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(54) Title: HOT MELT ADHESIVE COMPOSITIONS COMPRISING LOW MOLECULAR WEIGHT ETHYLENE COPOLYMERS (57) Abstract <p>Hot melt adhesive compositions which include a base polymer constituent, a tackifying constituent, a wax constituent, and which further includes a low molecular weight polyethylene copolymer constituent which includes ketone functional moieties and/or hydroxyl functional moieties wherein the hot melt adhesive composition may be further characterized as providing improved adhesive strength to polar and non-polar substrates.</p>		

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HOT MELT ADHESIVE COMPOSITIONS COMPRISING LOW MOLECULAR WEIGHT ETHYLENE COPOLYMERS

BACKGROUND

5 1. Field of the Invention

The present invention is related to hot melt adhesive compositions; more particularly the present invention application is directed to improvements in hot melt adhesive compositions comprising low molecular weight ethylene copolymers having improved adhesive properties to a variety of substrate materials of both polar and non-polar characteristics.

2. Description of the Prior Art

15 As is known to the art, conventional hot melt adhesive compositions typically comprise three primary constituents; a base polymer which provides adhesion and toughness to the adhesive in its cooled state, a waxy material which acts to initiate the setting and solidification of the heated adhesive composition and to further minimize the viscosity, and a tackifying constituent which enhances the wetting and adhesion of the composition to the surfaces upon which it is applied. Ideally, a hot melt adhesive composition is useful for bonding a wide variety of substrates, including polar substrates such as metals, polycarbonates, polyesters including polyethylene terephthalate ("PET"), as well as halogenated polymer compositions, including PVC, and further, nonpolar substrates such as polyolefins, including polyethylene and polypropylene. Further, such hot melt adhesive compositions exhibit good compatibility of their

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individual constituents. The prior art proposes various solutions to these problems.

U.S. Patent 5,037,874 to Nuttens et al. a compatible wax which comprises a synthetic polyethylene wax which includes incorporated carbon monoxide ("CO") terminal groups and a method for its production. The advantage cited by the reference includes a novel process for the production of the synthetic polyethylene wax, and its compatibility with conventional hot melt adhesive compositions.

US Patent 4,601,948 to Lancaster provides adhesive compositions which are used in bonding materials utilizing high frequency radiation; the adhesives therein include ethylene/carbon monoxide copolymers and terpolymers which are cited as having melt indices of 0.5-2500, which are expected to be relatively higher weight materials.

US Patents 4,880,904 and 4,871,618 to Kinneberg provide adhesive compositions and laminated structures which consist essentially of a linear alternating polymer which is heat curable, and which is preferably of a number average molecular weight of the range of 10,000 to 30,000.

A paper entitled "Ethylene Copolymer for Adhesion to Plastics" by E. McBride and presented at an Adhesive and Sealant Council Seminar on April 16, 1991 describes hot melt adhesive systems which include as the base polymer constituent various high molecular weight copolymers and terpolymers including ethylene/carbon monoxide "E/CO", ethylene/vinyl acetate/carbon monoxide "E/VA/CO", and ethylene/acrylate/carbon monoxide "E/Ac/CO". The paper cites the need for improved waxes which exhibit compatibility with the aforementioned base polymers.

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Japanese Kokai 181557 of 1991, describes compositions which are similar to those described in the McBride paper above.

While these and other prior art references provide
5 useful hot melt adhesive compositions, there remains a continuing need for improved hot melt adhesive compositions featuring improved adhesive strength characteristics for both polar and non-polar type substrates.

10

SUMMARY

The present invention provides a hot melt adhesive composition which includes a base polymer constituent, a tackifying constituent, a wax constituent, and which
15 further includes a low molecular weight polyethylene copolymer constituent which includes ketone functional moieties and/or hydroxyl functional moieties wherein the hot melt adhesive composition may be further characterized as providing improved adhesive strength
20 to polar and non-polar substrates. Optionally, the hot melt adhesive composition further includes a minor amounts of one or more conventional additives, such as thermal stabilizing constituents and anti-oxidants.

In a further aspect of the present invention there
25 is provided a process for improving the adhesive strength of conventional hot melt adhesive composition which includes a base polymer constituent, a tackifying constituent, and a wax constituent, the process improvement comprising the addition of an effective
30 amount of a low molecular weight polyethylene copolymer constituent which includes ketone functional moieties and/or hydroxyl functional moieties.

In a still further aspect of the invention there are provided laminar constructions which comprise two
35 substrate materials having a layer of the improved

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adhesive taught herein disposed between and interfacially contacting each of the substrate layers.

