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(54) Title: HOT-MELT ADHESIVE

(57) Abstract: To provide a hot-melt adhesive, a solidified coating of which is excellent in non-slip performance on cardboard, and with which the cardboard can be easily peeled off from a pallet without damaging the cardboard substrate. A hot-melt adhesive comprising a crystalline olefin polymer (A), a noncrystalline olefin polymer (B), a tackifying resin (C) and a wax (D), wherein the crystalline olefin polymer (A) comprises a metallocene-type propylene/ethylene copolymer (A1) having an ethylene content of 5 to 10% by weight.



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Description

Title of Invention: HOT-MELT ADHESIVE

Technical Field

- [0001] The present invention relates to a hot-melt adhesive, and cardboard to which the hot-melt adhesive is applied.
- Background Art
- [0002] A hot-melt adhesive is an adhesive not containing a solvent, it is heated, melted and applied to an adherend, and then, solidified by being cooled to develop adhesion. Therefore, the hot-melt adhesive has features of enabling instant bonding and high-speed bonding (high-speed setting), and is used in a wide variety of fields such as paper processing, woodworking, sanitary material and electronic fields.
- [0003] As a base polymer of the hot-melt adhesive, there have generally been used, according to the intended use, for example, ethylene/carboxylate copolymers such as ethylene-vinyl acetate copolymers (hereinafter also referred to as “EVA”), ethylene-ethyl acrylate copolymers (hereinafter also referred to as “EEA”); polyolefins such as polyethylene, polypropylene and copolymers of ethylene and α -olefins; synthetic rubbers such as styrene-based block copolymers (for example, styrene-isoprene-styrene block copolymers, styrene-butadiene-styrene block copolymers and their hydrogenated products); polyurethanes; and the like.
- [0004] Among these hot-melt adhesives, a hot-melt adhesive using noncrystalline poly- α -olefins (APAO) as a base polymer is sometimes used in cardboard processing as disclosed in Patent Documents 1 and 2.
- [0005] A cardboard is a sheet in which a paper board liner is laminated on one side or both sides of a paper board serving as an inner core formed in a corrugated shape. The paper board used for the liner includes kraft liner (K liner) made from kraft pulp and used paper, jute liner (C liner) made from used paper and the like. A typical example of the cardboard includes an exterior cardboard described in JIS 1516.
- [0006] The hot-melt adhesive for cardboard may be used as a non-slip member for cardboard besides cardboard processing. Cardboard surfaces are smooth and mutually slippery. A plurality of stacked cardboard boxes, for example, may collapse if they are slightly tilted while being moved, the risk is high when handling stacked packages, and the work efficiency is lowered.
- [0007] When a plurality of cardboard boxes are stacked, if a coating of the hot-melt adhesive is formed on cardboard surfaces, the coating of the hot-melt adhesive makes the cardboard surfaces non-slip, and even if they are tilted, the stacked packages will not collapse. The coating of the hot-melt adhesive is formed, for example, by heating and melting the hot-melt adhesive, applying it to a cardboard surface, and cooling and so-

lidifying the applied layer.

- [0008] A plurality of cardboard boxes are stacked on an olefin pallet, and these stacked packages are prevented from collapsing. Consequently, safety when handling the stacked packages is improved, and it becomes easy to move the packages with them being placed on the pallet. Therefore, the work efficiency is also improved.
- [0009] As described above, when cardboard boxes are stacked on the coating of the hot-melt adhesive, the stacked cardboard boxes are strongly stuck to each other if the cooled and solidified hot-melt adhesive still has excellent adhesion, and substrate damage may occur in the event of unpacking the stacked cardboard boxes.
- [0010] Therefore, it is desirable that the hot-melt adhesive for cardboard have at least two performances of making the stacked cardboard boxes non-slip, and not adhering to the cardboard in a cooled and solidified state.
- [0011] Patent Document 1 discloses a hot-melt adhesive containing a noncrystalline poly- α -olefin, a crystalline metallocene-type poly- α -olefin, and a tackifying resin ([claim 1], [Table 1]-[Table 8]). In the hot-melt adhesive of Patent Document 1, a cooled and solidified coating has excellent frictional properties on cardboard, and has excellent non-slip performance. However, stacked cardboard packages with a coating of this hot-melt adhesive may be difficult to be peeled off from a pallet, and there is still room for improvement regarding peel-off performance.
- [0012] Patent Document 2 discloses a hot-melt adhesive comprising an ethylene- α -olefin copolymer, polypropylene having a softening point of 80 to 100°C, a tackifying resin having a softening point of 110 to 150°C, and a wax, and paper packaging materials ([claim 1], [claim 6], [Table 1]). In the hot-melt adhesive of Patent Document 2, adhesive performance is maintained even in a wide temperature range environment of -20 to 55°C, particularly by using an ethylene-1-octene copolymer as the ethylene- α -olefin copolymer. However, non-slip performance or peel-off performance on cardboard with the solidified coating is not described in Patent Document 2.
- [0013] Furthermore, in the hot-melt adhesive of Document 2, depending on its composition, thread formation or exudation to a paper substrate such as cardboard may occur when discharged from a hot melt gun and applied to an adherend.

