

NON-CORROSIVE, LOW VOLATILES-CONTAINING
PRESSURE SENSITIVE ADHESIVE

BACKGROUND OF THE PRESENT INVENTION

The present invention is directed to a
5 pressure sensitive adhesive composition comprised
of a polymerized acrylic or methacrylic acid ester
backbone having grafted thereto pendant polymeric
moieties.

Polymeric compositions are known which are
10 comprised of backbone polymers having grafted
thereto pendant polymeric moieties. The type of
backbone polymer and graft polymeric moiety
employed varies depending upon the desired
characteristics of the end product. See, for
15 example, U.S. Patent Nos. 3,786,116; 3,832,423;
3,842,146; 3,862,077; 3,879,494; 3,928,255;
3,989,768; 4,085,168; 4,551,388; 4,554,324;
4,656,213; 4,693,776; 4,732,808; and 4,871,812
which disclose various types of such polymers
20 which may or may not exhibit pressure sensitive
adhesive properties.

Typical of the type of polymeric compositions
disclosed in the above patents are compositions
comprised of a backbone polymer such as an acrylic
25 or methacrylic backbone polymer having attached
thereto a graft polymer comprised of a
polymerizable macromolecular monomer such as
styrene or alpha-methylstyrene. See, for example,
U.S. Patent No. 4,554,324, among others, in this
30 regard.

The acrylic pressure sensitive adhesives such
as described in U.S. Patent No. 4,554,324 may be
made from an acrylic ester and a polar acrylic

monomer. The polar acrylic monomer can be one or a mixture of acrylic acid, acrylamide, acrylonitrile, itaconic acid, etc. The acrylic ester can be any aliphatic ester of acrylic acid.

5 Such monomers are typically polymerized free radically by solution, suspension or emulsion polymerization. The acrylate portion of the copolymer is generally present in a generally high concentration and renders the polymer tacky. The

10 polar monomer increases the ability of the adhesive to bond to a surface.

While such polymeric compositions have been found to have utility as pressure sensitive adhesives, one area that has not heretofore been

15 addressed with much success is providing high performance pressure sensitive adhesives which may be suitable for use in high temperature environments (i.e., environments where the temperature exceeds about 250°F.).

20 By way of example, the aerospace and automotive industries are experiencing an increased demand for adhesives with the capability to withstand temperature extremes of -200°F. to as high as 400°F. It has been found that typical

25 acrylic pressure sensitive adhesives, while performing satisfactorily at temperatures as low as -45°F., fail at temperatures of about 150-200°F. (and sometimes at lower temperatures) as the adhesive becomes too soft and is unable to

30 retain acceptable adhesive properties. Attempts have been made to enhance the performance of such adhesives by cross-linking procedures.

Recent advances in the electronics industry also require the use of non-corrosive pressure

35 sensitive adhesives due to the sensitivity of the

electronic components. It is also desirable for the adhesive to have a low-volatiles content to minimize contamination during use of such adhesives during the manufacture of computer assemblies.

However, it has been found that the use of conventional polar monomer-containing pressure sensitive adhesives do not provide satisfactory performance at high temperatures. It has also been found that such adhesives exhibit undesirable corrosive properties as well as contain an undesirable volatiles content (thus leading to potential contamination during electronics manufacturing).

OBJECTS AND SUMMARY OF THE PRESENT INVENTION

It is accordingly an object of the present invention to provide a pressure sensitive adhesive composition which exhibits high performance properties.

It is further an object of the present invention to provide a pressure sensitive adhesive composition which retains sufficient adhesive strength at high temperatures.

It is still yet an object of the present invention to provide a pressure sensitive adhesive composition that has a low volatiles content.

It is still yet another object of the present invention to provide a pressure sensitive adhesive composition that is non-corrosive.

In accordance with the present invention, there is provided a normally tacky non-polar monomer-containing phase-separated graft copolymer exhibiting pressure sensitive adhesive properties comprised of a backbone polymer having a polymeric

moiety grafted thereto, comprising the reaction product of

(1) at least one A monomer consisting of a monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol, said alcohol having from 1 to 3 carbon atoms,

(2) at least one B monomer consisting of a monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol, said alcohol having from 4 to 12 carbon atoms,

(3) a graft polymeric moiety C having a T_g greater than $20^\circ\text{C}.$, and

wherein the weight ratio of said at least one A monomer to said at least one B monomer ranges from about 1:2 to 2:1, and the average number of carbon atoms present in the alcohol portion of the total acrylic or (meth)acrylic acid esters of monomers A and B present ranges from about 2.5 to 3.5, with the proviso that when the molecular weight of the graft polymeric moiety C ranges from 2,000 to 13,000 the graft polymeric moiety C is present in an amount of up to about 20% by wt., and when the molecular weight of the graft polymeric moiety C is greater than 13,000, then the graft polymeric moiety C is present in an amount of up to about 30% by wt.

