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**EMULSION PRESSURE-SENSITIVE ADHESIVE POLYMERS
EXHIBITING EXCELLENT GUILLOTINE PERFORMANCE****Background of the Invention**

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The present invention relates to acrylic polymers which are formed by emulsion polymerization and as formed, are inherently tacky and functional as pressure-sensitive adhesives. More particularly, the adhesives of the instant invention have excellent guillotinability, room- and elevated-temperature adhesive performance, and provide an ecologically safe replacement for solvent adhesives and other acrylic- and rubber-based emulsion adhesives.

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Guillotinability is a critical requirement in film applications where pressure-sensitive adhesive (PSA) coated products are cut into sheet stock. During the process of guillotining it is expected that the adhesive will not build on the blades so that subsequent cutting is not affected and the cut sheets separate individually without sticking together. Solvent adhesives are commonly used in such applications due to the performance benefits they offer. Environmental constraints imposed on the use of solvents has caused the PSA industry to move away from solvent systems. The best alternative to day is the water borne adhesive technology due to adhesive user friendliness and the cost advantages. Obtaining high



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1 performance from water borne adhesive systems is the
major task which the PSA industry is facing.

In terms of the instant invention U.S. Patents Nos.
4,507,429, 4,694,056, and 4,725,639 to Lenney, and
5 assigned to Air Products, Inc., pertain to a
pressure-sensitive adhesive compositions and disclose
increasing cohesive strength by use of polyfunctional
monomers which include polyvinyl and polyallyl
compounds including triallyl isocyanurate. Product
10 glass transition temperature may be as high as -15°C ,
limiting utility at reduced temperature.

We have sought to provide pressure-sensitive
adhesives of improved properties which have broad
utility including excellent guillotinability.

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Summary of the Invention

According to the present invention, there is
provided inherently tacky acrylic emulsion adhesive
polymers which exhibit excellent guillotinability and
20 have excellent adhesion to a wide variety of surfaces
ranging from polar, relatively high energy surfaces
such as stainless steel to nonpolar, relatively low
energy surfaces such as polyethylene and to
difficult-to-bond surfaces such as corrugated board.
25 Moreover, cohesion and adhesion at room and elevated
temperatures is excellent and, when part of a laminate
stock such as pressure-sensitive adhesive label stock,
provides excellent high-speed converting
characteristics such as die cutting, matrix stripping
30 and fan folding. Superior properties are obtained even
at lower-than-normal coat weights. In sum, the
adhesive polymers are broad-based and serve to replace
many solvent-based adhesives on an ecologically safe
basis as well as many emulsion-based adhesives, thus
35 serving a variety of markets.

The inherently tacky, emulsion pressure-sensitive
adhesive polymers of the instant invention comprise, on



1 a polymerized basis and based on the total weight of
the polymer of at least one soft monomer having a glass
transition of less than -25°C . Preferably the soft
monomer is an alkyl acrylate containing from about 4 to
5 about 12 carbon atoms in the alkyl group, most
preferably a mixture of 2-ethylhexyl acrylate and butyl
acrylate. The total of the soft monomers are present
in an amount of from about 35 to about 95 percent by
weight of the polymer.

10 The polymer contains at least one hard monomer
having a glass transition temperature greater than 0°C
and preferably further includes a soft diester monomer
such as maleates and fumarates.

15 The emulsion polymers of this invention are formed
in the presence about 0.1 to about 1 percent of a
multifunctional monomer having a cyanurate or phosphate
functionality with tris(2-hydroxyethyl) isocyanurate
triacylate and bis(methacryloxyethyl) phosphate
presently preferred. The emulsion polymers of the
20 invention are high performance polymers preferably
having a gel content in excess of about 60 percent by
weight of the polymer.

25 The emulsion adhesive polymers of the instant
invention are preferably prepared using a reactive
surfactant which polymerizes and becomes part of the
emulsion polymer and which has been observed to enhance
cohesive strength and aid in copolymerization of the
monomers in forming the emulsion pressure-sensitive
adhesive polymers of the instant invention. The amount
30 of reactive surfactant employed in the preparation of
the emulsion pressure-sensitive adhesives of the
present invention is a positive amount up to about 0.4
percent by weight of the total monomers, preferably
from about 0.1 to about 0.25 percent by weight. The
35 preferred reactive surfactants are anionic vinyl
functional surfactants, such as sodium vinyl sulfonate
and sodium styrene sulfonate.