Citation List

Patent Literature

- [0014] [PTL1]Patent Document 1:JP 2016-159916 A
[PTL2]Patent Document 2:JP 2014-208812 A
Summary of Invention
- [0015] Problems to be solved by Invention
The present invention solves the above conventional problems, and it is an objective

of the present invention to provide a hot-melt adhesive, a solidified coating of which is excellent in non-slip performance on cardboard, and with which the cardboard can be easily peeled off from a pallet at the same time without damaging the cardboard substrate.

Means for solving Problems

[0016] The present invention provides a hot-melt adhesive comprising a crystalline olefin polymer (A), a noncrystalline olefin polymer (B), a tackifying resin (C) and a wax (D), wherein

the crystalline olefin polymer (A) comprises a metallocene-type propylene/ethylene copolymer (A1) having an ethylene content of 5 to 10% by weight.

[0017] In one embodiment, the metallocene-type propylene/ethylene copolymer (A1) has a density of 0.87 to 0.95 g/cm³, a melt viscosity at 190°C of 1000 to 2000 mPas.

[0018] In one embodiment, the noncrystalline olefin polymer (B) comprises a propylene/ethylene/butene copolymer (B1).

[0019] In one embodiment, 10 to 70 parts by weight of (A1) are contained, based on 100 parts by weight in total of (A) to (D).

[0020] In one embodiment, 2 to 20 parts by weight of (B1) are contained, based on 100 parts by weight in total of (A) to (D).

[0021] The present invention also provides a cardboard having a coating of the hot-melt adhesive according to any one of claims 1 to 5, which has been bonded and solidified at its coated portion.

Effects of Invention

[0022] According to the present invention, there is provided a hot-melt adhesive, a solidified coating of which is excellent in non-slip performance on cardboard, and with which the cardboard can be easily peeled off from a palette at the same time without damaging the cardboard substrate. Even when stacked cardboard boxes with a coating of the hot-melt adhesive of the present invention are placed on a pallet, they are less likely to slip when handled by a worker, and there is no substrate damage. Furthermore, when cardboard boxes are unloaded from the pallet, the cardboard boxes are easily peeled off from the pallet, which improves the unpacking work.

[0023] The cardboard is a sheet in which a paper board liner is laminated on one side or both sides of a paper board serving as an inner core formed in a corrugated shape. The paper board used for the liner includes kraft liner (K liner) made from kraft pulp and used paper, jute liner (C liner) made from used paper and the like. A typical example of the cardboard includes an exterior cardboard described in JIS 1516.

Description of Embodiments

[0024] A hot-melt adhesive of the present invention comprises, as essential components, a crystalline olefin polymer (A), a noncrystalline olefin polymer (B), a tackifying resin

(C) and a wax (D).

[0025] In the present specification, the "hot-melt adhesive" refers to an adhesive, which is solid at normal temperature, but has fluidity by being heated and melted, can be applied to an object such as a substrate or an adherend, is cured and bonded by being cooled.

[0026] Here, "crystalline" means what is usually called "crystalline", and more specifically refers to a state in which polymers are regularly arranged. Although "noncrystalline" usually means not crystalline, and more specifically it is defined as a state in which molecular chains of the polymer are randomly arranged.

