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(21) International application number: PCT/FR96/01425 (22) International filing date: 13 September 1996 (13.09.96) (30) Data relating to the priority: 95/11.253 26 September 1995 (26.09.95) FR (71) Applicant (for all designated States except US): ATO FINDLEY S.A. [FR/FR]; 4/8, cours Michelet, La Défense 10, F-92800 Puteaux (FR). (72) Inventors: and (75) Inventors/Applicants (US only): François BAUDUIN [FR/FR]; 12, rue d'Alsace, F-60200 Compiègne (FR). Thierry DREYFUS [FR/FR]; 304, rue du Maréchal- Foch, F-60280 Margny-les-Compiègne (FR). Jean- Marie BORDAT [FR/FR]; 19, rue de la Batterie- Hennequin, F-60170 Bailly (FR). (74) Representative: Patricia CHOSSON; Elf Atochem S.A., Industrial Property Department, Cours Michelet - La Défense 10, F-92091 Paris-La Défense Cédex (FR).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO Patent (KE, LS, MW, SD, SZ, UG), Eurasian Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI Patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With the International Search Report.

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(54) Title: HOT-MELT PRESSURE SENSITIVE ADHESIVE FOR ADHESIVE STRIPS

(54) Titre: COLLE THERMOFUSIBLE AUTO-ADHESIVE POUR RUBANS ADHESIFS

(57) Abstract

The invention discloses a hot-melt pressure sensitive adhesive composition characterised in that it includes (a) at least one ethylene-vinyl acetate, ethylene-methyl acrylate or ethylene-butyl acrylate copolymer, (b) a solid tackifying resin, (c) a liquid tackifying resin, (d) an anti-oxidant and optionally (d) a fluidising agent. The invention also discloses a hot-melt pressure sensitive adhesive composition for the preparation of labels and adhesive strips, more particularly for skin-contacting adhesive strips.

(57) Abrégé

La présente invention a pour objet une composition thermofusible auto-adhésive caractérisée en ce qu'elle comprend: a) au moins un copolymère éthylène-acétate de vinyle, éthylène-acrylate de méthyle ou éthylène-acrylate de butyle, b) une résine tackifiante solide, c) une résine tackifiante liquide, d) un anti-oxydant, e) et éventuellement un fluidifiant. L'invention concerne également l'utilisation de la composition thermofusible auto-adhésive pour la préparation d'étiquettes et de rubans adhésifs et plus particulièrement des rubans destinés à être en contact avec la peau.

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PRESSURE-SENSITIVE HOT-MELT ADHESIVE
FOR ADHESIVE TAPES

The invention relates to a pressure-sensitive hot-melt adhesive composition and to its use for the manufacture of labels and adhesive tapes and more particularly of tapes intended to come into contact with the skin.

Adhesives in suspension or in solution in organic solvents are conventionally employed in the manufacture of adhesive tapes. When these adhesives are used it is necessary to carry out a stage of evaporation of the solvent, and this has the result of, on the one hand, limiting the production rate and, on the other hand, producing effluents of toxic character, the removal of which is found to be costly and tricky.

In order to avoid the use of solvents it has been proposed to employ pressure-sensitive hot-melt adhesives.

In WO 93/23488 an adhesive is proposed permitting the adhesive bonding of materials of low surface energy, for example a polyethylene film and a nonwoven fabric. This adhesive includes 75-98 % of a diblock copolymer A-B, in which A consists predominantly of polystyrene or its derivatives and B is poly-1,3-butadiene, and a mixture consisting of a solid tackifying resin and of a liquid or oily tackifying resin.

In US 5,290,842, a composition is described for the adhesive pasting of labels, which has good cohesion at ambient temperature. This composition includes a first elastomer, for example polybutadiene, and a second elastomer which has a glass transition temperature that is higher than that of the first elastomer, for example polyisoprene, and a tackifying agent which is miscible with the second elastomer.

Patent EP 0104005-A describes an adhesive composition for the adhesive bonding of female protections to garments. This composition includes a viscoelastic polymer of A-B-A type in which B denotes a polyolefin, for example an ethylene-butylene copolymer, and A denotes a polystyrene, and a tackifying resin.