1 The emulsion adhesives of the instant invention may
be prepared with excellent conversions at reaction
temperatures ranging from 70 to about 85°C in the
presence of from about 0.5 to about 1 percent by
5 weight, based on the weight of the monomers, of a
persulfate or equivalent catalyst, with the monomer mix
being fed over a period of about 4 to about 5 hours.
Reaction pH is from about 2.5 to about 7.0. Conversion
is high, approaching 100 percent at the reaction
10 conditions set forth above.

 The use of the multifunctional monomers of this
invention having cyanurate or phosphate moieties give
a significant improvement in cohesive strength without
much loss of peel and tack. The multifunctional
15 monomers may be used with or without a chain transfer
agent, and cross-linking agents, e.g. metal salts such
as aluminum acetate. It has been found that
copolymerizing multifunctional acrylate monomers
without said moieties are not effective in improving
20 guillotinability and elevated temperature performance.

 The present invention provides low cost water borne
pressure-sensitive adhesives which exhibit high
guillotinability and excellent adhesive performance at
room temperature and after elevated temperature aging.
25 The multifunctional monomers used in this invention
provide hydrogen bonding with functional groups such as
carboxy groups and enhance adhesion to polar substrates
without affecting peel and tack. Shear performance is
further enhanced by metal cross-linking. This creates
30 a highly cohesive net work which enhances guillotine
performance.

Detailed Description

 The present invention relates to pressure-sensitive
35 adhesive compositions based on emulsion polymers which
provide excellent processability including
guillotinability and high adhesion and high tack to



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1 polar, nonpolar and difficult-to-bond substrates with
excellent cohesion. The adhesives have properties
sufficient to make them useful for replacing solvent
polymers, tackified styrene-butadiene emulsion
5 pressure-sensitive adhesives, and nontackified and
tackified acrylic pressure-sensitive adhesives. An
improvement exhibited over tackified styrene-butadiene
resin adhesives include better aging and no edge ooze
or bleed as part of a release liner adhesive face stock
10 laminate. In addition, being functional as a single
polymer, there is a minimal or no need for compounding
and tackification. The improved performance
characteristics of the adhesive of the instant
invention enable them to be used on almost any
15 available face stock. Properties induced in the
adhesive by proper selection of monomers and
surfactants give excellent moisture resistance.

As compared to prior art acrylic pressure-sensitive
adhesives which do not give good adhesion to nonpolar
20 surfaces, such as polyolefins and certain other
surfaces such as recycled corrugated board, without
tackification with attendant sacrifice in cohesive
strength and elevated-temperature performance, the
adhesives prepared in accordance with the instant
25 invention have excellent adhesion to both polyolefins
and corrugated board and good elevated-temperature
performance. The adhesives are more universal in their
use, a result not heretofore achieved in single polymer
adhesives.

30 The emulsion based pressure-sensitive adhesives of
the instant invention contain, on a percent by weight
basis from about 35 to about 95 percent by weight total
monomers of at least one soft monomer preferably an
alkyl acrylate or vinate containing about 4 to about 12
35 carbon atoms in the alkyl group and which have a glass
transition temperature (T_g) of less than -25°C.
Preferably, a mixture of alkyl acrylates are employed



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1 with the total alkyl acrylate concentration, in an
amount of from about 35 to 60 more preferably 40 to
about 50 percent by weight of the monomers. Useful
alkyl acrylates include n-butyl acrylate, 2-ethylhexyl
5 acrylate, isooctyl acrylate and the like, with a
mixture 2-ethylhexyl acrylate and butyl acrylate being
preferred. These are "soft monomers" because of low
glass transition temperature. Other soft monomers
of the instant invention are one or more diesters of a
10 dicarboxylic acid and mixtures thereof, present in a
total amount of from about 0 to about 30 percent by
weight based on the total weight of the monomers
preferably from 5 to about 30 percent by weight of the
monomers. Each ester group of the diester of the
15 dicarboxylic acid independently contains from about 4
to about 12, preferably from about 8 to about 12 carbon
atoms. The preferred diesters are di-2-ethylhexyl
maleate, di-2-ethylhexyl fumarate and mixtures thereof.
The diester monomers improve tack and overall adhesive
20 properties.

The balance of the monomers are "hard monomers"
having a T_g greater than about 0°C. They include vinyl
esters, carboxylic acids and methacrylates.