[0027] <(A) Crystalline Olefin Polymer>

(A) As the crystalline olefin polymer, for example, polyethylene, polypropylene, an ethylene/propylene copolymer, an ethylene/ α -olefin copolymer, a propylene/ α -olefin copolymer, an ethylene/propylene/ α -olefin copolymer, an ethylene/1-butene copolymer and a propylene/1-butene copolymer may be cited. These copolymers may be used alone or two or more may be mixed.

[0028] As an example of a commercially available product of the crystalline olefin polymer (A), Affinity GA1900 (trade name), Affinity GA1950 (trade name), Affinity EG8185 (trade name), Affinity EG8200 (trade name), Engage 8137 (trade name), Engage 8180 (trade name), Engage 8400 (trade name) and the like manufactured by The Dow Chemical Company; Vistamaxx 2330 (trade name), Vistamaxx 6202 (trade name), Vistamaxx 8880 (trade name) manufactured by Exxon Mobil Corporation; Evolve SP1071C (trade name), Evolve SP2030 (trade name), and Evolve SP2530S (trade name) manufactured by Prime Polymer Co. Ltd.; L-MODU S400 (trade name), L-MODU S600 (trade name), L-MODU S901 (trade name) manufactured by Idemitsu Kosan Co., Ltd., and the like are cited.

[0029] The crystalline olefin polymer (A) includes a metallocene-type propylene/ethylene copolymer (A1). The metallocene-type propylene/ethylene copolymer (A1) is a polymer produced by polymerizing ethylene and propylene using a metallocene catalyst. The polymer produced using the metallocene catalyst has a very narrow molecular weight distribution and does not cause deviation in crystallinity. The metallocene-type propylene/ethylene copolymer is uniform in the arrangement of ethylene moieties and propylene moieties, the content ratio of each structural unit, and the like, and therefore a low molecular weight compound hardly occurs. As a result, it is considered that, the hot-melt adhesive of the present invention, a solidified coating of which has low adhesion, has excellent peelability, and also has excellent thermal resistance.

[0030] By including the component (A1) in the hot-melt adhesive of the present invention, non-slip performance at high temperatures (about 50°C) is improved, the cardboard

substrate is less likely to be damaged at the time of peeling off, and peelability of the cardboard from an olefin substrate (pallet) is improved.

[0031] The ethylene content of the metallocene-type propylene/ethylene copolymer (A1) is 5 to 10% by weight, preferably 6 to 9% by weight, and most preferably 7 to 8% by weight. The ethylene content of the component (A1) in the above range favorably keeps a good balance between thermal resistance and non-slip performance in the hot-melt adhesive of the present invention, and it becomes useful for non-slip applications to the cardboard surface.

[0032] The ethylene content is a ratio of ethylene structures with respect to the total weight of ethylene and α -olefin polymers, and is taken as a value measured by the Exxon Mobil method based on ASTM method.

[0033] The metallocene-type propylene/ethylene copolymer (A1) preferably has a density of 0.87 to 0.95 g/cm³. The density of (A1) in the above range makes it possible for the hot-melt adhesive of the present invention to maintain an appropriate hardness. When applied to cardboard, the cardboard substrate is made less likely to be damaged, resulting in better non-slip performance.

[0034] In the present specification, the density is a weight per unit volume and defined as a value measured based on ASTM D1505-03.

[0035] The metallocene-type propylene/ethylene copolymer (A1) preferably has a viscosity at 190°C of 1000-2000 mPas, and particularly preferably of 1100-1900 mPas.

[0036] The viscosity of the (A1) in the above range makes it possible for the hot-melt adhesive of the present invention to maintain the appropriate shape (spread and height) when applied to a cardboard surface, and improves non-slip performance more. The viscosity of the (A1) at 190°C is a value measured based on JAI 7-1991, Method B. A Brookfield viscometer, No. 27 rotor was used as a measuring device.

[0037] (A1) An example of a commercially available product of the metallocene-type propylene/ethylene copolymer (A1) includes Vistamaxx 8880 manufactured by Exxon Mobil Corporation. Vistamaxx A (prototype) described below also corresponds to the (A1).

