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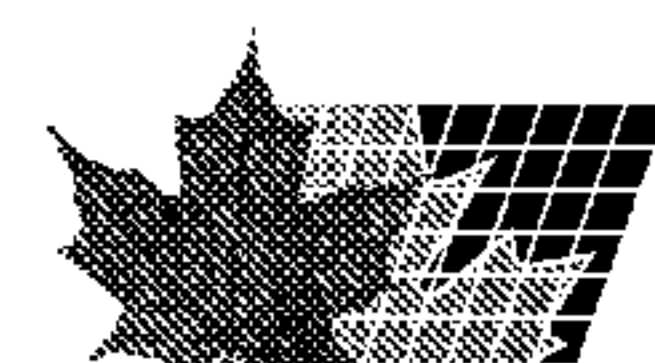
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(72) Inventeurs/Inventors:  
BERNARD, MARGARET MALLIKA, US;  
SCHNIEDERS, LAWRENCE JOSEPH, US  
(73) Propriétaire/Owner:  
AVERY DENNISON CORPORATION, US  
(74) Agent: FETHERSTONHAUGH & CO.

(54) Titre : COMPOSITION AUTO-ADHESIVE LAVABLE POUR SUPPORTS RECYCLABLES  
(54) Title: REMOVABLE PRESSURE-SENSITIVE ADHESIVES FOR RECYCLABLE SUBSTRATES

(57) **Abrégé/Abstract:**

There is provided hot water and alkali removable pressure-sensitive adhesive composition based on emulsion pressure-sensitive adhesive polymers used in combination with a rosin based acidic tackifier and a rosin based surfactant.





## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| <b>(51) International Patent Classification <sup>5</sup> :</b><br>C09J 133/08, C08L 93/04<br>C08L 31/02, 33/08<br>C08F 220/10                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | <b>A1</b> | <b>(11) International Publication Number:</b> <b>WO 93/13181</b><br><b>(43) International Publication Date:</b> 8 July 1993 (08.07.93)<br><b>2126351</b>                                                                                                                                                                                             |
| <b>(21) International Application Number:</b> PCT/US92/11161<br><b>(22) International Filing Date:</b> 22 December 1992 (22.12.92)<br><br><b>(30) Priority data:</b><br>813,354 24 December 1991 (24.12.91) US<br><br><b>(71) Applicant:</b> AVERY DENNISON CORPORATION [US/<br>US]; 150 N. Orange Grove Boulevard, Pasadena, CA<br>91109 (US).<br><br><b>(72) Inventors:</b> BERNARD, Margaret, Mallika ; 5479 Finch<br>Street, LaVerne, CA 91750 (US). SCHNIEDERS, Law-<br>rence, Joseph ; 1151 East 344th Street, East Lake, OH<br>44095 (US).<br><br><b>(74) Agent:</b> GRINNELL, John, P.; Christie, Parker & Hale,<br>P.O. Box 7068, Pasadena, CA 91109-7068 (US). |           | <b>(81) Designated States:</b> AU, BB, BG, BR, CA, CS, FI, HU, JP,<br>KP, KR, LK, MG, MN, MW, NO, PL, RO, RU, SD, Eu-<br>ropean patent (AT, BE, CH, DE, DK, ES, FR, GB, GR,<br>IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF,<br>CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).<br><br><b>Published</b><br><i>With international search report.</i> |
| <b>(54) Title:</b> REMOVABLE PRESSURE-SENSITIVE ADHESIVES FOR RECYCLABLE SUBSTRATES<br><br><b>(57) Abstract</b><br><br>There is provided hot water and alkali removable pressure-sensitive adhesive composition based on emulsion pressure-sensitive adhesive polymers used in combination with a rosin based acidic tackifier and a rosin based surfactant.                                                                                                                                                                                                                                                                                                             |           |                                                                                                                                                                                                                                                                                                                                                      |

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10           **REMOVABLE PRESSURE-SENSITIVE ADHESIVES FOR**  
                  **RECYCLABLE SUBSTRATES**

**Field of Invention**

15           This invention relates to pressure-sensitive  
adhesives formulated to exhibit the properties of a  
permanent adhesive for use with paper and polymer film  
backed labels and which remove cleanly from nonpaper  
surfaces such as polymeric (plastic), glass and metal  
substrates under the action of hot water or with hot  
20           alkaline solutions such as household detergent  
solutions or caustic alkali solutions with or without  
use of some manual force to assist removal.

**Background of the Invention**

25           Pressure-sensitive adhesives which are used for  
label applications do not in general remove cleanly  
from nonpaper substrates. Some residue of the adhesive  
is left on the substrate thus making its cleaning less  
effective or more involved. There is a growing need in  
30           the market today for environmentally or user friendly  
pressure-sensitive adhesive labels which can be cleanly  
removed from the substrate during domestic or  
industrial cleaning processes. This is true in the  
case of price marking and product identification labels  
35           used on metals, polymers (plastics), glass, wood and  
painted or water resistant coated substrates.

          Attention in this regard has focused on water

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1 dispersible, water soluble, repulpable and wet stick  
adhesives. Most of the base polymers for such  
adhesives are not inherently pressure-sensitive  
adhesives. Being nontacky they require the addition of  
5 high levels of plasticizers and/or tackifiers.  
Carboxyl content of the base polymer is also high,  
exceeding 10% by weight of the polymer, such carboxyl  
groups are incorporated into the polymer during  
polymerization. When the base polymer used for a  
10 removable adhesive is pressure-sensitive, it is usually  
compounded with at least 10% by weight of a vinyl  
carboxylic acid polymer either in the acid or salt form  
and various amounts of plasticizers and/or tackifiers.

U.S. Patent 4,033,918 to Hauber discloses a water  
15 removable pressure-sensitive adhesive composition which  
comprises based on 100 parts weight of the total  
solids, of from 25 to 35 parts by weight of a  
crosslinked acrylic acid ester copolymer which contains  
10 to 20% by weight of unsaturated carboxylic acid,  
20 vinyl acetate, 2-ethyl hexyl acrylate, acrylonitrile,  
diethyl maleate and mixtures thereof, from 10 to 20  
parts by weight of an uncrosslinked acrylic acid ester  
copolymer, from 10 to 20 parts by weight of  
polyvinylmethyl ether, from 10 to 20 parts by weight of  
25 an alkali metal and/or ammonium salt of polyacrylic  
acid, polymethacrylic acid or a copolymer of acrylic  
and methacrylic acids; 10 to 20 parts by weight of  
monomeric plasticizer such as a polyvinyl methyl ether  
or phthalate ester and 10 to 15 parts by weight of an  
30 emulsifying agent such as ethoxylated phenols.

U.S. Patents 3,865,770, 4,413,080 and 4,569,960 to  
Blake disclose tapes providing water dispersible/water  
soluble pressure-sensitive adhesives for use as a  
repulpable splicing tape. The adhesives described are  
35 solvent polymerized alkyl acrylate and acrylic acid  
polymers, neutralized with alkanolamines, or potassium  
hydroxide used in combination with sodium hydroxide

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1 and/or lithium hydroxide. The polymer is further  
blended with acidic rosin or rosin derivatives and  
plasticized with hydrophilic polyoxyethylene compounds.  
Adhesive compositions comprise a polymer containing 60-  
5 85% alkyl acrylate and 10 to 40% vinyl carboxylic acid.  
The formulated adhesives have 35 to 150 parts by weight  
of acidic rosin, and/or 50 to 250 parts by weight of  
surfactant (ethoxylated alkyl phenols and/or complex  
acidic esters of phosphoric acid). High levels of  
10 plasticizer and high levels of rosin acid pose aging  
problems due to separation or migration thereby  
decreasing the adhesive properties. The adhesive tapes  
are sold in closed containers to preserve adhesive  
properties which are rapidly lost on exposure to  
15 atmospheric humidity.

U.S. Patent No. 4,492,724 to Albright, et al.  
describes a humidity resistant wet-stick  
pressure-sensitive adhesive made up of three  
components. Two are nonpressure-sensitive polymeric  
20 components containing high levels of polymerizable  
acids and the third component consisting of an  
ethoxylated alkyl arylphenol which serves as a  
plasticizer/tackifier to make the composition a  
pressure-sensitive adhesive. The first component is a  
25 copolymer of vinyl acetate, alkyl acrylate and acrylic  
acid in which the acrylic acid is present in an amount  
of from 20 to 55% by weight, the second component is an  
acrylic acid polymer which is present from 8 to 35% by  
weight and the plasticizer is present in an amount of  
30 from 20 to 65% by weight.