DETAILED DESCRIPTION OF THE INVENTION

The pressure sensitive adhesive graft copolymer of the present invention is comprised of a "hard" reinforcing graft polymeric moiety attached to or copolymerized with a "soft" backbone polymer to obtain a phase-separated adhesive graft copolymer. While graft copolymers are known which are comprised of a "soft" backbone polymer having an attached "hard" reinforcing

graft polymer, such prior art graft copolymers fail to exhibit the desired high performance adhesive properties such as high strength in elevated temperature environments, with the graft copolymer also being non-corrosive and having a low volatiles content.

Specifically, the adhesive of the present invention comprises a phase-separated non-polar monomer-containing graft copolymer comprised of the reaction product of copolymerized monomers A and B to form a backbone polymer having a polymeric moiety C grafted thereto, wherein monomer(s) A is a monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol having from 1 to 3 carbon atoms, and monomer(s) B is a monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol having from 4 to 12 carbon atoms.

The average number of carbon atoms present in the alcohol portion of the total acrylic or (meth)acrylic acid esters of monomers A and B present in the copolymer will be less than 4, and preferably about 2.5 to 3.5 (calculated on mole percent basis). Most preferably, the average number of carbon atoms is about 3.0.

Importantly, it has been found that the presence of a polar monomer(s) (such as acrylic acid) in pressure sensitive adhesives is a disadvantage to the extent that a non-corrosive adhesive is desired or that the volatiles content of the adhesive is to be minimized. The graft copolymer of the present invention thus contains no polar monomers. Any disadvantage which would normally result from the absence of the polar monomer is addressed by providing for a particular

composition of A monomers based on the carbon atom content of the ester.

Exemplary A monomers include but are not limited to one or more of methyl(meth)acrylate, ethyl(meth)acrylate, n-propyl(meth)acrylate and iso-propyl(meth)acrylate. Such monomers are known to those skilled in the art.

Exemplary B monomers include but are not limited to esters of acrylic acid or methacrylic acid with non-tertiary alcohols such as 1-butanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 2-ethyl-1-butanol, 3,5,5-trimethyl-1-hexanol, 3-heptanol, 2-octanol, 1-decanol, 1-dodecanol, etc. Such monomers are known to those skilled in the art.

The weight ratio of said A monomer(s) to said B monomer(s) in said copolymer ranges from about 1:2 to 2:1, and preferably is about 1:1.

The A monomer will preferably be present in the graft copolymer in an amount within the range of from about 20 to 65 percent by weight, based on the total weight of the copolymer, with any additional monomers employed (such as the B monomer) and the polymeric graft moiety comprising the remaining portion of the copolymer. Desirably, the graft copolymer consists solely of monomers A and B and graft polymeric moiety C.

Polymeric graft moiety C has a Tg greater than 20°C. The graft moiety is preferably present in an amount of from 1.5 to 2.5 polymeric moieties per polymer backbone on average, and most preferably in an amount of 2 polymeric moieties per chain on average. The presence of the graft polymeric moiety within the noted range assists in

enabling the copolymer to exhibit sufficient cohesive strength even in view of the presence in the copolymer of significant amounts of the A monomer which might otherwise reduce the cohesive strength of the copolymer. The amount of the A monomer employed may accordingly be optimized without otherwise diminishing the adhesive properties of the copolymer.

The molecular weight of the graft polymeric moiety must be sufficient to result in the formation of a "phase-separated" graft copolymer. Generally, the molecular weight (number average) of the graft polymeric moiety will range from 2,000 to 60,000. In order to enhance the high temperature resistance of the copolymer, the molecular weight of the graft polymeric moiety will preferably range from greater than 30,000 to 60,000.

When the molecular weight of the graft polymeric moiety C ranges from 2,000 to 13,000, the graft polymeric moiety is present in an amount of from about 2 to about 20% by wt. When the molecular weight of the graft polymeric moiety C is greater than 13,000, then the graft polymeric moiety is present in an amount of from about 2 to about 30% by weight, based on the total weight of components A, B and C.