Vinyl esters may be present in a total amount of
25 from about 0 to about 35 percent by weight, preferably
from about 20 to about 25 percent by weight based on
total weight of the monomers, said vinyl esters
containing from 2 to about 16 carbon atoms in the alkyl
group of the ester. Representative of the vinyl esters
30 include vinyl acetate, vinyl butyrate, vinyl
propionate, vinyl isobutyrate, vinyl valerate, vinyl
versitate, and the like. Vinyl acetate is preferred.
The vinyl esters aid in the copolymerization of maleate
and fumarate monomers and enhance cohesive strength and
35 peel adhesion.

The inclusion of one or more unsaturated carboxylic
acids containing from about 3 to about 5 carbon atoms



1 enhances cohesive strength, adhesion to polar surfaces
and stabilizes the particles formed during emulsion
polymerization. The unsaturated carboxylic acids are
provided in a positive amount of up to about 10 percent
5 by weight of the polymer, preferably from 1 to about 5
percent by weight. The unsaturated carboxylic acids
include, among others, acrylic acid, methacrylic acid,
itaconic acid, and the like. Acrylic acid, methacrylic
acid, and more preferably mixtures thereof, are
10 presently preferred.

Cohesive strength may be enhanced by inclusion of an
alkyl methacrylate containing from 1 to about 8 carbon
atoms in the alkyl group and present in an amount of
from 0 to 10 percent by weight of the monomers. Methyl
15 methacrylate is presently preferred.

The emulsion adhesives of the instant invention are
preferably prepared in the presence of a reactive
surfactant which polymerizes during formation of the
polymer and becomes an integral part of the polymer.
20 Preferred reactive surfactants include anionic vinyl
functional monomers such as sodium vinyl sulfonate and
sodium styrene sulfonate and the like. The reactive
surfactant is present as part of the total surfactant
system and in an amount up to about 0.4 percent by
25 weight of the total monomers, preferably about 0.1 to
about 0.25 percent by weight.

An essential component of the instant invention is
a reactive multifunctional monomer which is an acrylate
and/or methacrylate having a cyanurate or phosphate
moiety and present in an amount of from 0.1 to about 1
30 percent by weight of the monomers. The multifunctional
monomers improve guillotinability without adversely
affecting adhesive properties. The presently preferred
m u l t i - f u n c t i o n a l m o n o m e r s a r e
35 tris-(2-hydroxyethyl)isocyanurate triacrylate and
bis-(methacryloxyethyl) phosphate.



1 Presently preferred emulsion polymers contain,
exclusive of reactive monomers, about 25 to 35 percent
by weight 2-ethylhexyl acrylate, about 15 to 25 percent
by weight butyl acrylate, about 20 to 25 percent by
5 weight vinyl acetate, about 15 to 25 percent by weight
di-2-ethylhexyl maleate (dioctyl maleate), about 0.5
percent by weight tris-(2-hydroxyethyl) isocyanurate
triacylate, about 2 percent by weight acrylic acid,
and about 2 percent by weight methacrylic acid.

10 The monomer proportions are normally adjusted in
such a way that the adhesive has a glass transition
temperature less than about -20°C , giving a good
balance of adhesion and tack at room temperature and
elevated temperatures. The emulsion polymers of this
15 invention have a very broad glass transition
temperature range of from 15 to 30°C , which is unusual
among acrylic polymers. Conventional acrylic polymers,
for instance, have a glass transition temperature range
of only 10 to 15°C . Depending on polymerization
20 conditions, copolymers showing two distinct glass
transition temperatures, have been observed.

The preferred gel content or percent insolubles are
in excess of 60 percent by weight which provides
excellent cohesive strength and high performance. In
25 this regard, gel represents the amount of polymer which
is insoluble in tetrahydrofuran expressed in percent by
weight and determined by the membrane gel partitioning
method. In this method, about 600 to 800 milligrams of
100 percent solid polymer is weighed onto a millipore
30 membrane disk of 5 micrometer porosity. The disk is
heat sealed and transferred to a scintillation vial.
About 20 milliliters of tetrahydrofuran is added to the
vial and the vial is rotated on a shaker for 16 to 24
hours. The sealed disk is then removed, washed with
35 tetrahydrofuran, and dried first by placing it on a
Whatman No. 1 filter paper, followed by exposure to
 100°C in the oven for a few hours. The dried disk is



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1 weighed and the insoluble portion of the polymer
determined by the equation:

$$\text{Per cent insoluble} = \frac{(b - c) \times 100}{a} = \% \text{ gel}$$

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wherein

a = total weight of 100 percent solids
polymer

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b = the weight of the polymer plus
membrane before tetrahydrofuran
treatment

c = polymer plus membrane remaining after
tetrahydrofuran treatment.