U.S. Patent No. 4,413,082 to Gleichenhagen, et al.  
teaches a water soluble pressure-sensitive adhesive  
composition for repulpable splicing tape comprising  
from 30 to 80 parts of a copolymer of 70 to 88% by  
weight of butyl acrylate of which 5 to 25% can be a  
35 mixture of vinyl acetate and fumaric acid dialkyl ester  
and 12 to 30% by weight vinyl carboxylic acid blended

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1 with from 20 to 70 parts by weight of a water soluble  
plasticizer which is ethoxylated alkyl phenol,  
ethoxylated alkyl mono or diamine and from 2 to 30  
5 parts by weight of an acidic rosin. The adhesive is  
water soluble and contains more than 10% of vinyl  
carboxylic acid in the polymer.

U.S. Patent 4,418,120 to Kealy, et al. relates to a  
tackified crosslinked acrylic adhesive which display  
improved adhesion to low energy substrates. The  
10 adhesive is based on a solution polymer of isooctyl  
acrylate and acrylic acid containing from 3 to 7% by  
weight acrylic acid, 100 parts of which is blended with  
20 to 50 parts of a tackifying rosin ester having an  
acid number less than 20, additionally the adhesive  
15 contains certain antioxidants and a crosslinking agent,  
is coated and dried at 70°C to allow for crosslinking.  
The composition is required to be free of surfactants  
to achieve the designated performance.

U.S. Patent 4,726,982 to Traynor, et al. relates to  
20 a tackified acrylic pressure-sensitive adhesive for  
application to high solids automotive paints. The  
adhesive is also a solution polymer of acrylic acid  
ester of nontertiary alcohol containing from 4 to 14  
carbon atoms, which polymers contain from 10 to 40  
25 parts of N-vinyl lactam and is tackified with 5 to 50  
parts, based on the weight of the polymer, of  
tackifying resins such as isobornyl methacrylate, rosin  
ester, and/or mixed aliphatic/aromatic polymeric  
tackifier resins. A suitable combination of the N-  
30 vinyl lactam and the tackifier is needed to provide  
high adhesion to automotive paint. Compositions with  
less than 10% N-vinyl lactam do not provide the high  
adhesion. The tackifying resins are either esters or  
hydrocarbon resins with no carboxyl functionality.

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**Summary of the Invention**

The present invention pertains to water insoluble pressure-sensitive emulsion polymers which on blending with low levels of a surfactant and a tackifier provide a pressure-sensitive adhesive, when applied with a paper or film backing, which can be removed clean from a nonpaper surface under at least the action of hot water or hot alkaline conditions such as detergent or caustic alkali. It aids in label removal from the substrate at the time of acquisition or at the time of substrate recycling or recovery. The formulated adhesive exhibits excellent adhesion to and clean removal from a wide variety of substrates including metal, glass and polymeric substrates (plastics). Clean removability includes self-separating, hand peeling without leaving an adhesive residue or if some residue is left, removability for the residue with no more than moderate thumb rubbing.

Accordingly, the present invention provides a pressure-sensitive adhesive composition which comprises:

(a) an acrylic, pressure-sensitive adhesive polymer formed by emulsion polymerization, which polymer comprises, on a polymerized basis and based on the total weight of the monomers:

(i) at least one alkyl acrylate containing from 4 to 8 carbon atoms in the alkyl group, the total amount of alkyl acrylate monomers being at least about 35 percent by weight of the monomers; and

(ii) at least one unsaturated carboxylic acid containing from 3 to 5 carbon atoms, present in a total positive amount up to about 5 percent by weight of the monomers, or a rubber-based emulsion polymer which is sufficiently polar to be compatible with a rosin acid tackifier and rosin-based surfactant, and

(b) as additives for each 100 parts by weight of the polymer:

(i) from about 3 to about 20 parts by

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weight of a rosin acid tackifier, and

(ii) from about 1 to about 10 parts by  
5 weight of a rosin-based surfactant,  
said pressure-sensitive adhesive composition when applied  
to paper backing being capable of clean removability from  
a nonpaper surface of a polar or nonpolar substrate on  
exposure to the action of hot water or alkali for less  
10 than about 5 minutes.

According to the present invention, there is  
provided an emulsion pressure-sensitive adhesive polymer  
which is acrylic or elastomeric-based and which is  
blended with one or more acidic rosin-based tackifiers  
15 and one or more rosin-based surfactants to provide a  
pressure-sensitive adhesive system which displays  
excellent adhesion to a wide variety of surfaces ranging  
from polar, relatively high energy surfaces such as  
stainless steel to nonpolar, relatively low energy  
20 surfaces such as polyethylene. The pressure-sensitive  
adhesive composition displays permanent adhesive  
characteristics yet removes clean from nonpaper surfaces  
of substrate under the action of hot water or an alkaline  
solution.

25 The preferred inherently tacky, acrylic emulsion  
pressure-sensitive adhesive polymers of the instant  
invention comprise, on a polymerized basis and, based on  
the total weight of the monomers, at least one alkyl  
acrylate containing from about 4 to about 8 carbon

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1 atoms in the alkyl group, preferably 2-ethyl hexyl  
acrylate, the alkyl acrylate present being in a total  
amount of at least about 35 percent by weight of the  
monomers, and at least one unsaturated carboxylic acid  
5 present in a positive amount up to 5 per cent by weight  
of the acrylic-based pressure-sensitive adhesive  
polymer. It is preferred that the alkyl acrylate be  
present in a total amount of from about 35 to about 60  
percent by weight; and that there also be present at  
10 least one vinyl ester containing from 2 to about 16  
carbon atoms in the alkyl chain of the ester,  
preferably vinyl acetate, said vinyl ester present in  
a total amount of from about 15 to about 35 percent by  
weight; at least one diester of a dicarboxylic acid  
15 wherein each alkyl group of the diester independently  
contains from about 6 to about 16 carbon atoms, with  
di-2-ethyl hexyl maleate or di-2-ethyl hexyl fumarate  
being preferred, said diesters being present in a total  
amount of from about 20 to about 40 percent by weight.  
20 It is preferred that the adhesive contain 1 to 3  
percent, of an unsaturated carboxylic acid containing  
from 3 to about 5 carbon atoms, preferably acrylic  
and/or methacrylic acid, and that said emulsion polymer  
have a glass transition temperature of less than about  
25 -30°C and a gel content of from about 50 to about 70  
percent by weight of the polymer.

Although the acrylic emulsion adhesive polymers of  
the instant invention can be prepared by using  
conventional surfactants, it is preferred to  
30 additionally employ a reactive surfactant which  
polymerizes and becomes part of the emulsion polymer.  
If employed, the amount of reactive surfactant used in  
the preparation of the emulsion pressure-sensitive  
adhesives of the present invention may be in an amount  
35 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 preferred reactive surfactants

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1 are anionic vinyl functional surfactants, such as  
sodium vinyl sulfonate and sodium styrene sulfonate.

5 The preferred acrylic emulsion polymer system  
comprises a copolymer of about 15 to about 35% by  
weight vinyl acetate, about 20 to about 40% by weight  
of di-2-ethylhexyl maleate, about 35 to about 60% by  
weight of 2-ethylhexyl acrylate and 1 to 3% by weight  
of one or more vinyl unsaturated carboxylic acids and  
for each 100 parts by weight of the polymer from about  
10 3 to about 20 parts by weight of acidic rosin or rosin  
derivative provided as a tackifier and about 1 to about  
10 parts by weight of rosin-based surfactant preferably  
an ethoxylated rosin-based surfactant.

15 The adhesives have wide applicability as an  
aggressive adhesive for paper and film labels and tapes  
which can be removed clean from the nonpaper  
substrates, thus making recycling/recovering operations  
or simply the removal of a price label at substrate  
acquisition easy. The base polymer of the present  
20 invention as compared to the '918 patent has a  
different composition in that the adhesive of this  
invention is preferably not externally crosslinked and  
preferably contain more than 20% dialkyl maleate and  
more than 20% vinyl acetate besides acrylic acid ester.  
25 The formulated adhesive contains more than 80% by  
weight of polymer, less than 5% of surfactant and less  
than 10% tackifier the later being rosin-based as  
opposed to polyvinylmethyl ether or phthalate esters.

30 The preferred elastomeric pressure-sensitive  
adhesive copolymer is a styrene-butadiene copolymer  
containing from about 20 to about 50% by weight styrene  
and is especially useful in adhering to polypropylene  
and polystyrene surfaces.