[0038] <(B) Noncrystalline Olefin Polymer>

In the present invention, the “noncrystalline olefin polymer (B) (hereinafter, also referred to as the “component (B)”) is a noncrystalline α -olefin polymer, and generally referred to as a noncrystalline poly- α -olefin. The noncrystalline olefin polymer (B) is not particularly limited as long as the hot-melt adhesive of the present invention can be obtained.

[0039] Here, “noncrystalline” usually means not crystalline, but more specifically, it refers to a state in which molecular chains of a polymer are randomly arranged. By blending the noncrystalline olefin polymer (B) with the hot-melt adhesive, the hot-melt adhesive

has an increased coefficient of friction, and the adherend (cardboard) surface becomes less likely to slip.

[0040] Friction is a force acting in a direction in which, when an object attempts to move or is moving in contact with a surface of another object, this movement is disturbed at a contact surface. The friction is classified into static friction which, until one object starts to slide due to a relative movement state of two objects, attempts to stop it (the maximum frictional force that is a frictional force when the object is about to slide), and dynamic friction (sliding friction, rolling friction, and the like) that attempts to stop the moving object.

[0041] In this specification, the friction means static friction, and the friction coefficient means a coefficient of static friction.

[0042] As the noncrystalline olefin polymers (B), for example, noncrystalline polypropylene, noncrystalline polyethylene, or a copolymer of noncrystalline propylene and other α -olefins may be cited. These polymers may be used alone or in combination of two or more.

[0043] As the noncrystalline olefin polymer (B), specifically, a polypropylene (homopolymer), a propylene/ethylene copolymer, a propylene/1-butene copolymer, a terpolymer of propylene/ethylene/1-butene, a terpolymer of propylene/1-hexene/1-octene, a terpolymer of propylene/1-hexene/ methylpentene, 1-polybutene (homopolymer) and the like may be cited.

[0044] In the present invention, the noncrystalline olefin polymer (B) preferably has a chemical structure derived from propylene. The chemical structure derived from propylene is meant to include both pure propylene and propylene derivatives having other functional groups. When the hot-melt adhesive of the present invention contains a chemical structure derived from propylene, the maximum static frictional force increases and it becomes less likely to slip. Therefore, cardboard boxes can be prevented from collapsing, and the cardboard substrate can also be prevented from being damaged.

[0045] Examples of the noncrystalline olefin polymer (B) include Vestoplast 703 (trade name), Vestoplast 704 (trade name), Vestoplast 708 (trade name) manufactured by Evonik Degussa Japan Co., Ltd.; Eastoflex (trade name) E1016PL-1, Eastoflex PP1010PL (trade name) manufactured by Eastman Chemical Company; Rexentac 2304 (trade name) manufactured by Huntsman Corporation, and the like.

[0046] In the present invention, the density of the noncrystalline olefin polymer (B) is preferably 1.00 g/cm³ or less, particularly preferably 0.80 g/cm³ to 0.90 g/cm³, and most preferably 0.85 g/cm³ to 0.88 g/cm³. The density of the noncrystalline olefin polymer (B) in the above range makes the hot-melt adhesive of the present invention less likely to slip, and prevents cardboard boxes from collapsing more reliably.