These and other aspects of the invention will be more apparent from the following detailed description
5 of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides hot melt adhesive compositions which feature improved adhesive strength
10 to both polar and non-polar substrates which composition includes a conventionally used base polymer constituent, a conventional tackifying constituent, a wax constituent, and a low molecular weight polyethylene copolymer constituent which includes
15 ketone functional moieties and/or hydroxyl functional moieties. The wax constituent described may be partially or completely substituted by the low molecular weight polyethylene copolymer constituent described above. Optionally, effective of
20 conventional additives, such as thermal and/or oxidative stabilizers.

It is to be understood that the term "copolymer" as used throughout this description of the invention is to be understood to define a constituent comprised
25 essentially of two monomeric constituents, as well as constituents comprised essentially of three monomeric constituents, sometimes interchangeably referred to as "terpolymers", as well as constituents comprised essentially of four or more monomeric constituents.

30 Conventional base polymer constituents may be one or more base polymers which are known to the art as useful in hot melt adhesive compositions. Preferred base polymers include ethylene copolymers including ethylene/carbon monoxide "E/CO", ethylene/vinyl
35 acetate/carbon monoxide "E/VA/CO", ethylene/vinyl

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acetate "E/VA", ethylene/acrylate/carbon monoxide "E/Ac/CO", and ethyl/acrylate "E/Ac". The acrylate portions of the E/Ac/CO or E/Ac copolymers may be methyl acrylate, ethyl acrylate, n-butyl acrylate, as well as 2-ethylhexylacrylate. The base polymer constituents include characteristic properties including a melt index of 0.2 - 3000 dg/min according to ASTM D-1238. These ethylene copolymers may comprise varying weight proportions of the monomers from which they are produced. By way of example, the E/VA copolymer may comprise between 0.1-99.9% by weight of ethylene, and 99.9-0.1% by weight of vinyl acetate. Similarly, the E/CO may comprise between 0.1-99.9% by weight of ethylene, and 99.9-0.1% by weight of carbon monoxide. For terpolymers, (i.e., copolymers comprising three or more constituents) the weight percentages of the individual monomers may be in any percentage, such as as in the case of E/Ac/CO the weight percentages of the three monomers may vary as follows: 0.1-99.8 wt.% E, 0.1-99.8 wt.% Ac, and 0.1-99.8 wt.% CO. As will be apparent to skilled practitioners, the relative weight percentages of each of the monomers comprising the base polymer effects variation in the adhesive, physical and processing characteristics of these materials. Selection of a suitable base polymer will be dependent upon the final end use application of the hot melt adhesive composition; an appropriate base polymer should be selected in accordance which satisfies these technical considerations.

Conventional tackifying constituents include one or more constituents presently known as useful in hot melt adhesive compositions. Useful conventional tackifying constituents include but are not limited to one or more rosin, rosin esters, derivatives thereof,

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polyterpenes, as well as aliphatic and/or aromatic hydrocarbon materials which are known useful tackifying constituents.

Conventional wax constituents useful in the practice of the present invention include one or more waxes which are presently known to the art as useful in hot melt adhesive compositions. Such useful waxes include one or more paraffin waxes, microcrystalline waxes, low molecular weight polyethylene waxes, Fisher-Tropsch type waxes, as well as others not recited here.

In accordance with the present invention, a hot melt adhesive composition includes one or more low molecular weight polyethylene copolymers which includes ketone functional moieties and/or hydroxyl functional moieties. These copolymers may be characterized as having a very high melt flow index according to ASTM D-1238, generally in excess of about 3000 dg/min and even higher which makes them difficult to measure; such high values are indicative of low molecular weight materials. Useful ethylene copolymers which include ketone functionality include ethylene/carbon monoxide copolymers which consist of between 0.01 - 99.99 wt.% ethylene and 0.01 - 99.99 wt.% carbon monoxide "CO"; preferably useful ethylene copolymers consist of up to 50 wt.% of CO and the remainder consisting of ethylene. Further useful ethylene copolymers which include hydroxyl functionality include at least partially saponified ethylene/vinyl acetate copolymers which are comprised of between 0.01 - 99.99 wt.% ethylene and 0.01 - 99.99 wt.% vinyl alcohol; preferred useful ethylene copolymers consist of up to 85 wt.% of vinyl alcohol and the remainder consisting of ethylene units and unsaponified vinyl acetate units. The degree of saponification of an ethylene/vinyl acetate copolymer may be from 1 - 100%; preferably the degree of

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saponification is 25% and greater. The ethylene copolymers described may be either random, block, or repeating type copolymers; preferably they are random copolymers.