35 The acrylic-based adhesives of the present invention  
are different than the adhesives of Blake in that the  
base polymer preferably contains vinyl esters and alkyl  
diesters besides the alkyl acrylate and has low levels

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1 of vinyl carboxylic acid, i.e., much less than 10%  
contrary to the high acid requirement of Blake. The  
adhesive compositions of the present invention are not  
cold water dispersible or water soluble as taught by  
5 Blake. Blake also does not disenable the use of a  
rubber-based polymer in the adhesive composition.  
However, labels made from the composition of the  
invention remove clean from the substrate in hot water.

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1     Detailed Description

5       The present invention relates to pressure-sensitive adhesive compositions based on emulsion acrylic and rubber polymers which provide high adhesion and high tack to polar and nonpolar substrates with excellent cohesion which polymers are modified by rosin-based acidic tackifiers and rosin-based surfactants which allow retention of permanent adhesion characteristics, but which enable clean removability from a wide variety of nonpaper surfaces including metal, glass and polymeric substrates under the action of hot water and alkali solution.

15       By the expression "nonpaper surface," as used herein, there is meant a surface which does not break up or absorb significant amounts of moisture and include polar and nonpolar surfaces such as metal, glass, plastics, wood, paint, coated surfaces, even coated paper substrate which allow hot water and alkaline solutions to cause clean removability of the adhesive coated label without an adverse effect on the substrate.

25       By the expression "clean removability", there is meant self-removability, hand removability by peeling leaving no adhesive residue and if an adhesive residue remains, removability of the residue by light to moderate thumb rubbing. This duplicates the action of easy label removability from a household product after purchase without sacrifice of permanent adhesion of label with a surface while the product is on display for sale.

35       The clean removable adhesive compositions of this invention are based on acrylic-based emulsion polymers and rubber-based or elastomeric emulsion polymers which are compatible with the rosin-based surfactants and rosin-based tackifiers.

      The acrylic-based emulsion pressure-sensitive adhesive polymers used in the invention are polymers

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1 which contain at least 35 percent by weight total of  
one or more alkyl acrylates containing from about 4 to  
about 8 carbon atom in the alkyl group and a positive  
amount up to about 5 percent by weight total of vinyl  
5 unsaturated carboxylic acids containing from about 3 to  
about 5 carbon atoms.

The emulsion-based acrylic pressure-sensitive  
adhesive polymers of the instant invention are  
preferably inherently tacky polymers which contain, on  
10 a percent by weight basis, from about 35 to about 60  
percent by weight total of one or more alkyl acrylates  
containing about 4 to about 8 carbon atoms in the alkyl  
group. Preferably the total alkyl acrylate  
concentration, including mixtures of alkyl acrylates,  
15 is from about 40 to about 50 percent by weight of the  
monomers. Useful alkyl acrylates include n-butyl  
acrylate, 2-ethyl hexyl acrylate, isooctyl acrylate,  
and the like, with 2-ethyl hexyl acrylate being  
preferred.

20 The second monomeric component of the acrylic  
emulsion polymers is one or more vinyl esters present  
in a total amount of from about 15 to about 35 percent  
by weight, preferably from about 20 to about 25 percent  
by weight based on total weight of the monomers, said  
25 vinyl esters containing from 2 to about 16 carbon atoms  
in the alkyl group of the ester.

Representative of the vinyl esters include vinyl  
acetate, vinyl butyrate, vinyl propionate, vinyl  
isobutyrate, vinyl valerate, vinyl versitate, and the  
30 like. Vinyl acetate is preferred.

The third component of the acrylic emulsion polymer  
used in the instant invention is one or more diesters  
of a dicarboxylic acid and mixtures thereof, present in  
a total amount of from about 20 to about 35 percent by  
weight based on the total weight of the monomers. Each  
35 ester group of the diester of the dicarboxylic acid  
independently contains from about 6 to about 16,

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1 preferably from about 6 to about 12, carbon atoms. The  
preferred diesters are di-2-ethyl hexyl maleate,  
di-2-ethyl hexyl fumarate and mixtures thereof.

5 A fourth component of the acrylic emulsion polymers  
of the instant invention is at least one unsaturated  
carboxylic acid containing from about 3 to about 5  
carbon atoms and present in a total amount of up to  
about 5 percent by weight of the polymer, preferably  
10 from 1 to about 3 percent by weight. The unsaturated  
carboxylic acid includes, among others, acrylic acid,  
methacrylic acid, itaconic acid, and the like. Acrylic  
acid, methacrylic acid, and more preferably mixtures  
thereof, are presently preferred.

The acrylic emulsion polymers of the instant  
15 invention may be prepared in the presence of 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,  
20 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  
weight of the total monomers, preferably about 0.1 to  
about 0.25 percent by weight.

25 The presently preferred acrylic emulsion polymer  
contains, about 48 percent by weight 2-ethyl hexyl  
acrylate, about 21 percent by weight vinyl acetate,  
about 29 percent by weight di-2-ethyl hexyl maleate,  
about 1 percent by weight acrylic acid, and about 1  
30 percent by weight methacrylic acid and are formed as an  
emulsion having a solids content of about 59.6% and a  
pH of about 3.8.

The monomer proportions are preferably adjusted in  
such a way that the adhesive has a glass transition  
35 temperature less than about  $-30^{\circ}\text{C}$ , preferably less than  
about  $-34^{\circ}\text{C}$ , giving a good balance of adhesion and tack  
at room temperature and low temperatures. Depending on

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1 polymerization conditions, copolymers showing two  
distinct glass transition temperatures, one in the  
region of -45 to -60°C and the other in the region of  
-15 to -30°C, have been observed.

5 Gel content or percent insolubles maybe and are  
preferably in the range of 50 to 65 percent by weight  
which provides excellent cohesive strength without the  
use of multifunctional monomers or external  
crosslinking. In this regard, gel represents the  
10 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\* membrane disk of 5  
15 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  
20 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  
weighed and the insoluble portion of the polymer  
determined by the equation:

25

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

wherein

a = total weight of 100 percent solids polymer;  
30 b = the weight of the polymer plus membrane before  
tetrahydrofuran treatment; and  
c = polymer plus membrane remaining after  
tetrahydrofuran treatment.

35 The acrylic emulsion polymers of the instant  
invention are prepared by emulsion polymerization under  
conditions of agitation in an autogenous atmosphere in

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1 the presence of suitable polymerization initiators such  
as peroxydisulfate and peroxides. Depending on desired  
polymer properties including gel content, the preferred  
5 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.  
10 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  
15 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  
can be achieved by the use of buffers such as sodium  
20 bicarbonate and sodium acetate, typically in amounts up  
to 0.3 percent by weight based on the weight of the  
monomer.

The stabilizer system used during polymerization  
contains a combination of anionic and nonionic  
25 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  
ethoxylated nonylphenol sulfate, and a suitable  
nonionic surfactant is ethoxylated nonylphenol. The  
30 best balance of properties is achieved by maintaining  
the anionic to nonionic surfactant ratio approximately  
3 to 1.

The acrylic emulsion polymers of the instant  
invention are produced at high solids level content,  
35 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

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1 weight of the total monomers, 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.

5 The presently preferred acrylic emulsion polymer  
used for removability purposes is the pressure-  
sensitive adhesive described in Example 3 of US Patent  
No. 5,164,444. Good conversion is obtained by  
feeding a pre-emulsified monomer mix along with  
10 potassium persulfate as catalyst into the reactor over  
a period of 4 to 5 hours at temperatures ranging from  
70 to 85°C. The adhesive polymer as such is a  
permanent electronic data processing label adhesive  
used on (EDP) and other paper facestock and build in  
15 adhesion over a period of time causing the facestock to  
tear in 180 or 90° peel tests. The adhesive has low  
levels of vinyl carboxylic acid unlike polymers taught  
in the prior art.

The elastomeric or rubber-based polymers which can  
20 be employed in the removable permanent adhesive  
compositions are any rubber-based emulsion polymer  
which is sufficiently polar to be compatible with the  
rosin-based surfactants and tackifiers used to induce  
clean removability. The presently preferred rubber-  
25 based polymers are carboxylated styrene-butadiene  
random copolymers of from about 20 to about 50% styrene  
content. Block copolymers based on styrene and  
butadiene or isoprene which exhibit a sufficient degree  
of polarity may also be used.

30 It is possible to modify the rheology of the polymer  
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  
35 the properties by the use of tackifiers and the like.  
For general purpose applications, it is desirable to  
have good adhesion to both hydrophobic substrates such

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1 as polyethylene and hydrophilic substrates such as  
stainless steel.