- [0047] The noncrystalline olefin polymer (B) preferably contains a propylene/ethylene/1-butene copolymer (B1). By blending the propylene/ethylene/1-butene copolymer, stacked cardboard boxes can be prevented from collapsing reliably, and at the same time, the cardboard substrate can also be prevented from being damaged.
- [0048] Examples of commercialized products of the propylene/ethylene/1-butene copolymer (B) include Vestoplast series, such as Vestoplast 703 (trade name), Vestoplast 704 (trade name), and Vestoplast 708 (trade name), manufactured by Evonik Degussa Japan Co., Ltd.
- [0049] <Tackifying Resin (C)>
The "tackifying resin (C)" is not particularly limited as long as it is one usually used for a hot-melt adhesive and the hot-melt adhesive intended by the present invention can be obtained.
- [0050] Examples of the tackifying resin include, for example, natural rosins, modified rosins, hydrogenated rosins, glycerol esters of natural rosins, glycerol esters of modified rosins, pentaerythritol esters of natural rosins, pentaerythritol esters of modified rosins, pentaerythritol esters of hydrogenated rosins, copolymers of natural terpenes, three-dimensional polymers of natural terpenes, hydrogenated derivatives of copolymers of hydrogenated terpenes, polyterpene resins, hydrogenated derivatives of phenol-based modified terpene resins, aliphatic petroleum hydrocarbon resins, hydrogenated derivatives of aliphatic petroleum hydrocarbon resins, aromatic petroleum hydrocarbon resins, hydrogenated derivatives of aromatic petroleum hydrocarbon resins, cyclic aliphatic petroleum hydrocarbon resins and hydrogenated derivatives of cyclic aliphatic petroleum hydrocarbon resins. These tackifying resins may be used alone or in combination. For the tackifying resin, liquid type tackifying resins may also be used as long as they are colorless to pale yellow in color tone, have substantially no odor, and have good thermal stability. Considering these properties comprehensively, hydrogenated derivatives of the above resins and the like are preferred as the tackifying resin.
- [0051] As the tackifying resin, commercialized products may be used. Examples of such commercial products include ECR 231C (trade name), ECR 179 EX (trade name), ECR 5600 (trade name) manufactured by Exxon Mobil Corporation, MARUKACLEAR H (trade name) manufactured by Maruzen Petrochemical Co., Ltd., Clearon K100 (trade name), Clearon K4090 (trade name), Clearon K4100 (trade name) and Clearon P105 manufactured by YASUHARA CHEMICAL Co., Ltd., ARKON M100 (trade name), ARKON P90 manufactured by Arakawa Chemical Industries, Ltd., I MARV S100 (trade name), I MARV Y135 (trade name), I MARV P125 and I MARV P100 (trade name) manufactured by Idemitsu Kosan Co., Ltd., T-REZ HC103 (trade name), T-REZ HA103 (trade name), T-REZ HA125 (trade name), T-REZ

HB103 (trade name), T-REZ HA085 (trade name) manufactured by JXTG Nippon Oil & Energy Corporation, and REGALITE R7100 (trade name) manufactured by Eastman Chemical Company. These commercialized products may be used alone or in combination.

[0052] <Wax (D)>

In the present invention, the hot-melt adhesive contains a wax (D). In the present specification, "wax" refers to an organic substance having a weight-average molecular weight of less than 15000 which is solid at normal temperature, becomes liquid when heated, and is generally referred to as "wax". If it has waxy properties, it is not particularly limited as long as the hot-melt adhesive of the present invention can be obtained. The wax may be a synthetic wax or a natural wax.

[0053] Examples of the synthetic wax include Fischer-Tropsch waxes, polyolefin waxes (e.g., polyethylene wax, polypropylene wax, polyethylene/polypropylene wax) and the like.

[0054] "Fischer Tropsch waxes" refers to those which are synthesized by the Fischer-Tropsch method and generally referred to as Fischer-Tropsch waxes. The Fischer-Tropsch wax is a wax fractionated such that its component molecules have a narrow carbon number distribution from a wax whose component molecules relatively have a wide carbon number distribution.

[0055] As Fischer Tropsch wax, SASOL H1 (trade name), SASOL C80 (trade name) manufactured by Sasol Wax Corporation, and FT-115 (trade name) manufactured by NIPPON SEIRO CO., LTD. are commercially available.

[0056] The natural wax includes paraffin waxes, microcrystalline waxes and petrolatum.

[0057] The paraffin waxes are waxes which are solid at room temperature, and separated from vacuum distillation extracted oil. Examples of representative paraffin waxes include Paraffin Wax series manufactured by NIPPON SEIRO CO., LTD.

[0058] Microcrystalline waxes are waxes which are solid at room temperature, and separated and produced from a vacuum distillation bottom or heavy extract oil. Examples of representative microcrystalline waxes include Hi-Mic series manufactured by NIPPON SEIRO CO., LTD.

[0059] Petrolatum is a wax which is semi-solid at normal temperature, and separated and produced from the vacuum distillation bottom. Representative examples of the petrolatum include Centon CP series manufactured by CHUO YUKA Co., Ltd.

[0060] These waxes may be used alone, or two or more may be mixed.