The graft copolymer of the present invention is characterized as being "phase-separated". That is, the backbone of the copolymer and the attached graft are incompatible and thus do not mix together to form a homogeneous phase. Instead, the copolymer backbone forms a continuous phase within which is dispersed the attached graft phase. The dispersed graft discontinuous phase

thus acts to mechanically reinforce the continuous phase, thus inhibiting the flow of the continuous phase at an elevated temperature.

The polymer graft may be attached to the polymer backbone by conventional techniques such as (1) copolymerization with the respective monomers of the backbone polymer or (2) attachment to a preformed backbone polymer via a suitable functional group subsequent to formation of same by copolymerization of monomers A and B.

With regard to technique (1) which comprises the preferred technique, the graft copolymer of the present invention may be formed from copolymerized monomers A, B and C, wherein

monomers A and B are as defined above and monomer C has the general formula X-Z wherein X is a group copolymerizable with said monomers A and B (preferably a vinyl group), and

Z is a polymeric graft moiety having a T_g greater than 20°C., said moiety Z being essentially unreactive under copolymerization conditions,

wherein said group X of said monomer C and said monomers A and B are copolymerized to form a polymeric backbone chain having pendant therefrom polymeric moiety Z.

The graft polymeric moiety may be prepared as a macromer and copolymerized with one or more A and B monomers which form the backbone polymer. See, for instance, the disclosure of U.S. Patent No. 3,786,116, incorporated by reference in its entirety, in this regard.

Typical copolymerization techniques include but are not limited to conventional free radical initiated copolymerization techniques in the

presence of a solvent. Suitable copolymerization temperatures range from about 20°C to 150°C for periods of time of from 2 to 24 hours until the desired degree of conversion occurs.

5 Upon completion of the polymerization process, the solvent is removed and a tacky acrylate copolymer results having an acceptable balance of tack and shear adhesive properties at high temperatures.

10 Depending upon the properties imparted to the backbone polymer as a result of the molecular weight of the particular graft employed, the resulting adhesive may need to be used in solution or emulsion form rather than as a melt adhesive.
15 That is, if the molecular weight of the graft is sufficiently high, the resultant adhesive may be applied to a backing material or substrate in emulsion or solution form, with the water or solvent being removed upon application to the
20 substrate.

 With regard to the polymeric graft moiety portion of the copolymer, U.S. Patent Nos. 3,786,116; 3,842,057; 3,842,058; 3,842,059; 3,862,098; 3,862,101, 3,862,102 and 4,554,324
25 disclose polymerizable macromers which are suitable for use as graft moieties on a backbone polymer as defined.

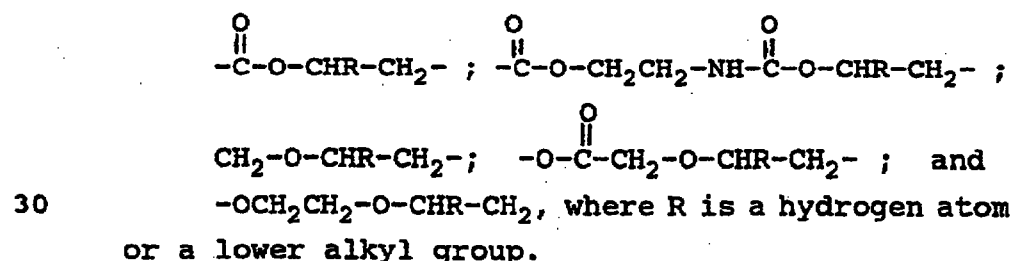
 The polymeric moiety Z may be formed from a vinyl aromatic monomer such as styrene, alpha-
30 methylstyrene, indene and p-tert-butylstyrene. However, the polymeric moiety Z may also be formed from vinyl toluene, acenaphthalene, acrylonitrile and methacrylonitrile, organic isocyanates including lower alkyl, phenyl, lower alkyl phenyl
35 and halophenyl isocyanates, organic diisocyanates

including lower alkylene, phenylene, and tolylene diisocyanates, lower alkyl and allyl acrylates and methacrylates, including methyl, t-butyl acrylates, and methacrylates; lower olefins, such as ethylene, propylene, butylene, isobutylene, pentene, hexene, etc.; vinyl esters of aliphatic carboxylic acids such as vinyl acetate, vinyl propionate, vinyl octoate, vinyl oleate, vinyl stearate, vinyl benzoate, vinyl lower alkyl ethers; conjugated dienes such as isoprene and butadiene, 2-oxazolines such as 2-ethyl-2-oxazoline, and vinyl unsaturated amides such as acrylamide, methacrylamide, N,N-di(lower alkyl) acrylamides such as N,N-dimethylacrylamide.