By formulating the adhesive with suitable rosin acid  
and rosin based tackifiers and rosin based surfactant  
5 systems labels and tapes made with the formulated  
adhesive composition remove clean from substrates in  
hot water or in hot alkaline wash cycle either by use  
of household detergents such as Cascade® or caustic  
alkali (2-3% by weight of solution). The blended  
10 product essentially consists of 100 parts of the  
emulsion polymer, about 3 to about 20 parts rosin acid  
tackifier and from about 1 to about 10 parts  
surfactant. The preferred composition consists of 100  
parts of the emulsion polymer, about 3 to about 15  
15 parts of rosin acid tackifier, and from about 1 to  
about 5 parts by weight surfactant.

Surfactants useful in the present invention include  
nonionic ethyleneoxide adducts of pale wood rosin  
containing about 15 moles of ethylene oxide, sold by  
20 Hercules, Inc. under the trade name AR-150. Being  
rosin based, this surfactant differs from surfactants  
disclosed in the prior art which are mainly  
polyoxyalkylene alkyl phenols, polyoxyalkylene glycols  
and polyoxyalkylene phenols. When present as per the  
25 prior art, they are required to be used in greater than  
20 parts by weight based on 100 parts by weight of  
polymer and in most cases >50 parts by weight to give  
the required performance. The level of rosin based  
surfactant used in the instant invention is less than  
30 10 parts by weight per 100 parts polymer, the optimum  
level being about 1.0 to about 5.0 parts by weight.  
The other rosin based surfactants which may be useful  
are Dresinates\* made by Hercules, Inc. which are  
potassium or sodium salts of modified rosin. Suitable  
35 surfactants include Dresinate 81, 90-95 and Dresinate  
214, 515, and 731. Higher amounts of surfactant tend  
to reduce the shear and adhesion values on the required

Trade-mark\*

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1 substrates.

2 The tackifying resins suitable for this application  
3 are noncrystallizing resins and include fully or  
4 partially polymerized rosins, modified rosins,  
5 disproportionate rosins, stabilized rosins,  
6 hydrogenated rosins and the like, preferably having an  
7 acid number (Acid No.) greater than 50 and less than  
8 210 (acid no. expressed as mg. of KOH/gram of resin)  
9 with a softening point of about 50 to about 170°C. The  
10 most preferred resins have a softening point of about  
11 60 to about 95°C and an Acid No. of 100 to 140. The  
12 preferred resins are Sylvatac<sup>\*</sup>R-85, R-95 and R-295 sold  
13 by Arizona Chemicals, Unitac<sup>\*</sup>70 sold by Union Carbide,  
14 Foral<sup>\*</sup>AX, Hercules 731D resin, Pentalyn<sup>\*</sup>261 supplied by  
15 Hercules, Snowtack<sup>\*</sup> 301A, 342A, 820A, 380A, 380B and  
16 385F sold by EKA Nobel. The resins with acid number in  
17 excess of 160 and softening points exceeding 100°C tend  
18 to create partial incompatibility with the polymer when  
19 used in levels higher than 10 parts per 100 parts of  
20 the polymer. Resin levels exceeding 20 parts reduce  
21 the shear values and cause zippiness during peel.

22 The tackifying resins can be used in the dispersion  
23 form or in the solubilized form. Resin dispersions are  
24 commercially available from the supplier and are used  
25 as such. For solid resins, solubilization is effected  
26 either by dissolving the resin by water and ammonium  
27 hydroxide with a suitable anionic surfactant or by  
28 dissolving the resin in isopropyl alcohol and ammonium  
29 hydroxide then diluting the solution with water and  
30 adding a suitable anionic surfactant. The total solid  
31 content of the tackifying resin is maintained between  
32 about 40 to about 60% by weight. The optimum level for  
33 the application is about 5 to about 20 parts by weight  
34 and the preferred level is 5 to about 15 parts for 100  
35 parts of the polymer.

36 The tackifying resin by itself or the surfactant by  
37 itself when combined with the polymer do not promote

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1       removability in hot water or under hot alkaline  
          conditions. When blended in suitable ratios and coated  
          on paper facestock the adhesives afford clean  
          removability as defined above in less than 5 minutes  
5       from the surface of the substrate when immersed in  
          agitated hot water or in hot alkaline solutions such as  
          detergent solutions or 2-3% caustic alkali, held at 40  
          to about 60°C. They may be and preferably are  
          formulated to resist cold water removal in a reasonable  
10       amount of time. This allows them use on labels adhered  
          to substrates which contract cold water for extended  
          periods of time. The label remains intact, although it  
          may in some instances be peeled from the substrate. In  
          any event the bond is not undermined and will recover  
15       on drying. The appropriate pH of the blended product  
          is maintained between about 6.5 and about 8 by the  
          addition of ammonium hydroxide. Use of alkali metal  
          hydroxides in the place of ammonium hydroxide tends to  
          adversely affect peel and tack adhesion by inducing  
20       zippiness on peel which is unacceptable.

          A preferred adhesive composition of the invention  
          consists of 100 parts by weight of the emulsion  
          polymer, 1 to about 10 parts by weight of the  
          surfactant and about 3 to about 20 parts by weight of  
25       the tackifying resin. The preferred composition  
          consists of 100 parts by weight of the emulsion  
          polymer, about 1 to about 10 parts of AR<sup>\*</sup>-150  
          surfactant, and about 3 to about 20 parts of Snowtack  
          385F or a combination of Snowtack 385F with 380A or  
30       380B or 820A or 301A.

          In a preferred method of formulation, the surfactant  
          is added to an emulsion containing the polymer with  
          agitation followed by the addition of the tackifying  
          resin solution or dispersion. pH is then adjusted to  
35       about 6.5 to about 7.5. The emulsion is then coated at  
          20 to 25 g/m<sup>2</sup> coat weight on a release paper, dried at  
          70°C for 10 minutes and laminated to the backing

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1 preferably high gloss, DSX paper and dual print paper.  
Polymeric film backing or face stocks may also be used.

5 In the following Examples (Ex) and Controls (Cont)  
2.5 x 10 cm paper backed labels were applied to the  
substrate and tested for removability after 1 week  
dwell by immersing the total construction in the  
respective solutions at the required temperatures and  
observing the time the label self-separates from the  
substrate. For purposes of Tables 1 to 4, a  
10 formulation is considered excellent if the label self  
separates from a given substrate in less than about 5  
minutes without leaving any adhesive residue in hot  
water or alkali and excellent if self removal is from  
multiple substrates. Controls have a removal time of  
15 more than 5 minutes for all substrates evaluated.  
Table 1 illustrates the different acrylic-based  
compositions based on solubilized tackifier resin.  
Table 2 is for water dispersions of tackifier resins.  
The numbers are parts by weight in grams of the  
20 components which went into the formulation for each 100  
parts of the preferred polymer. Removability data  
indicate the time in minutes for the label to cleanly  
self-separate from the substrate without a residue.  
The temperatures of the hot water and the alkali were  
25 maintained between 50 to about 60°C. All formulations  
which pass the removability test on polyethylene (PE)  
and stainless steel (SS) are considered capable and  
pass the same test on polyester (PET) and glass (GL)  
and vice a versa. All samples which pass in hot water  
30 also pass in hot alkaline conditions. Table 3 provides  
adhesive properties of some of Exemplary Example  
compositions and Control compositions.

Table 4 gives cold water removability.

35 Clean removability includes the added task of  
peeling a label from a substrate with or without  
leaving some adhesive residue which can be removed with  
light to moderate thumb rubbing. This mimics removal

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1 of label by soaking in water after purchase. Systems  
based on styrene-butadiene random copolymers are  
illustrated as to performance in Tables 5 and 6 and are  
particularly utile for the purpose of adhering to  
5 polystyrene and polypropylene substrates.

While adhesives are intended as hot water and alkali  
removable adhesives, they have been found to have  
utility in binding grips to golf shafts. when formed  
as a double sided tape and adhered to the shaft the  
10 outside can be wetted, the grip slid over the wet  
adhesive and the bond formed on evaporation of water.  
This eliminates the use of organic solvents to activate  
the adhesive. The acrylic-based compositions are  
preferred for this special application.