[0061] The hot-melt adhesive of the present invention preferably contains "paraffin wax" that is a natural wax. When the paraffin wax is blended, the cohesion force of the hot-melt adhesive of the present invention is improved and cured, so that the cardboard substrate can also be prevented from being damaged when stacked cardboard packages

are unpacked.

[0062] <Hot-Melt Adhesive>

In the hot-melt adhesive of the present invention, the metallocene-type propylene/ethylene copolymer (A1) is preferably blended in an amount of 10 to 70 parts by weight, particularly preferably 30 to 70 parts by weight, and most desirably 40 to 65 parts by weight, based on 100 parts by weight in total of the components (A) to (D).

[0063] The blending amount of the metallocene-type propylene/ethylene copolymer (A1) in the above range makes the cardboard substrate less likely to be damaged when the hot-melt adhesive of the present invention is applied to cardboard, and the cardboard becomes easy to be peeled off from the pallet.

[0064] In the hot-melt adhesive of the present invention, the blending amount of the propylene/ethylene/butene copolymer (B1) is preferably 2 to 20 parts by weight, particularly preferably 5 to 20 parts by weight, and most desirably 5 to 15 parts by weight, based on 100 parts by weight in total of the total weight of the components (A) to (D).

[0065] The blending amount of the propylene/ethylene/butene copolymer (B1) in the above range makes the hot-melt adhesive of the present invention better in non-slip performance on the cardboard surface when it is applied to the cardboard.

[0066] In the hot-melt adhesive of the present invention, the blending amount of the tackifying resin (C) is preferably 10 to 40 parts by weight, particularly preferably 15 to 40 parts by weight, and most desirably 20 to 30 parts by weight, based on 100 parts by weight in total of the components (A) to (D).

[0067] The blending amount of the tackifying resin (C) in the above range improves the hot-melt adhesive in initial adhesion, improves it in non-slip performance, makes the cardboard substrate less likely to be damaged, and can make it easy for the cardboard to be peeled off from the pallet.

[0068] In the hot-melt adhesive of the present invention, the blending amount of the wax (D) is preferably 5 to 20 parts by weight, particularly preferably 5 to 15 parts by weight, and most desirably 5 to 10 parts by weight based on 100 parts by weight in total of the components (A) to (D).

[0069] The blending amount of the wax (D) in the above range reduces the viscosity of the hot-melt adhesive, and also improves the cohesion force, with the compatibility of each component being improved. Therefore, it is excellent in non-slip performance, and the cardboard substrate can also be prevented from being damaged.

[0070] The hot-melt adhesive of the present invention preferably includes a plasticizer. The “plasticizer” is blended for the purpose of lowering the melt viscosity of the hot-melt adhesive, imparting flexibility, and improving wettability to the adherend. There is no particular limitation as long as it is compatible with an ethylene-based copolymer, and the hot-melt adhesive intended by the present invention can be obtained. Examples of

the plasticizer include paraffinic oils, naphthenic oils and aromatic oils. Particularly preferred are colorless, odorless paraffinic oils.

- [0071] When oil is blended, the compatibility of the components (A) to (C) is improved. Therefore, flexibility is imparted to the hot-melt adhesive of the present invention, slipperiness on the cardboard surface, and damage to the cardboard substrate are prevented. In addition, thread formation can be reduced, and application properties are improved.
- [0072] As the plasticizer (D), commercialized products may be used. Examples thereof include, for example, White Oil Broom 350 (trade name) manufactured by Kukdong Oil & Chemicals Co., Ltd.; Diana Fresia S32 (trade name), Diana Process Oil PW-90 (trade name) and DN Oil KP-68 (trade name) manufactured by IDEMITSU KOSAN CO., LTD.; Enerper M1930 (trade name) manufactured by BP Chemicals, Inc.; Kaydol (trade name) manufactured by Crompton Corporation; Primol 352 (trade name) manufactured by ESSO; and SUNPURE N90 manufactured by Japan Sun Oil Company, Ltd. These plasticizers (D) may be used alone or in combination.
- [0073] The hot-melt adhesive of the present invention may further include various additives. As such additives, for example, a stabilizer (an ultraviolet absorber, an antioxidant), and a particulate filler may be cited.
- [0074] The "stabilizer" is blended to prevent molecular weight decrease, gelation, coloring, generation of odor and the like of the hot-melt adhesive due to heat, air, light and the like, thereby improving the stability of the hot-melt adhesive. It is not particularly limited as long as the hot-melt adhesive intended by the present invention can be obtained. As a stabilizer, for example, an antioxidant and an ultraviolet absorber may be cited.
- [0075] "UV absorbers" are used to improve light resistance of the hot-melt adhesive. "Antioxidants" are used to prevent oxidative degradation of the hot-melt adhesive. Antioxidants and UV absorbers are not particularly limited as long as they are generally used in hot-melt adhesives, and the intended paper product described later can be obtained.
- [0076] As an "antioxidant", for example, a phenol-based antioxidant, a sulfur-based antioxidant, and a phosphorus-based antioxidant may be cited. As an ultraviolet absorber, for example, a benzotriazole-based ultraviolet absorber and a benzophenone-based ultraviolet absorber may be cited. Furthermore, a lactone-based stabilizer may also be added. These may be used alone or in combination.
- [0077] Commercialized products may be used as stabilizers. Examples thereof include Sumilyzer GM (trade name), Sumilyzer TPD (trade name) and Sumilyzer TPS (trade name) manufactured by Sumitomo Chemical Company, Limited; Irganox 1010 (trade name), Irganox HP2225FF (trade name), Irgafos 168 (trade name) and Irganox 1520