The selection of the specific polymerizable monomer for the polymer graft is not critical, since as the above listing suggests, a wide variety of monomers (and the resulting polymeric moieties) can be used with success as a polymeric graft in the copolymer.

A variety of functional groups may be employed to attach the graft Z to the polymer backbone.

Exemplary functional groups include but are not limited to



Various graft copolymers prepared according to the present invention are exemplified in Examples 1-3 below:

EXAMPLE 1

A polyacrylate polymer having a polystyrene graft (having a molecular weight of 13,000) is prepared by the following method. In a glass 1 liter reaction vessel the following charge stock was incrementally polymerized under a nitrogen atmosphere at 160-165°F over 8 hours with agitation:

	Ethyl acetate (solvent)	254.44 grams
10	Butyl acetate (solvent)	70.72 grams
	Heptane (solvent)	99.84 grams
	2-ethylhexyl acrylate (B monomer)	132.79 grams
	Butyl acrylate (B monomer)	63.78 grams
	Ethyl acrylate (A monomer)	73.15 grams
15	Methyl acrylate (A monomer)	96.00 grams
	Polystyrene methacrylate macromer (graft)	18.28 grams
	Benzoyl peroxide (initiator)	1.12 grams

Note: The average number of carbons in the alcohol portion of the acrylic or (meth)acrylic acid esters of the A and B monomers is calculated to be 3.4.

EXAMPLE 2

A polyacrylate polymer having a polystyrene graft (having a molecular weight of 13,000) is prepared by the method of Example 1 from the following charge stock:

5	Ethyl acetate (solvent)	254.44 grams
	Butyl acetate (solvent)	70.72 grams
	Heptane (solvent)	99.84 grams
	2-ethylhexyl acrylate (B monomer)	111.36 grams
10	Butyl acrylate (B monomer)	55.68 grams
	Ethyl acrylate (A monomer)	96.00 grams
	Methyl acrylate (A monomer)	96.00 grams
	Polystyrene methacrylate macromer (graft)	24.96 grams
15	Benzoyl peroxide (initiator)	1.12 grams

Note: The average number of carbons in the alcohol portion of the acrylic or (meth)acrylic acid esters of the A and B monomers is calculated to be 3.1.

EXAMPLE 3

In order to demonstrate the advantages of the graft copolymer of the present invention, comparisons were made of the adhesive properties of graft copolymers formed from the following three compositions:

Composition 1 (Invention):

30	2-ethylhexyl acrylate	29.00 wt. %
	butyl acrylate	14.50
	ethyl acrylate	25.00
	methyl acrylate	25.00
	polystyrene methacrylate macromer	6.50
	(molecular weight = 13,000)	

Composition 2 (Comparison):

35	butyl acrylate	93.50 wt. %
	polystyrene methacrylate macromer	6.50
	(molecular weight = 13,000)	

Composition 3 (Comparison):

	ethyl acrylate	93.50 wt. %
	polystyrene methacrylate	6.50
	macromer	
5	(molecular weight = 13,000)	

The average number of carbon atoms in the alcohol portion of the total (meth)acrylic acid esters in compositions 1, 2 and 3 is 3.0855, 4.0 and 2.0, respectively.

10 Each of the above compositions was used to produce corresponding graft copolymers 1, 2 and 3 according to the procedure described in Example 1.

Once produced, each of copolymers 1, 2 and 3 was tested for adhesive properties with the
15 following results:

	Copolymer 1	Copolymer 2	Copolymer 3
5' peel	57.6 oz NT	32.0 oz NT	12.8 oz NT
500 g.	925.5 min ST	22.45 min ST	>300 min
20 shear (Ave.)			
Probe tack (Ave.)	1145.8 grams	934.6 grams	575.2 grams
Plasticity	2.59 mm	2.18 mm	3.25 mm

The above comparative data indicates that
25 copolymer 1 of the present invention exhibits acceptable pressure sensitive adhesive properties. By contrast, copolymers 2 and 3 exhibit unacceptable pressure sensitive adhesive properties, thus confirming that use of an average
30 number of carbon atoms outside the claimed range of 2.5 to 3.5 yields an unacceptable adhesive.