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Table 1

| 5  | Ex/<br>Cont | Surfactant   | wt. % | Tackifying<br>Resin | wt.  | Hot Water<br>Removal<br>Time, Min |     | 3% NaOH<br>Removal<br>Time, Min |    |
|----|-------------|--------------|-------|---------------------|------|-----------------------------------|-----|---------------------------------|----|
|    |             |              |       |                     |      | PE                                | PET | SS                              | GL |
| 5  | Ex1         | AR-150       | 5.0   | Pentalyn 261        | 5.0  | <2.0                              | -   | <3                              | <2 |
|    | Ex2         | AR-150       | 5.0   | Pentalyn 261        | 10.0 | <3.0                              | -   | <3                              | <3 |
|    | Ex3         | AR-150       | 2.5   | Pentalyn 261        | 5.0  | 2.0                               | -   |                                 | -- |
|    | Ex4         | AR-150       | 2.5   | Pentalyn 261        | 7.5  | 2.5                               | -   |                                 | -- |
|    | Ex5         | AR-150       | 5.0   | Unitac 70           | 10.0 | 2.0                               | -   |                                 | -- |
| 10 | Ex6         | AR-150       | 5.0   | Unitac 70           | 20.0 | 2.0                               | -   |                                 | -- |
|    | Ex7         | AR-150       | 5.0   | Unitac 70           | 15.0 | 2.0                               | -   | 3                               | -  |
|    | Ex8         | AR-150       | 5.0   | Unitac 70           | 5.0  | -                                 | -   | <5                              | -  |
|    | Ex9         | AR-150       | 2.5   | Unitac 70           | 7.5  | <2.0                              | -   | -                               | -  |
|    | Ex10        | AR-150       | 5.0   | Sylvatac R85        | 5.0  | <5.0                              | -   | -                               | -  |
| 15 | Ex11        | AR-150       | 2.5   | Sylvatac R85        | 5.0  | -                                 | -   | 5                               | -  |
|    | Ex12        | AR-150       | 5.0   | Sylvatac R85        | 7.5  | <3.0                              | -   | -                               | -  |
|    | Ex13        | AR-150       | 2.5   | Sylvatac R85        | 7.5  | 7                                 | -   | 4                               | -  |
|    | Ex14        | AR-150       | 5.0   | Sylvatac R85        | 10.0 | <4.0                              | -   | -                               | -  |
|    | Ex15        | AR-150       | 2.0   | Sylvatac R85        | 5.0  | >2.0                              | -   | -                               | -  |
| 20 | Ex16        | AR-150       | 2.25  | Sylvatac R85        | 7.5  | <5.0                              | -   | -                               | -  |
|    | Ex17        | AR-150       | 2.0   | Sylvatac R85        | 10.0 | <4.0                              | -   | -                               | -  |
|    | Ex18        | AR-150       | 2.25  | Sylvatac R85        | 10.0 | <2.0                              | -   | -                               | -  |
|    | Ex19        | AR-150       | 5.0   | Resin* 731D         | 10.0 | <3.0                              | -   | -                               | -  |
|    | Ex20        | AR-150       | 2.5   | Resin* 731D         | 10.0 | <3.0                              | -   | -                               | -  |
| 25 | Ex21        | AR-150       | 5.0   | Foral AX            | 10.0 | <4.0                              | -   | -                               | -  |
|    | Ex22        | AR-150       | 2.5   | Foral AX            | 10.0 | <4.0                              | -   | -                               | -  |
|    | Ex23        | Dresinate731 | 5.0   | Snowtack 301A       | 5.0  | <3.0                              | -   | -                               | -  |
|    | Ex24        | Dresinate515 | 5.0   | Snowtack 301A       | 5.0  | <4.0                              | -   | -                               | -  |
|    | Cont1       | AR-150       | 0.0   | Unitac 70           | 10.0 | >10.0                             | -   | >10                             | -  |
| 30 | Cont2       | AR-150       | 5.0   | Unitac 70           | 0.0  | >10.0                             | -   | >10                             | -  |
|    | Cont3       | AR-150       | 10.0  | Unitac 70           | 0.0  | >10.0                             | -   | >10                             | -  |
|    | Cont4       | AR-150       | 1.0   | Sylvatac R85        | 5.0  | >15.0                             | -   | -                               | -  |
|    | Cont5       | AR-150       | 1.75  | Sylvatac R85        | 5.0  | >15.0                             | -   | -                               | -  |
|    | Cont6       | AR-150       | 1.5   | Sylvatac R85        | 7.5  | >15.0                             | -   | -                               | -  |
| 35 | Cont7       | Dresinate91  | 5.0   | Sylvatac R85        | 0.0  | >30.0                             | -   | -                               | -  |
|    | Cont8       | Dresinate91  | 2.5   | Sylvatac R85        | 5.0  | >15.0                             | -   | -                               | -  |
|    | Cont9       | Dresinate91  | 1.5   | Sylvatac R85        | 5.0  | >15.0                             | -   | -                               | -  |
|    | Cont10      | AR-150       | 5.0   | Resin 731D          | 5.0  | <10.0                             | -   | -                               | -  |
|    | Cont11      | AR-150       | 2.5   | Resin 731D          | 5.0  | >30.0                             | -   | -                               | -  |
| 35 | Cont12      | AR-150       | 5.0   | Foral AX            | 5.0  | 10.0                              | -   | -                               | -  |
|    | Cont13      | AR-150       | 2.5   | Foral AX            | 5.0  | >15.0                             | -   | -                               | -  |

Trade-mark\*

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## 1 Table 1 Continued

| Ex/<br>Cont | Surfactant       | wt. % | Tackifying<br>Resin | wt. | Hot Water<br>Removal<br>Time, Min |     | 3% NaOH<br>Removal<br>Time, Min |    |
|-------------|------------------|-------|---------------------|-----|-----------------------------------|-----|---------------------------------|----|
|             |                  |       |                     |     | PE                                | PET | SS                              | GL |
| 5           | Cont14 Dresinate |       |                     |     |                                   |     |                                 |    |
|             | 731              | 3.0   | Snowtack 301A       | 5.0 | <7.0                              | -   | -                               | -  |
|             | Cont15 Dresinate |       |                     |     |                                   |     |                                 |    |
|             | 515              | 3.0   | Snowtack 301A       | 5.0 | >10.0                             | -   | -                               | -  |