(trade name) manufactured by BASF SE, Japan; Adekastab AO-60 (trade name) of ADEKA CORPORATION; JF77 (trade name), JP-650 (trade name) manufactured by JOHOKU CHEMICAL CO., LTD. These stabilizers may be used alone or in combination.

- [0078] The hot-melt adhesive of the present invention may further contain a fine particle filler. The fine particle filler may be commonly used one, and it is not particularly limited as long as the hot-melt adhesive intended by the present invention can be obtained. As the "fine particle filler" include mica, calcium carbonate, kaolin, talc, titanium oxide, diatomaceous earth, urea resin, styrene beads, calcined clay, starch and the like may be cited. These shapes are preferably spherical, and the dimensions (diameter in the case of a spherical shape) are not particularly limited.
- [0079] The hot-melt adhesive of the present invention may be prepared, using a generally known method for producing a hot-melt adhesive, by blending a crystalline olefin polymer (A), a noncrystalline olefin polymer (B), a tackifying resin (C), a wax (D), and, if necessary, a plasticizer, the above-mentioned various additives.
- [0080] For example, it may be produced by blending predetermined amounts of the above components, and heating and melting them. The order of adding each component, the heating method, and the like are not particularly limited as long as the intended hot-melt adhesive can be obtained.
- [0081] <Cardboard to which the hot-melt adhesive is applied>
The hot-melt adhesive of the present invention is heated and melted, applied to a coated portion of cardboard, cooled and solidified to form a coating of the hot-melt adhesive on the cardboard surface.
- [0082] The method of applying the hot-melt adhesive is not particularly limited as long as the objective of the present invention product can be achieved, but a hot melt applicator is widely used. As the hot melt applicator, for example, ProBlue P4 Melter (trade name), ProBlue P10 Melter (trade name) manufactured by Nordson Corporation and the like may be cited.
- [0083] The application method is roughly categorized into, for example, contact application and non-contact application. "Contact application" refers to an application method in which a jet machine is brought into contact with a member or film when applying a hot-melt adhesive, whereas "non-contact coating" refers to a method in which a hot-melt adhesive is not brought into contact with a member or film when applying a hot-melt adhesive. As the contact application method, for example, slot coater application, roll coater application and the like may be cited, whereas as the non-contact application method, for example, spiral application which enables applying in a spiral form, omega application and control seam application which enable applying in a wavy form, slot spray application and curtain spray application which enable surface

applying, dot application which enables dot-like applying, bead application which enables linear applying, and the like may be cited.