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Other aids which may be used to develop
cross-linking include thermal cross-linking and
cross-linking by actinic and electron beam radiation.

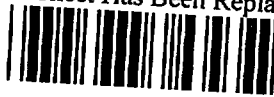
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The polymers of the instant invention are prepared
by emulsion polymerization under conditions of
agitation in an autogenous atmosphere in the presence
of suitable polymerization initiators such as
peroxydisulfate and peroxides. Depending on desired
polymer properties including gel content, the preferred
levels of these initiators are in the range of from
about 0.5 to about 1.0 percent by weight based on the
total weight of the monomers. The presently preferred
initiators are potassium persulfate, t-butyl hydrogen
peroxide, and the like. Level of agitation will vary
depending on the system and will influence conversion.
Typically, about 30 to 50 percent of the total
initiator is added along with an initial monomer charge
to the reactor, and the rest is added along with the
balance monomers during polymerization over a period of
from about 4 to about 5 hours. For the polymer to be
free from coagulum and to maintain grit levels less
than 20 ppm, it is desirable to maintain the pH of the
emulsion during polymerization between from about 2 to
about 4, preferably from about 2.5 to about 4. This



1 can be achieved by the use of buffers such as sodium bicarbonate and sodium acetate, typically in amounts up to 0.3 percent by weight based on the weight of the monomer.

5 The stabilizer system used during polymerization contains a combination of anionic and nonionic surfactants present in an amount up to about 3.5 percent by weight based on the weight of the monomers. A suitable anionic surfactant is the sodium salt of an
10 ethoxylated nonylphenol sulfate, and a suitable nonionic surfactant is ethoxylated nonylphenol. The best balance of properties is achieved by maintaining the anionic to nonionic surfactant ratio approximately 3 to 1.

15 Polymers of the instant invention are produced at high solids level content, typically about 50 to about 70 percent by weight. Reaction is carried out at temperatures from 70 to 85°C with an initial charge of up to about 10 percent by weight of the total monomers,
20 with the balance of the monomers being added to the emulsion reaction system over a period of about 4 to about 5 hours, with total monomer conversion approaching 100 percent.

It is possible to modify the rheology of the polymer
25 for coating purposes by use of conventional thickeners such as SCT-270 manufactured and sold by Union Carbide and present in an amount up to 0.2 percent by weight. Although not required, it is also feasible to modify the properties by the use of tackifiers and the like.
30 For general purpose applications, it is desirable to have good adhesion to both hydrophobic substrates such as polyethylene and hydrophilic substrates such as stainless steel and difficult-to-bond recycled corrugated board. Prior art acrylic polymers do not
35 have good adhesion to such substrates unless they are modified by addition of a tackifier. This is not required using the pressure-sensitive adhesive polymer



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1 of this invention although tackifiers can be effectively used to tailor adhesion to a substrate.

5 In accordance with the present invention, there is also provided emulsion pressure-sensitive adhesive polymers with high shear performance even at elevated temperature with little or no detriment in peel and tack adhesion which can be used to replace high cost solvent acrylic polymers used in film applications. The di-2 ethylhexyl maleate in the composition provides
10 tackiness to the adhesive and allows the use of vinyl acetate which provides good peel adhesion without the use of high levels of acid monomer which tends to reduce tack.

15 The presence of the multifunctional monomer in the copolymer itself provides some improvement in shear performance which may not be sufficient for high performance film applications. Further cross-linking by complex formation with metal salts dramatically enhances the shear in excess of 10,000 min. Elevated
20 temperature (70°C) shear is also greatly improved, with performance of the emulsion polymers being equivalent to solvent acrylic polymers. Adding multifunctional monomers to the copolymer may alter the gel content and/or glass transition temperature of the adhesive.
25 Accordingly, when multifunctional monomers are used, they are added in an amount that yields an adhesive that is pressure-sensitive, i.e., the glass transition temperature is sufficiently low as to enable use as a PSA.

30 To maintain good balance of peel and tack with high shear it may be desirable to lower the molecular weight of the polymer by the use of chain transfer agents such as n-dodecyl mercaptan(n-DDM) and to use higher levels of initiator than what is commonly used. An optimum
35 level of n-DDM in this invention is up to about 0.025 percent by weight of the monomers, preferably about 0.005 to about 0.01 percent by weight, and to employ a



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1 level of initiator of about 0.6 to about 0.75 percent
by weight based on the weight of the monomer
composition. Amounts exceeding these levels can result
in cohesive failure in peel adhesion on certain
5 substrates which will be detrimental to the product
application. Aluminum acetate, if present, is normally
present in an amount up to about 0.25 percent by weight
of the monomers.