HW = hot water

PE = high density poly ethylene milk cans

PET = polyester film

SS = Stainless steel

GL = Glass

The sign > indicates that the test was discontinued  
after that period of time

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Table 2

|    | Ex/<br>Cont | Surfactant | wt. % | Tackifying<br>Resin | wt. % | Hot Water<br>Removal<br>Time, Min |     | 3% NaOH<br>Removal<br>Time, Min |    |
|----|-------------|------------|-------|---------------------|-------|-----------------------------------|-----|---------------------------------|----|
|    |             |            |       |                     |       | PE                                | PET | SS                              | GL |
| 5  | Ex25        | AR-150     | 5.0   | Snowtack 301A       | 5.0   | <2                                | <2  | <3                              | -  |
|    | Ex26        | AR-150     | 5.0   | Snowtack 301A       | 20.0  | <5                                | <2  | <3                              | -  |
|    | Ex27        | AR-150     | 5.0   | Snowtack 301A       | 10.0  | <5                                | -   | <3                              | -  |
|    | Ex28        | AR-150     | 2.5   | Snowtack 301A       | 10.0  | <5                                | -   | -                               | -  |
|    | Ex29        | AR-150     | 5.0   | Snowtack 301A       | 15.0  | <2                                | -   | <1                              | -  |
| 10 | Ex30        | AR-150     | 2.5   | Snowtack 301A       | 15.0  | <3                                | -   | <2                              | -  |
|    | Ex31        | AR-150     | 3.25  | Snowtack 301A       | 5.0   | <4                                | -   | -                               | -  |
|    | Ex32        | AR-150     | 3.0   | Snowtack 301A       | 7.5   | 3                                 | -   | -                               | -  |
|    | Ex33        | AR-150     | 2.75  | Snowtack 301A       | 7.5   | -                                 | -   | 2                               | -  |
|    | Ex34        | AR-150     | 1.5   | Snowtack 301A       | 10.0  | <4                                | -   | -                               | -  |
|    | Ex35        | AR-150     | 1.25  | Snowtack 301A       | 10.0  | <4                                | -   | -                               | -  |
|    | Ex36        | AR-150     | 2.82  | Snowtack 301A       | 8.0   | 1                                 | -   | 5                               | -  |
| 15 | Ex37        | AR-150     | 1.75  | Snowtack 301A       | 12.25 | 2                                 | -   | 5                               | -  |
|    | Ex38        | AR-150     | 2.95  | Snowtack 301A       | 7.5   | 2                                 | -   | 2                               | -  |
|    | Ex39        | AR-150     | 3.1   | Snowtack 301A       | 5.0   | <3                                | -   | <5                              | -  |
|    | Ex40        | AR-150     | 3.15  | Snowtack 301A       | 5.0   | <5                                | -   | <5                              | -  |
|    | Ex41        | AR-150     | 5.0   | Snowtack 385F       | 10.0  | <2                                | -   | -                               | -  |
| 20 | Ex42        | AR-150     | 2.5   | Snowtack 385F       | 10.0  | <5                                | -   | -                               | -  |
|    | Ex43        | AR-150     | 5.0   | Snowtack 385F       | 15.0  | 3                                 | -   | -                               | -  |
|    | Ex44        | AR-150     | 2.5   | Snowtack 385F       | 15.0  | <5                                | -   | -                               | -  |
|    | Ex45        | AR-150     | 3.75  | Snowtack 385F       | 5.0   | <1                                | -   | -                               | -  |
|    | Ex46        | AR-150     | 3.3   | Snowtack 385F       | 5.0   | <2                                | <2  | <2                              | -  |
|    | Ex47        | AR-150     | 2.82  | Snowtack 385F       | 8.0   | <2                                | -   | <5                              | -  |
|    | Ex48        | AR-150     | 2.85  | Snowtack 385F       | 7.5   | 3                                 | -   | <5                              | -  |
| 25 | Ex49        | AR-150     | 2.95  | Snowtack 385F       | 7.5   | 2                                 | -   | <5                              | -  |
|    | Ex50        | AR-150     | 3.5   | Snowtack 380A       | 10.0  | <3                                | <4  | -                               | <2 |
|    | Ex51        | AR-150     | 3.25  | Snowtack 380B       | 7.5   | <3                                | <5  | -                               | <2 |
|    | Ex52        | AR-150     | 3.25  | Snowtack 820A       | 6.85  | <5                                | <5  | -                               | <2 |
|    | Ex53        | AR-150     | 3.2   | Snowtack 385F       | 5.0   | 2                                 | 1   | 3                               | -  |
|    | Ex54        | AR-150     | 3.15  | Snowtack 385F       | 5.0   | 6                                 | -   | 3                               | -  |
| 30 | Cont16      | AR-150     | 2.5   | Snowtack 301A       | 5.0   | 10-15                             | -   | -                               | -  |
|    | Cont17      | AR-150     | 2.75  | Snowtack 301A       | 5.0   | <10                               | -   | -                               | -  |
|    | Cont18      | AR-150     | 2.5   | Snowtack 301A       | 7.5   | <10                               | -   | -                               | -  |
|    | Cont19      | AR-150     | 0.0   | Snowtack 301A       | 10.0  | >15                               | -   | <4                              | -  |
|    | Cont20      | AR-150     | 0.0   | Snowtack 301A       | 20.0  | >15                               | -   | -                               | -  |
|    | Cont21      | AR-150     | 2.5   | Snowtack 385F       | 5.0   | 10-15                             | -   | -                               | -  |
|    | Cont22      | AR-150     | 2.75  | Snowtack 385F       | 5.0   | >10                               | -   | -                               | -  |
| 35 | Cont23      | AR-150     | 2.5   | Snowtack 385F       | 7.5   | 9                                 | -   | -                               | -  |
|    | Cont24      | AR-150     | 3.0   | Snowtack 385F       | 7.5   | <7                                | -   | -                               | -  |

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## 1      Table 2 Continued

| Ex/<br>Cont | Surfactant    | wt. % | Tackifying<br>Resin | wt. % | Hot Water<br>Removal<br>Time, Min |     | 3% NaOH<br>Removal<br>Time, Min |    |
|-------------|---------------|-------|---------------------|-------|-----------------------------------|-----|---------------------------------|----|
|             |               |       |                     |       | PE                                | PET | SS                              | GL |
| 5           | Cont25 AR-150 | 2.75  | Snowtack 385F       | 7.5   | <10                               | -   | -                               | -  |
|             | Cont26 AR-150 | 0.0   | Snowtack 385F       | 10.0  | >15                               | -   | <4                              | -  |
|             | Cont27 AR-150 | 0.0   | Snowtack 385F       | 20.0  | >15                               | -   | <4                              | -  |
|             | Cont28 AR-150 | 3.1   | Snowtack 385F       | 5.0   | 6                                 | -   | <6                              | -  |

10      The adhesive formulations provide good adhesion on all  
the application substrates building to permanency with  
facestock tear on most of the substrates. Illustrative  
examples are given in Table 3. All the samples were  
coated on release liner, dried at 70°C and transferred  
15      onto high gloss paper. The coat weights ranged from 20-  
24/gm<sup>2</sup>.

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Table 3

|    | Ex/Cont. | 90° Peel | N/m |         | RTS<br>500 g,min |
|----|----------|----------|-----|---------|------------------|
|    |          | SS       | PE  | PET     |                  |
| 5  | Ex3      | -        | 200 | -       | -                |
|    | Ex5      | 510      | 260 | 488     | 14               |
|    | Ex6      | 630pt    | 300 | 580pt   | 30               |
|    | Ex11     | pt       | 190 | pt      | 25               |
|    | Ex13     | -        | 180 | -       | 20               |
|    | Ex19     | -        | 170 | -       | 11               |
| 10 | Ex36     | -        | 236 | -       | 7                |
|    | Ex37     | -        | 275 | -       | 10               |
|    | Ex38     | -        | 200 | -       | 9                |
|    | Ex39     | pt       | 260 | pt      | 10               |
|    | Ex40     | pt       | 170 | pt      | 10               |
|    | Ex46     | 540pt    | 255 | 332slpt | -                |
| 15 | Ex47     | -        | 256 | -       | 17               |
|    | Ex48     | -        | 255 | -       | 18               |
|    | Ex49     | -        | 233 | -       | 7                |
|    | Ex50     | 400pt    | 185 | 400pt   | 22c              |
|    | Ex51     | 400pt    | 162 | 400pt   | 35c              |
|    | Ex52     | 420pt    | 214 | 470     | 24c              |
| 20 | Ex53     | pt       | 240 | pt      | 15               |
|    | Cont14   | -        | 200 | -       | 60               |
|    | Cont28   | pt       | 244 | pt      | 16               |
|    | Cont29   | pt       | 240 | pt      | 17               |

pt = facestock tear  
c = cohesive failure

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The adhesives of the invention are formulated to separate clean from a substrate within about 5 minutes under exposure to hot water or alkali at 50-60°C or more. This is to satisfy domestic and industrial needs of rapid separation without residue. It is preferred they resist cold water separation, except by peeling because on shelf presentation a labeled substrate may require ongoing resistance to exposure to cold water, although cold water attack at the adhesive-substrate interface may enable repositionable peeling during the period of cold water exposure. In addition, some

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1 applications permit cold water removability in addition  
 to hot water/alkali removability. The data in Table 4  
 establishes times in minutes of cold water separation  
 for some Examples and Controls as a point of reference  
 5 for other characteristics of label performance.