Finally, in WO 93/10734, a positioning adhesive is proposed for female protections on silk, cotton and synthetic fibres. This adhesive includes 6-25 % of a copolymer of formula $(A-B)_n-Y$, in which Y is a polyvalent coupling agent, A is a vinyl monomer substituted by an aromatic radical and B is polybutadiene, 30-70 % of a compatible tackifying resin and 10-40 % of a plasticizing oil.

The pressure-sensitive thermoplastic adhesives which have just been mentioned, while making it possible to avoid the use of solvent, are not, however, completely satisfactory. Thus, the adhesive tapes which are coated therewith exhibit, after being pulled off, a tendency to transfer the adhesive onto

the support. In addition, the adhesive tapes in contact with the skin exhibit poor resistance to perspiration.

The present invention proposes a new pressure-sensitive hot-melt adhesive composition
5 exhibiting high cohesion and good resistance to moisture, this composition being characterized in that it includes

a) at least one ethylene-vinyl acetate, ethylene-methyl acrylate or ethylene-butyl acrylate
10 copolymer

b) a solid tackifying resin

c) a liquid tackifying resin

d) an antioxidant

e) and optionally a diluent.

15 The term "solid tackifying resin" here denotes tackifying resins exhibiting a ring-and-ball softening point higher than 60°C.

The term "liquid tackifying resin" here denotes a tackifying resin exhibiting a ring-and-ball
20 softening point lower than 60°C.

Another subject of the present invention is the use of the said pressure-sensitive hot-melt adhesive composition for the manufacture of labels and adhesive tapes and more particularly of adhesive tapes
25 intended to be adhesively bonded to the skin, such as, for example, bandages and dressings.

The copolymer according to the invention is generally chosen from copolymers exhibiting a vinyl

acetate or methyl or butyl acrylate content of between 15 and 65 % and preferably 30 and 50 % by weight.

Copolymers exhibiting a melt index of between 1 and 1000 and preferably 2 and 500 are preferably
5 employed.

Such copolymers can be obtained conventionally by high-pressure radical polymerization from ethylene and from vinyl acetate or methyl or butyl acrylate (see, for example, US 5 298 582).

10 The solid tackifying resin according to the invention is generally chosen from natural or modified, for example dimerized, hydrogenated or polymerized, rosin esters, such as pentaerythritol, diethylene glycol and glycerol esters, polyterpene resins, for
15 example α -pinene dipentene, copolymers of terpenes and of aromatic monomers such as styrene, vinyltoluene and α -methylstyrene, terphenolic resins, for example Dertophene T marketed by DRT, hydrocarbon resins of aliphatic and/or aromatic nature which are
20 unhydrogenated or partially or completely hydrogenated, and mixtures of these compounds.

Hydrocarbon resins are preferably employed, and especially when the adhesive is intended to come into contact with the skin.

25 Such solid resins exhibiting a ring-and-ball softening point of between 60 and 140°C and preferably 80 and 120°C are advantageously employed.

The liquid tackifying resin according to the

invention is generally chosen from natural or modified, for example dimerized, hydrogenated or polymerized, rosin esters, for example glycerol and di- and triethylene glycol esters, polyterpene resins, for example α -pinene dipentene, copolymers of terpenes and of aromatic monomers such as styrene, vinyltoluene and α -methylstyrene, terphenolic resins, hydrocarbon resins of aliphatic and/or aromatic nature which are unhydrogenated or partially or completely hydrogenated and mixtures of these compounds.

Polyterpene resins and hydrocarbon resins are preferably employed, and especially when the adhesive is intended to come into contact with the skin.

Such liquid resins exhibiting a ring-and-ball softening point lower than 40°C are preferably employed.

The antioxidant is generally chosen from the compounds of the sterically hindered phenol type, such as Irganox, marketed by Ciba Geigy, amines, phosphites and mixtures of these compounds.