10 Examples 1 to 4 and Controls 1 and 2

To a one liter reactor equipped with a reflux
condenser, a thermocouple, a pitched turbine agitator
and a nitrogen inlet tube, there was charged a solution
containing 75 g of deionized water, 2.5 g of sodium
15 vinyl sulfonate (25 percent w/w solution in water) and
0.36 g of an anionic surfactant (Polystep B-27, a
sodium salt of ethoxylated nonylphenol sulfate
manufactured and sold by Stepan Chemical Co.). A
monomer mix consisting of 175 g of 2-ethylhexyl
20 acrylate, 75 grams of butyl acrylate, 125 g of di-2
ethylhexyl maleate, 105 g of vinyl acetate, 5 g of
acrylic acid, 5 g of methacrylic acid and 2.25 g of
tris (2-hydroxy-ethyl) isocyanurate was added to 117.6
g of water containing 43.6 g of Polystep B-27 and 6.37
25 g of Polystep F-9 and agitated to make a pre-emulsion.
The reactor charge was heated under nitrogen to
72-75°C, to which was added 20.93 g of a 4.46 w/w
potassium persulfate solution in deionized water.
After a few minutes 66 grams of the pre-emulsified
30 monomer and 10.46 g of potassium persulfate solution
were added to the reactor over 20 to 30 minutes. To
the remaining pre-emulsion there was added a pre-mixed
solution containing 2.4 g water, 0.9 g, Polystep B-27,
0.13 g Polystep F-9, 5 g each of methacrylic acid and
35 acrylic acid and 0.025 gm. n-DDM. After the
temperature reached a steady state, the remaining
monomer pre-emulsion and a 2.07% aqueous solution of



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1 potassium persulfate buffered with sodium bicarbonate
were introduced into the reactor at respective rates of
2.25 and 0.275 g/min. for a period of 270 - 280
minutes. The reactor temperature was maintained
5 between 79 to 82°C. Thirty minutes after the feed, a
2.625 g 4.8% solution of potassium persulfate was added
and maintained for 45 minutes. A second solution of
2.625 g was again added and maintained for 45 minutes.
Once the polymerization was complete, the contents were
10 cooled to ambient temperature neutralized with ammonia
to a pH of 5.5 - 6.5 and discharged. The polymer had
58.9 percent solids, and a Tg of -32°C.

Using the above procedure with n-DDM being omitted
the polymers listed in Table 1 were prepared.

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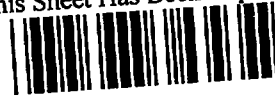
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Table 1

5 Example	Monomer Composition	Weight Ratio ‡	Solids
Ex. 2	2-EHA/DOM/VAC/BA/HEITA/AA/MAA	30/25/21/20/0.45/2/258.6	
Ex. 3	do	30/25/21/20/0.60/2/258.5	
Ex. 4	do	30/25/21/20/0.80/2/258.4	
10 Ex. 5	2-EHA/DOM/VAC/BA/HEITA/AA/MAA	25/25/21/25/0.45/2/258.6	
Ex. 6	do	25/25/21/25/0.60/2/258.6	
Ex. 7	do	25/25/21/25/0.80/2/259.1	
Ex. 8	do	26/20/25/25/0.60/2/258.0	
Ex. 9	2-EHA/DOM/VAC/BA/bisMOEP/AA/MAA	30/25/21/20/0.40/2/258.1	
15 Control 1	2-EHA/DOM/VAC/BA/AA/MAA	30/25/21/20/2/259.25	
Control 2	do	25/25/21/25/2/258.25	
20	2-EHA = 2-ethylhexyl acrylate DOM = di(2-ethylhexyl) maleate VAC = vinyl acetate BA = butyl acrylate HEITA = tris (2-hydroxyethyl)isocyanurate triacrylate bisMOEP = bis(methacryloxyethyl)phosphate		



1 For Examples 10 to 18 the monomers of Examples 2 to 9 were polymerized except that the monomer composition included 0.025 g of n-DDM as in Example 1.

5 Table 2 shows the guillotine performance of the emulsion polymer of Example 1 and some polymers from Table 1. The polymers were coated on a release liner at a coat weight of 22-24 g/sqm and then laminated to 60 pound per ream litho paper. 100 sheets measuring 2.5 mm x 200 mm were then cut using the guillotine press. As can be seen, from Table 2 most of the polymers show excellent guillotine performance. The lowest rating is very good indicative of the fact that these compositions will perform well on the guillotine press for sheeting of PSA constructions.