Table 4

|    | Ex/<br>Cont | Surfactant    | wt. % | Tackifying<br>Resin | wt.  | Cold Water<br>Removal<br>Time, Min |     |
|----|-------------|---------------|-------|---------------------|------|------------------------------------|-----|
|    |             |               |       |                     |      | PE                                 | PET |
| 10 | Ex1         | AR-150        | 5.0   | Pentalyn 261        | 5.0  | 7                                  | 4   |
|    | Ex2         | AR-150        | 5.0   | Pentalyn 261        | 10.0 | -                                  | -   |
|    | Ex3         | AR-150        | 2.5   | Pentalyn 261        | 5.0  | >10                                | >10 |
|    | Ex4         | AR-150        | 2.5   | Pentalyn 261        | 7.5  | >10                                | -   |
|    | Ex5         | AR-150        | 5.0   | Unitac 70           | 10.0 | -                                  | -   |
|    | Ex6         | AR-150        | 5.0   | Unitac 70           | 20.0 | -                                  | -   |
| 15 | Ex7         | AR-150        | 5.0   | Unitac 70           | 15.0 | -                                  | -   |
|    | Ex8         | AR-150        | 5.0   | Unitac 70           | 5.0  | -                                  | -   |
|    | Ex9         | AR-150        | 2.5   | Unitac 70           | 7.5  | >25                                | -   |
|    | Ex10        | AR-150        | 5.0   | Sylvatac R85        | 5.0  | 5                                  | -   |
|    | Ex11        | AR-150        | 2.5   | Sylvatac R85        | 5.0  | >10                                | -   |
|    | Ex12        | AR-150        | 5.0   | Sylvatac R85        | 7.5  | 3                                  | -   |
| 20 | Ex13        | AR-150        | 2.5   | Sylvatac R85        | 7.5  | 7                                  | -   |
|    | Ex14        | AR-150        | 5.0   | Sylvatac R85        | 10.0 | 4                                  | -   |
|    | Ex15        | AR-150        | 2.0   | Sylvatac R85        | 5.0  | >20                                | -   |
|    | Ex16        | AR-150        | 2.25  | Sylvatac R85        | 7.5  | >20                                | -   |
|    | Ex17        | AR-150        | 2.0   | Sylvatac R85        | 10.0 | 10                                 | -   |
|    | Ex18        | AR-150        | 2.25  | Sylvatac R85        | 10.0 | 9                                  | -   |
| 25 | Ex19        | AR-150        | 5.0   | Resin 731D          | 10.0 | 7                                  | -   |
|    | Ex20        | AR-150        | 2.5   | Resin 731D          | 10.0 | 10                                 | -   |
|    | Ex21        | AR-150        | 5.0   | Foral AX            | 10.0 | >15                                | -   |
|    | Ex22        | AR-150        | 2.5   | Foral AX            | 10.0 | >15                                | -   |
|    | Ex23        | Dresinate 731 | 5.0   | Snowtack 301A       | 5.0  | 10                                 | -   |
|    | Ex24        | Dresinate 515 | 5.0   | Snowtack 301A       | 5.0  | >10                                | -   |
| 30 | Ex25        | AR-150        | 5.0   | Snowtack 301A       | 5.0  | 12                                 | 5   |
|    | Ex26        | AR-150        | 5.0   | Snowtack 301A       | 20.0 | <10                                | <5  |
|    | Ex27        | AR-150        | 5.0   | Snowtack 301A       | 10.0 | 14                                 | -   |
|    | Ex28        | AR-150        | 2.5   | Snowtack 301A       | 10.0 | 14                                 | -   |
|    | Ex29        | AR-150        | 5.0   | Snowtack 301A       | 15.0 | <10                                | -   |
|    | Ex30        | AR-150        | 2.5   | Snowtack 301A       | 15.0 | 12                                 | -   |
| 35 | Ex31        | AR-150        | 3.25  | Snowtack 301A       | 5.0  | >20                                | -   |
|    | Ex32        | AR-150        | 3.0   | Snowtack 301A       | 7.5  | 13                                 | -   |
|    | Ex33        | AR-150        | 2.75  | Snowtack 301A       | 7.5  | >30                                | -   |

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1 Table 4 Continued

|    | Ex/<br>Cont | Surfactant    | wt. % | Tackifying<br>Resin | wt.           | Cold Water<br>Removal<br>Time, Min |      |
|----|-------------|---------------|-------|---------------------|---------------|------------------------------------|------|
|    |             |               |       |                     |               | PE                                 | PET  |
| 5  | Ex34        | AR-150        | 1.5   | Snowtack 301A       | 10.0          | 10                                 | -    |
|    | Ex35        | AR-150        | 1.25  | Snowtack 301A       | 10.0          | >15                                | -    |
|    | Ex36        | AR-150        | 2.82  | Snowtack 301A       | 8.0           | <10                                | -    |
|    | Ex37        | AR-150        | 1.75  | Snowtack 301A       | 12.25         | <10                                | -    |
|    | Ex38        | AR-150        | 2.95  | Snowtack 301A       | 7.5           | >15                                | -    |
|    | Ex39        | AR-150        | 3.1   | Snowtack 301A       | 5.0           | >20                                | -    |
| 10 | Ex40        | AR-150        | 3.15  | Snowtack 301A       | 5.0           | >20                                | -    |
|    | Ex41        | AR-150        | 5.0   | Snowtack 385F       | 10.0          | 12                                 | -    |
|    | Ex42        | AR-150        | 2.5   | Snowtack 385F       | 10.0          | >20                                | -    |
|    | Ex43        | AR-150        | 5.0   | Snowtack 385F       | 15.0          | <10                                | -    |
|    | Ex44        | AR-150        | 2.5   | Snowtack 385F       | 15.0          | >20                                | -    |
|    | Ex45        | AR-150        | 3.75  | Snowtack 385F       | 5.0           | 7                                  | -    |
| 15 | Ex46        | AR-150        | 3.3   | Snowtack 385F       | 5.0           | >30                                | -    |
|    | Ex47        | AR-150        | 2.82  | Snowtack 385F       | 8.0           | >15                                | -    |
|    | Ex48        | AR-150        | 2.85  | Snowtack 385F       | 7.5           | >20                                | -    |
|    | Ex49        | AR-150        | 2.95  | Snowtack 385F       | 7.5           | >20                                | -    |
|    | Ex50        | AR-150        | 3.5   | Snowtack 380A       | 10.0          | 10                                 | 10   |
|    | Ex51        | AR-150        | 3.25  | Snowtack 380B       | 7.5           | >20                                | 10   |
| 20 | Ex52        | AR-150        | 3.25  | Snowtack 820A       | 6.85          | >20                                | 10   |
|    | Ex53        | AR-150        | 3.2   | Snowtack 385F       | 5.0           | >30                                | -    |
|    | Ex54        | AR-150        | 3.15  | Snowtack 385F       | 5.0           | >30                                | -    |
|    | Cont1       | AR-150        | 0.0   | Unitac 70           | 10.0          | >30                                | -    |
|    | Cont2       | AR-150        | 5.0   | Unitac 70           | 0.0           | >30                                | -    |
|    | Cont3       | AR-150        | 10.0  | Unitac 70           | 0.0           | >30                                | -    |
| 25 | Cont4       | AR-150        | 1.0   | Sylvatac R85        | 5.0           | >25                                | -    |
|    | Cont5       | AR-150        | 1.75  | Sylvatac R85        | 5.0           | >30                                | -    |
|    | Cont6       | AR-150        | 1.5   | Sylvatac R85        | 7.5           | >30                                | -    |
|    | Cont7       | Dresinate 91  | 5.0   | Sylvatac R85        | 0.0           | >30                                | -    |
|    | Cont8       | Dresinate 91  | 2.5   | Sylvatac R85        | 5.0           | >15                                | -    |
|    | Cont9       | Dresinate 91  | 1.5   | Sylvatac R85        | 5.0           | >15                                | -    |
| 30 | Cont10      | AR-150        | 5.0   | Resin 731D          | 5.0           | 19                                 | -    |
|    | Cont11      | AR-150        | 2.5   | Resin 731D          | 5.0           | >30                                | -    |
|    | Cont12      | AR-150        | 5.0   | Floral AX           | 5.0           | >15                                | -    |
|    | Cont13      | AR-150        | 2.5   | Floral AX           | 5.0           | >15                                | -    |
|    | Cont14      | Dresinate 731 |       | 3.0                 | Snowtack 301A | 5.0                                | >30- |
|    | Cont15      | Dresinate 515 |       | 3.0                 | Snowtack 301A | 5.0                                | >30- |
| 35 | Cont16      | AR-150        | 2.5   | Snowtack 301A       | 5.0           | >60                                | -    |
|    | Cont17      | AR-150        | 2.75  | Snowtack 301A       | 5.0           | >30                                | -    |
|    | Cont18      | AR-150        | 2.5   | Snowtack 301A       | 7.5           | >20                                | -    |

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1 Table 4 Continued

|    | Ex/<br>Cont | Surfactant | wt. % | Tackifying<br>Resin | wt.  | Cold Water<br>Removal<br>Time, Min |     |
|----|-------------|------------|-------|---------------------|------|------------------------------------|-----|
|    |             |            |       |                     |      | PE                                 | PET |
| 5  | Cont19      | AR-150     | 0.0   | Snowtack 301A       | 10.0 | >30                                | -   |
|    | Cont20      | AR-150     | 0.0   | Snowtack 301A       | 20.0 | >30                                | -   |
|    | Cont21      | AR-150     | 2.5   | Snowtack 385F       | 5.0  | >60                                | -   |
|    | Cont22      | AR-150     | 2.75  | Snowtack 385F       | 5.0  | >30                                | -   |
|    | Cont23      | AR-150     | 2.5   | Snowtack 385F       | 7.5  | >30                                | -   |
|    | Cont24      | AR-150     | 3.0   | Snowtack 385F       | 7.5  | >20                                | -   |
| 10 | Cont25      | AR-150     | 2.75  | Snowtack 385F       | 7.5  | >30                                | -   |
|    | Cont26      | AR-150     | 0.0   | Snowtack 385F       | 10.0 | >30                                | -   |
|    | Cont27      | AR-150     | 0.0   | Snowtack 385F       | 20.0 | >30                                | -   |
|    | Cont28      | AR-150     | 3.1   | Snowtack 385F       | 5.0  | >30                                | -   |

> means that test was discontinued at the stated time

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The adhesive formulations provide good adhesion on all the application substrates building to permanency with facestock tear on most of the substrates. Illustrative examples are given in table III. All the samples were coated on release liner, dried at 70°C and transferred onto High Gloss paper. The coat weights ranged from 20-24g/sqm.