The diluent according to the invention may be chosen from any type of diluent which is compatible with the copolymer employed. Polybutene, phthalates such as dioctyl phthalate (DOP), diisononyl phthalate (DINP) or diisodecyl phthalate (DIDP) and naphthenic or paraffinic oils are preferably employed.

The pressure-sensitive hot-melt adhesive composition according to the invention is obtained by

mixing the various abovementioned constituents at a temperature which is generally between 120 and 150°C.

The pressure-sensitive hot-melt adhesive composition according to the invention generally includes from 30 to 50 % by weight and preferably 30 to 40 % of copolymer, from 10 to 40 % and preferably 15 to 35 % of solid tackifying agent, from 10 to 40 % and preferably 15 to 35 % of liquid tackifying resin, from 0.1 to 2 % of antioxidant and from 0 to 20 % of diluent.

When the composition is intended to be in contact with the skin the use of diluent is preferably avoided.

The pressure-sensitive hot-melt adhesive composition in accordance with the invention may be employed for the preparation of labels and adhesive tapes of any type. Purely by way of illustration it is possible to mention the coating, for example by means of a book nozzle, of substrates such as films based on polyethylene, polypropylene and polyvinyl chloride.

As a result of its properties of resistance to perspiration, the composition in accordance with the invention is particularly recommended for the preparation of adhesive tapes for cutaneous use such as adhesive dressings and strappings. In addition, such tapes exhibit a greater adhesiveness at the temperature of use close to 37°C than at ambient temperature, and this allows easy repositioning of the tape on the skin

in the event of incorrect application.

The examples which follow enable the invention to be illustrated.

In the examples the shear strength under
5 stress (holding power) is measured according to PSTC standard 7.

The 180° peel is measured according to PSTC standard 1.

The T peel test is measured according to the
10 method which consists in folding back onto itself the substrate coated with the adhesive to be tested, applying a moderate manual pressure to the said folded-back substrate and unbonding the portions thus adhesively bonded. The test is satisfactory when the
15 substrate retains the appearance and adhesive properties of the substrate before bonding.

EXAMPLE 1

A pressure-sensitive hot-melt adhesive composition is produced by mixing the following
20 compounds (in % by weight):

- EVA 4055	:	32.0
(ethylene-vinyl acetate copolymer; vinyl acetate: 40 %; melt index: 55; Bayer)		
25 - Liquid petroleum resin (ECR 2520; Exxon)	:	38.8

- Solid petroleum resin (ECR 368 LC; : 29.0
Exxon)
- Antioxidant (IRGANOX 1010; : 0.2
Ciba Geigy)

5 The composition thus obtained is applied onto a polyvinyl chloride film at a rate of 40 g/m² to form a dressing.

 The coated substrate has a holding power equal to 50 mm and a 180° peel of 18 N/25 mm at 23°C
10 and 36 N/25 mm at 40°C.

 The T peel test is satisfactory.

 After application of the dressing to the skin it is found that the rupture on the skin is adhesive without transfer of adhesive onto the skin.

15 EXAMPLE 2

 The conditions of Example 1 are followed in the presence of the following compounds (in % by weight):

- EVA 4055 : 30.0
20 (ethylene-vinyl acetate copolymer;
vinyl acetate: 40 %; melt index: 55;
Bayer)
- Liquid petroleum resin (ECR 2520; : 36.8
Exxon)
- Solid petroleum resin (Escorez 5320; : 33.0
25 Exxon)
- Antioxidant (Irganox 1010; : 0.2
Ciba Geigy)

The coated substrate (dressing) exhibits a holding power equal to 80 mm and a 180° peel of 19 N/25 mm at 23°C.

The T peel test is satisfactory.

5 After application of the coated substrate onto the skin it is found that the rupture on the skin is adhesive without transfer of the adhesive onto the skin.