5 Optionally, the ethylene copolymers described above may be at least partially oxidized copolymers.

 It is also contemplated that additional comonomers may be included in the ethylene copolymers described, so to form terpolymers and the like. By way of example
10 the inclusion of vinyl acetate monomers as a comonomer (or alternately by non-saponified vinyl acetate moieties) is contemplated in order to impart a more flexible nature to the ethylene copolymer. Further comonomers which may be included include but are not
15 limited to: alkyl acrylates "AAc" to form low molecular weight E/AAc/CO or E/AAc/OH terpolymers including methyl acrylate, ethyl acrylate, n-butyl acrylate and 2-ethylhexylacrylate as the AAc comonomer, and acrylic acid "AA", methacrylic acid "MAA", and maleic anhydride
20 "MA" monomers to form low molecular weight E/AA/CO, E/MAA/CO and E/MA/CO terpolymers, respectively. These terpolymers are low molecular weight terpolymers having molecular weights within the ranges described above, and/or have high melt indicies as described above.

25 The above low molecular weight ethylene copolymers are random copolymers; what is meant to be understood is that these copolymers do not consist essentially of regularly repeating or block copolymer units. The random copolymer structure provides for the inclusion
30 of the ketone functional moieties as well as the hydroxyl functional moieties within the backbone of the copolymer as well as possible ketone and/or hydroxyl terminal group functionality. Such as an important effect as the random copolymer structure with the
35 incorporated ketone and/or hydroxyl functional groups

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enhances the compatability of the low molecular weight ethylene copolymers with the base polymer and the tackifying constituent.

The low molecular weight ethylene copolymers may
5 be produced by well known processes, such as by conventional free-radical polymerization process techniques.

Optional constituents which may be included in effective amounts include oxidative and thermal
10 stabilizers. Oxidative stabilizers include tetrakis [ethylene 3-(3', 5'-di-tert-butyl- 4'hydroxyphenyl) propionate]. These optional constituents may be included in any effective amount; generally they are included in an amount to comprise 5 wt.% and less of
15 the total weight of the hot melt adhesive composition.

Hot melt adhesive compositions comprise the base polymer constituent, a conventional tackifying constituent, a conventional wax, and a low molecular weight polyethylene copolymer constituent may be in a
20 range of weight proportions wherein the base polymer constituent may comprise between 1-98 wt.%, the tackifying constituent between 1-98 wt.%, and the sum total of the weight of the conventional wax constituent and of the low molecular weight polyethylene copolymer
25 constituent between 1-98 wt.%. It is to be understood that the low molecular weight polyethylene copolymer may be used to substitute a portion or all of the conventional wax constituent in a hot melt adhesive formulation, or alternately, may be considered as a
30 separate additive constituent. Selection of the appropriate proportions of these three constituents is best determined by experimental analysis; as is apparent to the skilled practitioner the relative proportion of each constituent imparts a different
35 physical and/or processing characteristic upon the

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ultimate hot melt adhesive composition formed.
Generally, these four constituents are present in the
ranges of between about 0.10 % wt. and up to about 95 %
wt. Further, the inclusion of effective amounts of the
5 one or more conventional additives is frequently
desirable; typically these comprise up to 5 % wt. based
on the sum of the weight of the base polymer
constituent, the conventional tackifying constituent,
the conventional wax constituent, and the low molecular
10 weight polyethylene copolymer constituent. Further
exemplary compositions are more particularly described
in the Examples below.

The hot melt adhesive compositions may be produced
according to conventional techniques, such as by
15 providing weighed amounts of the respective
constituents, heating the blended constituents to at
least the melting point of the lowest melting
constituent and effectively mixing the same.
Subsequently, the mixture may be cooled and the
20 adhesive composition recovered. In an alternative
method, a measured amount of at least one of the
constituents is provided to a vessel wherein it is
heated to its melting point, and afterwards weighed
amounts of the additional constituents are added and
25 blended to form a uniformly mixed composition which is
allowed to cool to room temperature (68°F, 20°C) and
solidify. Afterwards the cooled adhesive composition is
removed.

The present inventor has found that his inventive
30 hot melt adhesive compositions exhibit a striking
improvement in the adhesive strength when applied to a
wide variety of substrates, both polar substrates,
i.e., metals, polycarbonates, polyesters such as PET,
halogenated polymeric materials such as polyvinyl
35 chloride materials, and further to a wide variety of

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non-polar or moderately polar materials, including polyolefins.

The present inventor has further found that the improved hot melt adhesive compositions as being taught
5 herein are useful in the formation of structures and articles wherein two substrates either of the same or different polar characteristics may be joined by an intermediate layer of the hot melt adhesive compositions having interfacial contact with the
10 surfaces of the substrates; such structures may be formed by conventional techniques.

While not wishing to be bound by any theory, it is believed by the present inventor the inclusion of hydroxyl and ketone moieties provides polar moieties to
15 the ethylene copolymer molecule of which they form a part; the degree of polarity of these included moieties in an ethylene copolymer are comparable with the polarity of ethylene/vinyl acetate copolymers which are known to the art, and yet, unlike the ethylene/vinyl
20 acetate copolymers of the prior art wherein the acetoxy moieties used to impart polarity to the molecule are relatively sterically large and inhibit the formation of a crystallized form of the ethylene/vinyl acetate upon cooling, the inclusion of hydroxyl and ketone
25 moieties for providing polar moieties to the ethylene copolymer molecule of the present invention are relatively more polar than the acetoxy moieties, while simultaneously are sterically smaller, thus allowing for formation of a more crystallized form of the
30 ethylene copolymers upon cooling.