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#### Examples 55 to 66

There was employed as the emulsion polymer carboxylated styrene butadiene dispersions of about 49% solids content. Styrene was 25% (BASF NS 144), 35% (BASF NS 166) and 45% (BASF NS 222). The surfactant was AR-150 from Hercules, Inc., an ethylene oxide derivative of rosin, and as the tackifier Snowtack 301A from Eka Nobel, a 50% solids water-borne dispersion of rosin and having a high acid number of about 160 mg KOH/gm a particle size of about 0.5 microns and a melt point of 64°C. To facilitate coating, there was employed Polyphobe\* 102 thickener from Union Carbide Corp. While useful on a variety of substrates, the adhesive systems were particularly suitable as a removable adhesive for polypropylene and

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polystyrene substrates. The results of testing on such substrates is reported in Table 5, wherein

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Y = self separating or easy removability by hand with or without light to moderate thumb rubbing of adhesive residue after 5 minutes immersion;

M = marginal removability requiring heavy thumb rubbing to remove adhesive residue; and

N = adhesive residue non-removable even with heavy thumb rubbing.

15

None of the compositions were removable on soaking in ice water for 15 minutes.

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Table 6 shows that varying the styrene content of the polymer used in the dispersion of Example 57 had no significant effect on removability using the 50°C immersion test.

25

30

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Table 5

| EXAMPLE                          | 55   | 56   | 57   | 58   | 59   | 60   | 61   | 62   | 63   | 64   |
|----------------------------------|------|------|------|------|------|------|------|------|------|------|
| % dry weight                     | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    | 10   |
| NS 144                           | 84.3 | 86.1 | 79.4 | 82.6 | 90.0 | 86.9 | 79.7 | 89.7 | 84.4 | 82.0 |
| SNOWTACK 301A                    | 10.4 | 6.4  | 13.7 | 14.3 | 6.7  | 10.8 | 15.4 | 4.8  | 10.4 | 10.1 |
| AR-150                           | 5.2  | 7.5  | 6.9  | 3.1  | 3.3  | 2.3  | 4.9  | 5.5  | 5.2  | 7.9  |
| Hot Water (40°C)<br>Removability |      |      |      |      |      |      |      |      |      |      |
| Polypropylene                    | N    | N    | M    | M    | M    | M    | M    | Y    | Y    | Y    |
| Polystyrene                      | N    | Y    | Y    | N    | N    | N    | Y    | M    | M    | M    |
| Hot Water (50°C)<br>Removability |      |      |      |      |      |      |      |      |      |      |
| Polypropylene                    | Y    | N    | Y    | Y    | Y    | Y    | Y    | Y    | Y    | Y    |
| Polystyrene                      | M    | Y    | Y    | M    | M    | M    | Y    | M    | Y    | Y    |
| 24 Hr. Peel (N/m)                |      |      |      |      |      |      |      |      |      |      |
| Polypropylene                    | 123  | 123  | 158  | 175  | 123  | 158  | 175  | 123  | 140  | 158  |
| Polystyrene                      | 263  | 210  | 245  | 385  | 368  | 333  | 350  | 263  | 350  | 333  |

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Table 6

|               | Ex. 57<br>25% Styrene | Ex. 65<br>35% Styrene | Ex. 66<br>45% Styrene |
|---------------|-----------------------|-----------------------|-----------------------|
| Polypropylene | Y                     | Y                     | Y                     |
| Polystyrene   | Y                     | Y                     | Y                     |

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**WHAT IS CLAIMED IS:**

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1. A pressure-sensitive adhesive composition which comprises:

(a) an acrylic, pressure-sensitive adhesive polymer formed by emulsion polymerization, which polymer  
10 comprises, on a polymerized basis and based on the total weight of the monomers:

(i) at least one alkyl acrylate containing from 4 to 8 carbon atoms in the alkyl group, the total amount of alkyl acrylate monomers being at least about 35  
15 percent by weight of the monomers; and

(ii) at least one unsaturated carboxylic acid containing from 3 to 5 carbon atoms, present in a total positive amount up to about 5 percent by weight of the monomers, or a rubber-based emulsion polymer which is  
20 sufficiently polar to be compatible with a rosin acid tackifier and rosin-based surfactant, and

(b) as additives for each 100 parts by weight of the polymer:

(i) from about 3 to about 20 parts by  
25 weight of a rosin acid tackifier, and

(ii) from about 1 to about 10 parts by weight of a rosin-based surfactant,  
said pressure-sensitive adhesive composition when applied to paper backing being capable of clean removability from  
30 a nonpaper surface of a polar or nonpolar substrate on exposure to the action of hot water or alkali for less than about 5 minutes.

2. A pressure-sensitive adhesive composition as  
35 claimed in claim 1 in which the acrylic, pressure-sensitive adhesive is inherently tacky and comprises, on a polymerized basis and based on the total weight of the monomers:

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(a) at least one alkyl acrylate containing from 4 to 8 carbon atoms in the alkyl group, the total amount of alkyl acrylate present being from about 35 to 60 percent by weight;

(b) at least one vinyl ester containing from 2 to 16 carbon atoms in the alkyl group of the acid, the total amount of the vinyl ester present being from 15 to about 35 percent by weight;

(c) at least one diester of a dicarboxylic acid in which each alkyl group of the diester independently contains from 6 to 12 carbon atoms, the total of the diesters present being in amount from about 20 to about 40 percent by weight; and

(d) at least one unsaturated carboxylic acid containing from 3 to 5 carbon atoms, the total of the unsaturated carboxylic acid being present in a positive amount up to about 5 percent by weight, said polymer having a glass transition temperature of less than about  $-30^{\circ}\text{C}$  and a gel content of from about 50 to about 70 percent by weight of the polymer.

3. A pressure-sensitive adhesive as claimed in claim 1 in which the acrylic emulsion polymer is an inherently tacky pressure-sensitive adhesive polymer and comprises:

(a) at least one alkyl acrylate selected from the group consisting of 2-ethylhexyl acrylate, isooctyl acrylate, and mixtures thereof, the total amount of alkyl acrylate present being from about 40 to about 50 percent by weight;

(b) vinyl acetate in an amount of from 15 to about 35 percent by weight;

(c) at least one diester of a dicarboxylic acid selected from di-2-ethylhexyl maleate and di-2-ethylhexyl fumarate and mixtures thereof present in an amount from about 20 to about 40 percent by weight; and

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(d) an unsaturated carboxylic acid selected from the group consisting of acrylic acid, methacrylic acid and mixtures thereof present in an amount of from about 1 to about 3 percent by weight, said polymer having a glass transition temperature of less than about  $-30^{\circ}\text{C}$  and a gel content of from about 50 to about 70 percent by weight of the polymer.

10

4. A pressure-sensitive adhesive composition as claimed in claim 1 in which the inherently tacky, acrylic pressure-sensitive adhesive polymer comprises based on the total weight of the monomers:

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(a) about 48 percent by weight 2-ethylhexyl acrylate;

(b) about 21 percent by weight vinyl acetate;

(c) about 29 percent by weight di-2-ethylhexyl maleate; and

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(d) about 1 percent by weight acrylic acid and about 1 percent by weight methacrylic acid.

5. A pressure-sensitive adhesive as claimed in claim 1 in which the rubber-based emulsion polymer is a carboxylated styrene-butadiene random copolymer containing from about 20 to about 50% by weight styrene.

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6. A pressure-sensitive adhesive as claimed in any one of claims 1 to 5 in which the tackifier is provided in a concentration of about 3 to about 15 parts by weight.

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7. A pressure-sensitive adhesive as claimed in any one of claims 1 to 6 in which the surfactant is provided in an amount of from about 1 to about 5 parts by weight.

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8. A pressure-sensitive adhesive as claimed in any one of claims 1 to 7 in which the tackifier has an acid  
5 number greater than about 50 and less than about 210.

9. A pressure-sensitive adhesive as claimed in any one of claims 1 to 7 in which the tackifier is noncrystallizing, has an acid number greater than about  
10 50 and less than about 210 and is selected from the group consisting of at least partially polymerized rosins, modified rosins, disproportionate rosins, stabilized rosins, hydrogenated rosins and mixtures thereof.

15 10. A pressure-sensitive adhesive as claimed in any one of claims 1 to 9 in which the surfactant is a nonionic pale wood rosin containing about 15 mols of ethyleneoxide.