - line 66 ---	1-21
Y	EP,A,0 109 177 (MINNESOTA MINING AND MANUFACTURING COMPANY) 23 May 1984 cited in the application & US,A,4 599 265 see claims 1-5 see page 4, line 6 - page 5, line 22 ---	1-21
A	US,A,3 983 297 (ONO ET AL.) 28 September 1976 ---	1-11
	-/--	

° Special categories of cited documents :[10]

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

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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

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

"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

2 **IV. CERTIFICATION**

Date of the Actual Completion of the International Search 16 FEBRUARY 1993	Date of Mailing of this International Search Report 15. 03. 93
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer ANDRIOLLO G.R.

Form PCT/ISA/210 (second sheet) (January 1985)

International Application No PCT/US 92/10776

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,3 707 518 (BEMMELS ET AL.) 26 December 1972 see claim 1 see column 3, line 28 - line 43	1-11,20, 21
A	WO,A,8 102 261 (MINNESOTA MINING AND MANUFACTURING COMPANY) 20 August 1981 cited in the application see page 4, line 15 - page 5, line 16 & US,A,4 329 384	1-11,18, 19

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9210776
SA 68314

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3900674	19-08-75	BE-A- 788440	02-01-73
		CA-A- 991786	22-06-76
		CH-A- 545324	31-01-74
		DE-A,C 2243702	15-03-73
		FR-A,B 2152703	27-04-73
		GB-A- 1386482	05-03-75
		NL-A- 7212171	09-03-73
		US-A- 3738971	12-06-73
EP-A-0109177	23-05-84	AU-B- 566547	22-10-87
		AU-A- 2094283	10-05-84
		CA-A- 1219498	24-03-87
		DE-A- 3374944	28-01-88
		JP-A- 59098185	06-06-84
		US-A- 4522870	11-06-85
		US-A- 4513039	23-04-85
		US-A- 4599265	08-07-86
		US-E- RE32249	23-09-86
US-A-3983297	28-09-76	JP-C- 978099	29-11-79
		JP-A- 49018924	19-02-74
		JP-B- 54010976	11-05-79
		JP-C- 981183	27-12-79
		JP-A- 49032933	26-03-74
		JP-B- 54014607	08-06-79
		CA-A- 1012683	21-06-77
		DE-A,B 2330328	10-01-74
		GB-A- 1423633	04-02-76
		NL-A- 7308139	18-12-73
		US-A- 3971766	27-07-76
US-A-3707518	26-12-72	US-A- 3617362	02-11-71
WO-A-8102261	20-08-81	US-A- 4329384	11-05-82
		AU-B- 537310	14-06-84
		AU-A- 6780481	31-08-81
		CA-A- 1145294	26-04-83
		DE-A- 3105342	17-12-81
		EP-A,B 0045769	17-02-82

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82