EXAMPLE 3

10 The conditions of Example 1 are followed in the presence of the following compounds (in % by weight):

- | | | | |
|----|---|---|------|
| | - Lotryl 28MA175 | : | 32.0 |
| | (ethylene-methyl acrylate copolymer; | | |
| 15 | methyl acrylate: 28 %; melt index: 175; | | |
| | Elf Atochem S.A.) | | |
| | - Liquid petroleum resin (ECR 2520; | : | 29.0 |
| | Exxon) | | |
| | - Solid petroleum resin (ECR 385; | : | 38.8 |
| 20 | Exxon) | | |
| | - Antioxidant (IRGANOX; Ciba Geigy) | : | 0.2 |

The coated substrate (dressing) exhibits a holding power of 7 mm and a 180° peel of 25 N/25 mm at 23°C.

25 The T peel test is satisfactory.

After application of the coated substrate onto the skin it is found that the rupture on the skin is adhesive, without transfer of adhesive onto the

skin.

EXAMPLE 4

A self-adhesive hot-melt composition is prepared by mixing together the following compounds (in % by weight):

5	- Lotryl 28MA175	:	30.0
	(ethylene/methyl acrylate copolymer; 28 % methyl acrylate; melt index: 175; Elf Atochem S.A.)		
10	- Lotryl 35BA320	:	15.0
	(ethylene/butyl acrylate copolymer; 35 % butyl acrylate; melt index: 320; Elf Atochem S.A.)		
15	- Liquid petroleum resin (ECR 2520; Exxon)	:	25.0
	- Solid petroleum resin (ECR 6372; Exxon)	:	29.8
	- Antioxidant (Irganox 1010; Ciba-Geigy)	:	0.2

20 The composition thus obtained has a Brookfield viscosity at 160°C equal to 6000 mPa s and a ring-and-ball softening point equal to 66°C.

This composition is applied to a film of polyvinyl chloride at a rate of 40 g/m² to form a
25 dressing.

The T peel test is correct.

After applying the dressing to the skin, it is observed that the rupture on the skin is adhesive

without transfer of adhesive onto the skin.

**CLAIMS**

1. Pressure-sensitive hot-melt adhesive composition characterized in that it includes

- a) at least one ethylene-vinyl acetate, ethylene-
5 methyl acrylate or ethylene-butyl acrylate copolymer
- b) a solid tackifying resin
- c) a liquid tackifying resin
- d) an antioxidant
- e) and optionally a diluent.

10 2. Composition according to Claim 1, characterized in that the vinyl acetate, methyl acrylate or butyl acrylate content in the copolymer is between 30 and 50 %.

3. Composition according to Claim 2,
15 characterized in that the copolymer has a melt index of between 1 and 1000.

4. Composition according to one of Claims 1 to 3, characterized in that the solid tackifying resin has a ring-and-ball softening point of between 60 and
20 140°C.

5. Composition according to Claim 4, characterized in that the resin is chosen from rosin esters, pentaerythritol esters, polyterpene resins, copolymers of terpenes and of aromatic monomers,
25 terphenenolic resins, hydrocarbon resins of aliphatic and/or aromatic nature and mixtures of these compounds.

6. Composition according to one of Claims 1



to 5, characterized in that the liquid tackifying resin has a ring-and-ball softening point lower than 40°C.

7. Composition according to Claim 6, characterized in that the resin is chosen from rosin
5 esters, glycerol, di- or triethylene glycol esters, polyterpene resins, copolymers of terpenes and of aromatic monomers, terpenephenolic resins, hydrocarbon resins of aliphatic and/or aromatic nature and mixtures of these compounds.

10 8. Composition according to one of Claims 1 to 7, characterized in that it includes from 30 to 50 % by weight of copolymer, from 10 to 40 % by weight of solid tackifying resin, from 10 to 40 % by weight of liquid tackifying resin, from 0.1 to 2 % by weight of
15 antioxidant and from 0 to 20 % by weight of diluent.

9. Use of the composition according to one of Claims 1 to 8 for the preparation of labels and adhesive tapes.

10. Use according to Claim 9, characterized
20 in that the tape is intended to be applied to the skin.

11. Adhesive tape enclosing the composition according to any one of Claims 1 to 8.

12. Adhesive dressing enclosing the composition according to any one of Claims 1 to 8.

25 13. Adhesive strapping enclosing the composition according to any one of Claims 1 to 8.

14. Adhesive label enclosing the composition according to any one of Claims 1 to 8.