As discussed above, the graft copolymer of the present invention has particular utility as a pressure sensitive adhesive. As such, the
35 composition may be employed alone or in combination with a suitable backing material in a manner known to those skilled in the art.

For instance, exemplary backing materials include but are not limited to flexible or inflexible backing materials conventionally employed in the area of pressure sensitive adhesives such as creped paper, kraft paper, fabrics (knits, non-wovens, wovens), foil and synthetic polymer films such as polyethylene, polypropylene, polyvinyl chloride, poly(ethylene terephthalate) and cellulose acetate, as well as glass, ceramics, metallized polymeric films and other compatible sheet materials.

Such materials may be coated in any conventional manner with the adhesive composition of the present invention, such as by roll coating, spray coating, extrusion coating, co-extrusion coating, hot melt coating by use of conventional coating devices. When appropriate, the composition of the present invention may be applied as a solution and the solvent subsequently removed to leave a tacky adhesive residue on the backing material.

The coated backing material may take many forms, such as tapes, patches, strips, etc., with the choice and form of backing material being ultimately determined by the end use contemplated.

WHAT IS CLAIMED IS:

1. A normally tacky non-polar monomer-containing phase separated graft copolymer having pressure sensitive adhesive properties comprised
5 of a backbone polymer having a polymeric moiety grafted thereto, comprising the reaction product of

(1) at least one A monomer consisting of a monomeric acrylic or methacrylic acid ester of a
10 non-tertiary alcohol, said alcohol having from 1 to 3 carbon atoms,

(2) at least one B monomer consisting of a monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol, said alcohol having from 4
15 to 12 carbon atoms, and

(3) a graft polymeric moiety C having a T_g greater than $20^\circ\text{C}.$, and

wherein the weight ratio of said at least one A monomer to said at least one B monomer ranges
20 from about 1:2 to 2:1, and the average number of carbon atoms present in the alcohol portion of the total acrylic or (meth)acrylic acid esters of monomers A and B present ranges from about 2.5 to 3.5, with the proviso that when the molecular
25 weight of the graft polymeric moiety ranges from 2,000 to 13,000 the graft polymeric moiety is present in an amount of up to about 20% by wt., and when the molecular weight of the graft polymeric moiety is greater than 13,000, then the
30 graft polymeric moiety is present in an amount of up to about 30% by wt.

2. The copolymer of claim 1 wherein said graft is a polymerized monoalkenyl-substituted aromatic hydrocarbon.



3. The copolymer of claim 2 wherein said polymerized monoalkenyl-substituted aromatic hydrocarbon comprises polystyrene.

5 4. The copolymer of claim 1 wherein the molecular weight of said graft is in the range of from 2,000 to 13,000.

10 5. The copolymer of claim 1 wherein said graft is present in an amount of about 1.5 to 2.5 polymeric moieties per polymeric backbone chain on average.

6. The copolymer of claim 1 wherein the weight ratio of said at least one A monomer to said at least one B monomer is about 1:1.

15 7. The copolymer of claim 1 wherein said at least one B monomer comprises an ester of acrylic and methacrylic acid with a non-tertiary alcohol selected from the group consisting of 1-butanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 20 3-methyl-1-pentanol, 2-ethyl-1-butanol, 3,5,5-trimethyl-1-hexanol, 3-heptanol, 2-octanol, 1-decanol and 1-dodecanol.

8. The copolymer of claim 2 wherein said graft comprises poly-alpha-methylstyrene.

25 9. The copolymer of claim 1 wherein the molecular weight of said graft polymeric moiety is greater than 13,000.



10. The copolymer of claim 1 wherein the A monomer is present in the copolymer in an amount within the range of from about 20 to 65 percent by weight.

5 11. The copolymer of claim 1 wherein the average number of carbon atoms present in the alcohol portion of the total acrylic or (meth)acrylic acid esters of monomers A and B present in the copolymer is about 3.

10 12. The copolymer of claim 2 wherein the average number of carbon atoms present in the alcohol portion of the total acrylic or (meth)acrylic acid esters of monomers A and B present in the copolymer is about 3.

15 13. The copolymer of claim 4 wherein the average number of carbon atoms present in the alcohol portion of the total acrylic or (meth)acrylic acid esters of monomers A and B present in the copolymer is about 3.

20 14. The copolymer of claim 9 wherein the average number of carbon atoms present in the alcohol portion of the total acrylic or (meth)acrylic acid esters of monomers A and B present in the copolymer is about 3.