It is further believed by the inventor that these low molecular weight copolymers may provide faster setting speed adhesives than low molecular weight ethylene copolymer waxes of similar polarity, but,
35 containing comonomers such as vinyl acetate, methyl

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acrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate and acrylic acid because the latter types of copolymers are less crystalline than the E/CO or E/OH copolymers which are among the teaching of the present specification. It is believed that such E/Co and E/OH copolymers provide set speed comparable or better than conventional hydrocarbon waxes.

The foregoing invention will be more apparent by reference to specific embodiments which are representative of the invention. It is nonetheless to be understood that the particular embodiments described herein are provided for the purpose of illustration, and not be means of limitation, and that it is to be further understood that the present invention may be practiced in a manner which is not exemplified herein without departing from its scope.

EXAMPLES

In the following embodiments of the invention, it is to be understood that in the description of any composition, all percentages associated with a constituent used to form a composition are to be understood as to be "percentage by weight" of the particular constituent relative to the composition of which it forms a part. Exceptions to this convention will be particularly noted.

The following constituents were used in the Examples:

"E/n-butyl acrylate/CO" is an ethylene/n-butyl acrylate/carbon monoxide terpolymer which is characterized as having a melt index of 100 dg/minute according to ASTM D-1238, a ring and ball softening

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point of 205°F (95°C), and a glass transition temperature, "Tg" of -47°C.

It is presently commercially available from E.I. DuPont de Nemours, Inc., Delaware, USA as "EP-4043".

5 "Rosin Ester" is Foral® 85, a conventionally known tackifying constituent which includes the characteristics of: softening point of 80-88°C by the "Hercules Drop Method", and acid number of 3-10. It is presently commercially available from Hercules Inc.,
10 Delaware, USA.

"Microcrystalline wax" was Multiwax® 180W, a conventional microcrystalline wax commercially available from Witco Corp., New York, USA and characterized as featuring a melting point of 82-88°C
15 according to ASTM D-127, and a needle penetration at 25°C of 15-20 dmm according to ASTM D-1321.

"Stabilizer" was tetrakis [ethylene 3-(3', 5'-di-tert-butyl- 4'-hydroxyphenyl) propionate] commercially available as "Irganox® 1010", from Ciba-Geigy and used
20 as an oxidative stabilizer.

"E/VA copolymer I" was an ethylene/vinyl acetate copolymer used as the base polymer and characterized as being 27.2-28.8 % wt. of vinyl acetate groups, and having a Melt Index according to ASTM D-1238 of 365-440
25 dg/min. It is presently commercially available from E.I. DuPont de Nemours Co. as "ELVAX 210".

"E/VA copolymer II" was an ethylene/vinyl acetate copolymer used as the base polymer and characterized as being 27.2-28.8 % wt. of vinyl acetate groups, and
30 having a Melt Index according to ASTM D-1238 of 38-48 dg/min. It is presently commercially available from E.I. DuPont de Nemours Co. as "ELVAX 240".

The constituents illustrated on Table 1 and labeled in the column headed "Copolymers" were the
35 ethylene copolymers according to the present inventive

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teaching. All of the ethylene copolymers are low molecular weight random type ethylene/carbon monoxide copolymers.

TABLE 1

Copolymer	Mettler Drop Point, deg.C	Brookfield Viscosity, at 140 C	Penetrometer Hardness, dmm	carbon monoxide, %	density, g/cc
AX-1	106.6	385	3.2	1.4	0.921
AX-2	107.9	165	2.2	4.5	0.939
AX-3	96.5	230	7	13.7	0.958
AX-4	98.9	245	10.5	30	1.075
AX-5 *	102.8	217	4.5	2.6	--
AX-6 **	93.5	725	4	--	--
AX-7 ***	106.5	725	1.7	--	--
AX-8	100.6	300	3.4	8.3	0.944
AX-9	96.8	185	6.1	11	0.948

* Oxidized E-CO copolymer.

** AX-6 is reported as having a number average molecular weight by vapor phase osmometry of 2400, and 98% hydrolyzed, with a hydroxyl number of 150.

*** AX-7 is reported as having a number average molecular weight by vapor phase osmometry of 2910, and 95% hydrolyzed, with a hydroxyl number of 83.

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Preparation of the samples according to the Examples was in accordance with the following general procedure: weighed amounts of the individual
5 constituents used to formulate the respective Example composition were provided to a vessel which was then heated over a heating mantle until all of the constituents were melted, which was mixed with stirring rod to assure good mixing. Subsequently, the heat was
10 withdrawn and the composition allowed to cool until hard. The composition was then removed for subsequent melting operations and testing.