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Table 2
Guillotine Performance

	<u>Example</u>	<u>Rating¹ Blade</u>	<u>Smear²</u>
20	Ex 1	1.5	1.5
	Ex 1, plus 0.06% Al acetate	1-1.5	1-1.5
	Ex 2	2	2
	Ex 3	1-1.5	2
	Ex 4	1.5	1.5
25	Ex 5	1.5	1.5
	Ex 6	1.5	1.5

¹Ratings

- 30 1 = Excellent
2 = Very Good
3 = Good
4 = Fair
5 = Poor
6 = Very Poor

²Smear is the adhesive spread on the guillotined stack of labels.

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Table 3 shows the adhesive performance initially and after aging at 70°C for one week and three weeks using the same adhesive construction as was used for Table 2.

Table 3

Performance on Paper (Litho)

Sample #	Initial			1 Wk @ 70°C			3 Wks @ 70°C		
	Loop			Loop			Loop		
	90° Peel	Tack	RTS	90° Peel	Tack	RTS	90° Peel	Tack	RTS
	N/m	N/m	Min.500g	N/m	N/m	Min.500g	N/m	N/m	Min.500g
Ex 1	488pt	660	1660C	-	-	6430C			
Ex 1 0.12%AA	480pt	675	3200ps/c	-	-	8450ps			
Ex 2	354pt	574	4130ps/c	331pt	520	6185C	401pt	575	8600C
Ex 4	360pt	600	6924C	370pt	583	8000+	400pt	570	-
Ex 5	400pt	590	2350ps/c	383pt	640	-	360pt	615	3000+
Ex 6	470pt	710	6000+	425pt	660	6000+	425pt	617	10,000+
Ex 7	415pt	700	1600C	420pt	570	2300C			
Ex 8	480pt	700	1386ps	440pt	627	2400ps	420pt	655	-
Control 1	465pt	730	6200C	433pt	685p	4600ps	438pt	635	-

AA= Aluminum acetate

C = Cohesive failure

ps= Panel Stain

pt= Facestock Tear

RTS= Room Temperature Shear

It is evident from Table 3 that aging improves the shear performance without sacrificing the peel and tack adhesion, a phenomenon which is unusual and unique since normally all pressure-sensitive adhesives tend to loose adhesion properties on aging at elevated



1 temperatures, some drastically and some to a lesser extent, especially when there is a shear improvement.

Table 4 illustrates the performance using 2 mil mylar as the facestock, initially, as well as after
 5 70°C aging. All the samples were coated on mylar at a coat weight of 25-30 g/sqm. Again it is apparent that the adhesion properties are not affected by aging irrespective of the facestock, whereas the aceto-
 10 acetoxyl ethyl methacrylate (AAEMA) containing polymers do show some adhesion loss on aging (Table 8 in U.S. Application Serial No.393,970).

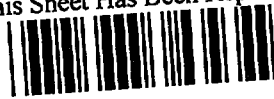
Table 4

15 Performance Using Polyester (mylar) as facestock

1Kg. Sample #	180° Peel N/m		Loop Tack N/m		RTS 500g	70°C Shear
	20 min.	1wk, @70°C	20 min.	1wk, @70°C	1/2x1/2" min.	1x1" min.
Ex 1	395	355	370	395	3000+	-
20 Ex 1 0.12AA	320	390	420	435	10000+	10000+
Ex 3	450	445	590	500	3225C	-
Ex 3 0.12AA	390	445	520	550	10000+	-
Ex 6	345	420	445	510	-	-
25 Control 1	385	430	355	375	2350C	-

The polymers of the present invention also exhibit very high elevated temperature shear exceeding 10000+ minutes showing its utility in high performance tapes such as automotive tapes. The elevated temperature shear was measured at 70°C using 1"x1" sample, with 24 hour dwell time, using a 1Kg load.

The adhesives of the present invention also show very good mandrel performance to make them suitable for pharmaceutical applications where solvent adhesives are currently being used. Examples 1, 3,4 and 6 were



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1 tested for mandrel on 0.25 inch diameter glass tube and
0.5 inch diameter polyethylene rod. All the samples
gave a rating of 3.5-4 indicative of very minimal lift
($<1/16$ inch) and the suitable applicability of the
5 polymer on curved substrates.