Testing of the Example compositions were in accordance with the following test protocols.

15 "SAFT" the shear adhesion failure temperature which includes the following protocol. First, using a 0.08 mm thick sheet of a film formed entirely of the hot melt adhesive compositions, 2.54 cm by 2.54 cm lap shear bonds were formed to 60 lb. weight kraft paper
20 using a Seal Model 210M press at 177°C for 3 seconds. Afterwards, 3 such prepared test samples were hung vertically in an air circulating oven at 32°C and a 1 kg mass was suspended from the bottom strip; the temperature was raised at a rate of 5°C per 15 minutes
25 and the sample observed; the time and temperature of the failure was determined and the average of the three test samples was reported.

Viscosity was determined by the use of a standard Brookfield Thermocel viscometer.

30 The Mettler Softening Point was determined according to the protocols of ASTM D-3954.

"T-Peel Adhesion" was in accordance with ASTM D-1876 testing procedures. The tested substrates included: aluminum foil, Lexan® (polycarbonate), Mylar®
35 (polyethylene terephthalate), untreated polypropylene

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film, having thicknesses of either 5 mil [0.02 cm] or 13 mil [0.051 cm], and polyvinyl chloride film having thickness of 8 mil [0.0031 cm]. The T-Peel Adhesion was evaluated for each substrate in accordance with the following: (a) a 0.08 mm thick film of the hot melt adhesive was formed; (b) the film was placed between 2 sheets of the tested substrate to form a multilayer structure therefrom; and (c) subsequently the multilayer structure was laminated by heat sealing it at 135°C for 15 seconds in the case of aluminium foil, Lexan®, or Mylar® substrates, or at 135°C for 20 seconds for the polypropylene substrate, or 110°C for 15 seconds for the PVC film substrate. Lamination was performed using a Seal® Model 210M press. The samples were allowed to cool, and afterwards tested.

Alternately, after the lamination step, certain of the samples were heat aged for 7 days in a hot air circulating oven maintained at a temperature of 135°F (56.5°C) after which these samples which are considered as the "heat aged" samples, were tested after they had been allowed to cool to room temperature, approx. 20°C.

Examples "Control", 1-5 as indicated on Table 2 illustrate various compositions. The Control example illustrates a composition as is known to the prior art, while Examples 1-5 illustrate compositions according to the present invention; various amounts of different ethylene/carbon monoxide random copolymers, including an oxidized ethylene/carbon monoxide random copolymer, as described in the foregoing description are used, both in conjunction with the conventional microcrystalline wax as well as without said wax. Table 3 reports the resultant physical properties of the respective Example compositions on the various substrates, including the SAFT, viscosity and adhesion properties. As may be seen from these reported

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results, modest to significant improvements in the adhesion for both initial and aged samples were realized, dependent upon the substrated used. Of particular note are the compositions according to

5 Examples 3 and 4 which surprisingly show significant improvements in adhesion to untreated polypropylene and aluminum foil, both initially and subsequent to heat aging. Example 3 also exhibits significantly improved adhesivity to the polyester substrate, Mylar®.

TABLE 2

Example:	Control	1	2	3	4	5
E/n-butyl acrylate/CO	34.8	34.8	34.8	34.8	34.8	34.8
rosin ester	40	40	40	40	40	40
microcrystalline wax	25	20	20	-	-	-
AX-1	-	5	-	-	-	-
AX-2	-	-	5	-	-	-
AX-3	-	-	-	25	-	-
AX-4	-	-	-	-	25	-
AX-5	-	-	-	-	-	25
stabilizer	0.2	0.2	0.2	0.2	0.2	0.2

TABLE 3

Example:	Control	1	2	3	4	5
Physical Properties:						
SFFT: seconds at (deg.F)	229 (131F)	110 (131F)	629 (122F)	305 (149F)	790 (122F)	250 (131F)
SFFT: seconds at (deg.C)	229 (54.5C)	110 (54.5C)	629 (49.5C)	305 (64.3C)	790 (49.5C)	250 (54.5)
Viscosity, cps at						
350 deg.F, 143 deg.C:	1325	975	1200	2650	7000	2500
Mettler Soft. Pt. (deg.C)	86.2	91	89.6	91.5	88.4	98.9
T-Peel Adhesion						
Aluminum Foil, Initial						
lb/in [g/cm] :	2 [357.2]	3 [535]	4.7 [840]	4.1 [732]	4.7 [840]	3.5 [625]
Aluminum Foil, 7 days						
lb/in [g/cm] :	1.15 [205]	3.02 [540]	4.28 [764]	5.23 [934]	5 [893]	4.36 [779]
Lexan, Initial						
lb/in [g/cm] :	6.9 [1232]	5.3 [947]	6.7 [1197]	6.2 [1107]	3.9 [696]	7 [1250]
Lexan, 7 days						
lb/in [g/cm] :	6.5 [1161]	5.2 [928]	7.7 [1375]	7.1 [1268]	4.04 [722]	7.5 [1400]
Mylar, Initial						
lb/in [g/cm] :	5.69 [1016]	5.27 [941]	6.47 [1155]	7.48 [1336]	4.7 [839]	6.66 [1190]
Mylar, 7 days						
lb/in [g/cm] :	5.89 [1051]	5.64 [1007]	7.15 [1277]	7.17 [1280]	7.46 [1332]	7.8 [1394]
untr. polypropylene, Init.						
lb/in [g/cm] :	0.94 [167]	2.1 [375]	0.17 [30.4]	2.01 [359]	3.49 [623.3]	0.45 [80.4]
untr. polyprop., 7 days						
lb/in [g/cm] :	0	0.93 [166]	0.27 [48.2]	5.06 [903]	4.92 [878.7]	0.46 [82.2]
PVC film *, Initial						
lb/in [g/cm] :	5.9 [1053]	5.6 [1000]	5.5 [982]	7.2 [1286]	6 [1071]	6.3 [1125]
PVC film*, 7 days						
lb/in [g/cm] :	0.26 [46.5]	0.32 [57.2]	0.38 [67.9]	0.07 [12.5]	0.29 [51.8]	0.32 [57.15]

* PVC film thickness, 13 mils [0.0051 cm]

TABLE 4

Example:	Control 2	6	7	8	9	10
E/VA copolymer I	42.7	42.7	42.7	42.7	42.7	42.7
rosin ester	32	32	32	32	32	32
microcrystalline wax	25	20	20	20	20	-
AX-1	-	5	-	-	-	25
AX-2	-	-	5	-	-	-
AX-6	-	-	-	-	5	-
AX-7	-	-	-	5	-	-
stabilizer	0.3	0.3	0.3	0.3	0.3	0.3

Example:	11	12	13	14	15
E/VA copolymer I	42.7	42.7	42.7	42.7	42.7
rosin ester	32	32	32	32	32
microcrystalline wax	-	-	20	-	-
AX-2	25	-	-	-	-
AX-6	-	25	-	-	-
AX-3	-	-	5	25	-
AX-4	-	-	-	-	25
stabilizer	0.3	0.3	0.3	0.3	0.3

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Examples Control 2, 6-15 indicated on Table 4 further illustrate further compositions, wherein Example "Control 2" is a further control composition according to the prior art, and Examples 6-15 are in accordance with the present invention's teaching. Examples 6-15 as indicated on Table 4 illustrates the use of an E/VA type base copolymer, characterized as having a melt index of 400 dg/minute, and further including the characteristics described above, with varying amounts of differing low molecular weight ethylene random copolymers as described above. The Examples Control 2, 6-15 were tested and the test results indicated on Table 5 illustrate the moderate to significant improvements in the adhesion for both initial and aged samples. Of particular note are the compositions according to Examples 9-15 which surprisingly show significantly improved adhesive characteristics for both as-applied adhesive samples as well as aged samples. The significant improvements in adhesion, particularly as shown to untreated polypropylene substrates, particularly shown by Examples 12, 14 and 15 are of especial note. The composition according to 12 shows significantly improved adhesion to a polycarbonate substrate, Lexan®. The composition according to 9 shows significantly improved adhesion to the polyester substrate, Mylar®.

TABLE 5

Example:	Control 2	6	7	8	9	10
Physical Properties:						
SFFT: seconds at (deg.F)	103 (149F)	196 (149F)	186 (149F)	332 (149F)	130 (140F)	702 (140F)
SFFT: seconds at (deg.C)	103 (64C)	196 (64C)	186 (64C)	332 (64C)	130 (59.4C)	702 (59.4C)
T-Peel Adhesion						
Aluminum Foil, Initial						
lb/in [g/cm] :	4.4 [786]	2.02 [360]	2.1 [375]	1.96 [350]	2 [357.2]	2.8 [500]
Aluminum Foil, 7 days						
lb/in [g/cm] :	1.32 [235.8]	1.32 [235.7]	1.28 [228.6]	1.59 [284]	2.33 [416.1]	2.99 [534]
Lexan, Initial						
lb/in [g/cm] :	4.66 [832.3]	5.36 [957.3]	5.15 [919.8]	5.34 [953.7]	5.77 [1030]	4 [714.4]
Lexan, 7 days						
lb/in [g/cm] :	2.83 [505]	1.99 [355]	2.46 [439.4]	2.1 [375]	2.5 [446.5]	3.63 [648.3]
Mylar, Initial						
lb/in [g/cm] :	3.79 [677]	4.3 [768]	4.58 [818]	5.11 [912.6]	5.03 [898.4]	5.75 [1026]
Mylar, 7 days						
lb/in [g/cm] :	2.28 [407]	2.07 [370]	2.61 [466]	2.73 [487.6]	4.57 [816.2]	3.77 [673.3]
untr. polypropylene, Init.						
5 mil, lb/in [g/cm] :	0.14 [25]	1.28 [228.6]	0.2 [35.7]	0.2 [35.7]	0.46 [82.2]	0.65 [116.1]
untr. polyprop., 7 days						
5 mil, lb/in [g/cm] :	1.42 [253.6]	0.87 [155.3]	0.3 [53.6]	0.41 [73.2]	4.18 [746.5]	0.67 [119.6]
PVC film*, Initial						
lb/in [g/cm] :	1.48 [264.3]	0.8 [142.8]	1.11 [198.2]	1.2 [214.3]	1.59 [284]	2.12 [378.6]
PVC film*, 7 days						
lb/in [g/cm] :	0.06 [10.7]	0.05 [8.9]	0.05 [8.9]	0.06 [10.7]	0.05 [8.93]	0.06 [10.7]