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Claims:

1. ~~In the formation of~~ ^{An} inherently tacky pressure-sensitive adhesive polymer ~~formed~~ ^{by} emulsion polymerization of at least one soft ~~alkyl acrylate or vinyl~~ ^{preferably an alkyl acrylate or vinyl} monomer having a glass transition temperature less than about -25°C and at least one hard monomer having a glass transition temperature greater than 0°C , ~~the improvement which comprises forming the polymer~~ in the presence of at least one reactive multifunctional monomer having at least two acrylate or methacrylate groups and a cyanurate or phosphate functionality, said multifunctional monomers being present in an amount of from 0.1 to about 1 percent by weight of the monomers, ^{wherein, preferably} ~~a pressure-sensitive adhesive as claimed in any one of the previous claims in which~~ the reactive multifunctional monomer is selected from the group consisting of tris(2-hydroxyethyl) isocyanurate triacrylate, bis(methacryloxyethyl) phosphate and mixtures thereof.

2. An inherently tacky, pressure-sensitive adhesive polymer formed by emulsion polymerization as claimed in claim 1, which polymer comprises, on a polymerized basis:

(a) at least of one alkyl acrylate containing from about 4 to about 12 carbon atoms in the alkyl group, the total amount of alkyl acrylate present in an amount of from about 35 to about 95 percent by weight of the monomers;

(b) at least one monomer selected from the group consisting of:

(i) vinyl ester containing from 2 to about 16 carbon atoms in the alkyl group of the ester,

^{preferably,}
~~5. A pressure-sensitive adhesive polymer as claimed in any one of claims 2 to 4 in which~~ the vinyl ester is present in a total amount of from about 20 to about 25 percent by weight based on the total weight of the monomers;



(ii) diesters of a dicarboxylic acid in which each alkyl group of the diester independently contains from about 4 to about 12 carbon atoms,

preferably,

~~6. A pressure-sensitive adhesive polymer as claimed in any one of claims 2 to 5 in which~~ the diester of the dicarboxylic acid is selected from the group consisting of di-2-ethylhexyl maleate, di-2-ethylhexyl fumarate, and mixtures thereof;

(iii) unsaturated carboxylic acids containing from about 3 to about 5 carbon atoms, *preferably*

~~7. A pressure-sensitive adhesive polymer as claimed in any one of claims 2 to 6 in which~~ the unsaturated carboxylic acid is present in an amount of from about 2 to about 5 percent by weight of the total monomers, *and further preferably*

~~8. A pressure-sensitive adhesive polymer as claimed in any one of claims 2 to 7 in which~~ the unsaturated carboxylic acid is selected from the group consisting of acrylic acid, methacrylic acid, and mixtures thereof;

(iv) methacrylates containing from 1 to about 8 carbon atoms in the alkyl group and,

(c) at least one reactive multifunctional monomer having at least two acrylate or methacrylate groups and a cyanurate or phosphate functionality, said multifunctional monomer being present in an amount from 0.1 to about 1 percent by weight of the monomers.

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3. An inherently tacky, pressure-sensitive adhesive polymer formed by emulsion polymerization as claimed in claim 1 or 2, which polymer comprises, on a polymerized basis and based on the total weight of the monomers:

(a) at least of one alkyl acrylates containing from about 4 to about 12 carbon atoms in the alkyl group, the total amount of alkyl acrylate present being from about 35 to about 95 percent by weight of the monomers; *and preferably*

(b) from 0 to 35 percent by weight of the monomers of at least one vinyl ester containing from 2 to about 16 carbon atoms in the alkyl group of the ester; *and further preferably*

(c) from 5 to about 30 percent by weight of the monomers of a diester of a dicarboxylic acid in which each alkyl group of the diester independently contains from about 8 to about 12 carbon atoms; *and*

further preferably (d) positive amount up to about 10 percent by weight of the monomers of at least one unsaturated carboxylic acid containing from about 3 to about 5 carbon atoms and; *and further preferably*

(e) an alkyl methacrylate containing from 1 to about 8 carbon atoms and present in an amount from 0 up to about 10 percent by weight of the monomers; *and*

further preferably (f) at least one reactive multifunctional monomer having at least two acrylate or methacrylate groups and a cyanurate or phosphate functionality, the total amount of multifunctional monomer present being from 0.1 to about 1 percent by weight of the monomers and said polymer being formed in the presence of a reactive surfactant.

4. A pressure-sensitive adhesive polymer as claimed in any one of the previous claims in which the alkyl acrylate is a mixture of 2-ethylhexyl acrylate and butyl acrylate.