* PVC film thickness, 13 mils [0.0051 cm]

TABLE 5 (continued)

Example:	11	12	13	14	15
Physical Properties:					
SAPT: seconds at (deg.F)	873 (158F)	709 (131F)	401 (140F)	517 (149F)	488 (131F)
SAPT: seconds at (deg.C)	873 (69.3C)	709 (54.5C)	401 (59.5C)	517 (64.5C)	488 (54.5C)
T-Peel Adhesion					
Aluminum Foil, Initial					
lb/in [g/cm] :	3.44 [614]	3.39 [605]	1.9 [339]	2.72 [486]	2.08 [371.5]
Aluminum Foil, 7 days					
lb/in [g/cm] :	3.6 [643]	3.54 [632]	1.36 [243]	3.24 [578.7]	2.08 [371.5]
Lexan, Initial					
lb/in [g/cm] :	5.62 [1003]	7.15 [1277]	5.37 [959]	2.93 [523]	1.12 [200]
Lexan, 7 days					
lb/in [g/cm] :	5.64 [1007]	6.53 [1166]	5.29 [943]	3.79 [677]	0.96 [171.5]
Mylar, Initial					
lb/in, [g/cm] :	5.75 [1027]	0.95 [169.7]	5.08 [907]	1.3 [232]	2.78 [496.5]
Mylar, 7 days					
lb/in [g/cm] :	4.8 [863]	5.37 [959]	1.24 [221]	4.7 [850]	4.17 [744.7]
untr. polypropylene, init.					
5 mil, lb/in [g/cm] :	0.98 [175]	4.94 [822]	0.24 [42.9]	4.7 [852]	3.78 [675]
untr. polyprop., 7 days					
5 mil, lb/in [g/cm] :	0.84 [150]	4.03 [719]	2.08 [371]	4.37 [780]	4.14 [740]
PVC film, Initial					
lb/in [g/cm] :	2.27 [405]	2.97 [530]	1.26 [225]	2.54 [454]	0.81 [144.6]
PVC film, 7 days					
lb/in [g/cm] :	0.07 [12.5]	0.06 [10.7]	0.07 [12.5]	0.06 [10.7]	0.09 [16]

* PVC film thickness, 13 mils [0.0051 cm]

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Examples Control 3, 16-21 indicated on Table 6 further illustrate further compositions, wherein Example "Control 3" is a further control composition according to the prior art, and Examples 16-21 are in accordance with the present invention's teaching. The Examples indicated on Table 6 illustrate the use of an E/VA type base copolymer, characterized as having a melt index of 43 dg/min, and further including the characteristics described above, with varying amounts of differing ethylene random copolymers as described above. The Examples Control 3, 16-21 were tested and the test results indicated on Table 7 illustrate the moderate to significant improvements in the adhesion for both initial and aged samples. Of particular note are the results reported for adhesion to the polycarbonate substrate, Lexan®, particularly by Examples 16-21.

It will be appreciated that the instant specifications and examples set forth herein are by way of illustration and not limitation, and that various modifications and changes may be made without departing from the spirit and scope of the present invention, whose limitations are bounded only by the appendant claims.

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TABLE 7

Example:	Control 3	16	17	18	19	20	21
Physical Properties:							
Viscosity, cps at 350 deg.F, 143 deg.C:	5125	3250	4600	3200	2700	2150	2150
Mettler Soft. Pt. (deg.C):	86.5	97.2	101	96.3	101.3	89.6	87
T-Peel Adhesion							
<u>Aluminum Foil, Initial</u>							
lb/in [g/cm] :	2.3 [411]	2.54 [453]	2.68 [479]	2.09 [373]	2.98 [532]	2.15 [384]	2.21 [395]
<u>Aluminum Foil, 7 days</u>							
lb/in [g/cm] :	1.61 [287.5]	1.92 [343]	2.34 [418]	1.97 [352]	2.26 [403]	1.16 [207]	1.6 [285]
<u>Lexan, Initial</u>							
lb/in [g/cm] :	5 [893]	5.68 [1015]	5.34 [954]	6.09 [1088]	6.01 [1073]	6.33 [1130]	5.78 [1032]
<u>Lexan, 7 days</u>							
lb/in [g/cm] :	3.41 [609]	5.14 [918]	4.72 [843]	5.17 [923]	5.94 [1061]	6.24 [1114]	4.8 [864]
<u>Mylar, Initial</u>							
lb/in [g/cm] :	2.89 [516]	2.96 [528]	3.27 [584]	2.83 [505]	3.4 [608]	3 [535.8]	2.91 [520]
<u>Mylar, 7 days</u>							
lb/in [g/cm] :	1.46 [260]	2.31 [413]	2.72 [486]	3.13 [559]	1.86 [332]	2.45 [437.6]	1.13 [202]
<u>untr. polypropylene, ink.</u>							
5 mils., lb/in [g/cm] :	0.24 [43]	0.2 [35.7]	0.41 [73.2]	0.2 [35.7]	0.32 [57.7]	0.22 [39.3]	0.83 [148]
<u>untr. polyprop., 7 days</u>							
5 mils., lb/in [g/cm] :	0.72 [129]	0.59 [105]	0.61 [109]	0.75 [134]	0.34 [60.7]	0.23 [41]	0.24 [43]
<u>PVC film, Initial</u>							
lb/in [g/cm] :	2.26 [403]	2.69 [480]	2.78 [497]	2.27 [405]	3.4 [607]	2.73 [487.6]	2.09 [373]

* PVC film thickness, 13 mils [0.0051 cm]

CLAIMS

1. A hot melt adhesive compositions which comprise:
a base polymer constituent,
5 a tackifying constituent,
a wax constituent, and
a low molecular weight polyethylene copolymer
constituent which includes ketone functional moieties
and/or hydroxyl functional moieties.
10
2. The hot melt adhesive composition according to
claim 1 wherein the low molecular weight polyethylene
copolymer has a melt index in excess of about 3000
dg/min according to ASTM D-1238.
15
3. The hot melt adhesive composition according to
claim 1 wherien the low molecular weight polyethylene
copolymer is an ethylene/carbon monoxide copolymer
which consist of between 0.01 - 99.99 wt.% ethylene and
20 0.01 - 99.99 wt.% carbon monoxide.
4. The hot melt adhesive composition according to
claim 3 wherein the low molecular weight polyethylene
copolymer is an ethylene/carbon monoxide copolymer
25 which consists of between about 50-99.9% ethylene, and
between about 0.1-50% carbon monoxide.
5. The hot melt adhesive composition according to
claim 1 wherien the low molecular weight polyethylene
30 copolymer is an ethylene/vinyl alcohol copolymer which
is comprised of between 0.01 - 99.99 wt.% ethylene and
0.01 - 99.99 wt.% vinyl alcohol.
6. The hot melt adhesive composition according to
35 claim 5 wherien the low molecular weight polyethylene

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copolymer is an ethylene/vinyl acetate copolymer is at least partially saponified.

7. The hot melt adhesive composition according to
5 claim 1 wherein the low molecular weight polyethylene
copolymer is a low molecular weight polyethylene
terpolymer selected from the group which consists of:
E/AAc/CO terpolymers or E/AAc/OH terpolymers wherein
the "AAc" comonomer is methyl acrylate, ethyl acrylate,
10 n-butyl acrylate or 2-ethylhexylacrylate, E/AA/CO,
E/MAA/CO and E/MA/CO terpolymers.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/02386

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C09J173/00; C09J123/08		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C09J ; C08L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	US,A,4 076 911 (D. M. FENTON) 28 February 1978 see column 3, line 27 - line 36; claims 1-3,10; example 3 ---	1-4
Y	PATENT ABSTRACTS OF JAPAN (C-0881)5 November 1991 & JP,A,31 81 557 (DU PONT MITSUI) 7 August 1991 cited in the application see abstract ---	1-4
A	WO,A,9 118 043 (DU PONT DE NEMOURS) 28 November 1991 see claims; tables --- -/--	1
<p>¹⁰ Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
25 MAY 1993	11. 05. 93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	KLIER E.K.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	RESEARCH DISCLOSURE no. 138, October 1975, page 8 13816 'novel uses for terpolymers of ethylene-vinyl acetate-carbon monoxide' & FR,A,2 149 932 (DU PONT DE NEMOURS) 30 March 1973 -----	1

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

US 9302386
SA 71540

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4076911	28-02-78	None	
WO-A-9118043	28-11-91	JP-A- 4227982	18-08-92

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