58. A pressure-sensitive adhesive polymer as claimed in ~~any one of~~ claims ~~3 to 8~~ ^{and 4} in which the reactive surfactant is selected from the group consisting of sodium vinyl sulfonate and sodium styrene sulfonate and present in an amount up to 0.4 percent by weight based on the total weight of the monomers, and preferably,

~~60. A pressure-sensitive adhesive polymer as claimed in claim 9 in which~~ the reactive surfactant is present in an amount of 0.1 to about 0.25 percent by weight of the total monomers.

62. A pressure-sensitive adhesive as claimed in any one of the previous claims in which the polymer is formed in the presence of a chain transfer agent, wherein preferably

~~63. A pressure-sensitive adhesive as claimed in claim 12 in which~~ the chain transfer agent is n-dodecyl mercaptan, and further preferably

~~64. A pressure-sensitive adhesive as claimed in claims 12 or 13 in which~~ the chain transfer agent is present in an amount up to about 0.025 percent by weight of the monomers.

7. A method for producing inherently tacky pressure sensitive adhesive polymers, comprising the steps of:

emulsion polymerisation of

(i) on a percent by weight

basis from about 35 to about 95 percent by weight total monomers of at least one soft monomer preferably an alkyl acrylate or vinate containing about 4 to about 12 carbon atoms in the alkyl group and which have a glass transition temperature (T_g) of less than -25°C. Preferably, a mixture of alkyl acrylates are employed with the total alkyl acrylate concentration, in an amount of from about 35 to 60 more preferably 40 to about 50 percent by weight of the monomers. Useful



alkyl acrylates include n-butyl acrylate, 2-ethylhexyl acrylate, isooctyl acrylate and the like, with a mixture 2-ethylhexyl acrylate and butyl acrylate being preferred, *and preferably*

(ii) about 0 to about 30 percent by

weight based on the total weight of the monomers preferably from 5 to about 30 percent by weight of the monomers, *where in* Each ester group of the diester of the dicarboxylic acid independently contains from about 4 to about 12, preferably from about 8 to about 12 carbon atoms, *and* The preferred diesters are di-2-ethylhexyl maleate, di-2-ethylhexyl fumarate and mixtures thereof,

(iii) hard monomers with a glass transition temperature greater than 0°C, such as vinyl

esters, carboxylic acids and methacrylates, *where the*

Vinyl esters may be present in a total amount of from about 0 to about 35 percent by weight, preferably from about 20 to about 25 percent by weight based on total weight of the monomers, said vinyl esters containing from 2 to about 16 carbon atoms in the alkyl group of the ester, *and* Representative of the vinyl esters include vinyl acetate, vinyl butyrate, vinyl propionate, vinyl isobutyrate, vinyl valerate, vinyl versitate, and the like, *and/or*

The inclusion of one or more unsaturated carboxylic acids containing from about 3 to about 5 carbon atoms

where in the unsaturated carboxylic acids *are* may be provided in a positive amount of up to about 10 percent by weight of the polymer, preferably from 1 to about 5 percent by weight, *and* The unsaturated carboxylic acids include, among others, acrylic acid, methacrylic acid, itaconic acid, and the like, *and* Acrylic acid, methacrylic acid, and more preferably mixtures thereof, are presently preferred, *and for the*



~~[Cohesive strength may be enhanced by]~~ inclusion of an alkyl methacrylate containing from 1 to about 8 carbon atoms in the alkyl group and present in an amount of from 0 to 10 percent by weight of the monomers, ^{wherein} Methyl methacrylate is presently preferred;

(iv) and preferably a reactive surfactant which polymerizes during formation of the polymer and becomes an integral part of the polymer. Preferred reactive surfactants include anionic vinyl functional monomers such as sodium vinyl sulfonate and sodium styrene sulfonate and the like, ^{wherein} The reactive surfactant is present as part of the total surfactant system and in an amount up to about 0.4 percent by weight of the total monomers, preferably about 0.1 to about 0.25 percent by weight;

(v) a reactive multifunctional monomer which is an acrylate and/or methacrylate having a cyanurate or phosphate moiety and present in an amount of from 0.1 to about 1 percent by weight of the monomers, and the

presently preferred multi-functional monomers are tris-(2-hydroxyethyl)isocyanurate triacrylate and bis-(methacryloxyethyl) phosphate.

8. The method of claim 7, wherein reaction temperatures range ~~from~~ from 70 to about 85°C in the presence of from about 0.5 to about 1 percent by weight, based on the weight of the monomers, of a persulfate or equivalent catalyst, with the monomer mix being fed over a period of about 4 to about 5 hours, and Reaction pH is from about 2.5 to about 7.0.