- [0084] When applying the hot-melt adhesive of the present invention with the hot melt applicator (even when the hot-melt adhesive is discharged in a horizontal direction with respect to the ground with the hot melt applicator to perform application), thread formation of the hot-melt adhesive is hardly observed. Therefore, the adherend or the applicator is not smeared with the tread-form material.
- [0085] The application amount of the hot-melt adhesive is not particularly limited, but is, for example, 1 to 5 g/m. Moreover, the application pattern of the hot-melt-adhesive may be determined as needed. For example, it is a bead shape.
- [0086] The coating of the hot-melt adhesive (after solidification) formed on the cardboard surface has a large frictional force against the cardboard. That can prevent cardboard boxes from collapsing even when they are moved or tilted in a state in which they are stacked on the coating of the hot-melt adhesive. The coating of the hot-melt adhesive preferably has a static friction coefficient of 14 or more, more preferably 16.5 or more, and still more preferably 18 or more, with respect to the cardboard surface.
- [0087] Also, the coating of the hot-melt adhesive (after solidification) has low adhesion to the cardboard. That prevents a portion of the cardboard substrate, which is in contact with the coating of the adhesive, from being damaged even when cardboard boxes are stored in a state in which they are stacked on the coating of the hot-melt adhesive.
- [0088] The hot-melt adhesive of the present invention is widely used, for example, for electronic parts, woodwork, building materials, sanitary materials, paper products, and the like. It is suitable where a plurality of cardboards are stacked and stored.
- [0089] The hot-melt adhesive of the present invention is useful as a "hot-melt adhesive for cardboard", which prevents stacked cardboard boxes from collapsing, and does not damage the cardboard substrate, and what is more, is excellent in application properties and reduction of thread formation.
- [0090] The cardboard of the present invention is a cardboard obtained using the above-mentioned hot-melt adhesive. As the cardboard of the present invention, a cardboard having a coating of the hot-melt adhesive formed on its surface is particularly preferred.
- [0091] The present invention will hereinafter be described by examples and comparative examples more specifically and in more detail. These examples are merely one aspect of the present invention, and not intended to limit the present invention at all. The ratios shown in the examples are based on the weight of non-volatile contents unless otherwise stated.

Examples

- [0092] Raw materials of the hot-melt adhesive, and formulations, evaluation methods are

described below.

(A) Crystalline olefin polymer

(A1-1) Metallocene-type propylene/ethylene copolymer (ethylene content: 7.1% by weight, melting point: 112°C, melt viscosity at 190°C: 1850 mPas, density 0.88 g/cm³, Vistamaxx A (prototype) manufactured by Exxon Mobil Corporation)

(A1-2) Metallocene-type propylene/ethylene copolymer (ethylene content: 6.0% by weight, melting point: 97°C, melt viscosity at 190°C: 1200 mPas, density 0.88 g/cm³, Vistamaxx 8880 (trade name) manufactured by Exxon Mobil Corporation)

(A2) Metallocene-type propylene homopolymer (melt flow rate: 350 g/10 min: 230°C, density 0.87 g/cm³, L-MODU S600 (trade name) manufactured by Idemitsu Kosan Co., Ltd.)

(A3) Metallocene-type ethylene/octene copolymer (1-octene content: 30 to 40% by weight, melting point: 68°C, melt flow rate: 1000 g/10 min, Affinity GA1900 (trade name) manufactured by Dow Chemical Co., Ltd.)

(A4) Low density polyethylene (melt flow rate: 145 g/10 min, Petrocene 353 (trade name) manufactured by Tosoh Corporation)

(A5) Metallocene-type ethylene/hexene copolymer (melting point: 95°C, Niporon Z HM510R (trade name) manufactured by Tosoh Corporation)

(A6) Metallocene-type propylene/ethylene copolymer (ethylene content: 15.0% by weight, melt flow rate: 20 g/10 min, density 0.86 g/cm³, Vistamaxx 6202 (trade name) manufactured by Exxon Mobil Corporation)

[0093] (B) Noncrystalline olefin polymer

(B1-1) Noncrystalline propylene/ethylene/butene copolymer (softening point: 124°C, melt viscosity at 190°C: 2700 mPas, Vestoplast 703 (trade name) manufactured by Evonik Degussa Japan Co., Ltd.

(B1-2) Noncrystalline propylene/ethylene/butene copolymer (softening point: 105°C, melt viscosity at 190°C: 3500 mPas, Vestoplast 704 (trade name) manufactured by Evonik Degussa Japan Co., Ltd.

(B2) Noncrystalline propylene homopolymer (melt viscosity at 190°C: 1000 mPas, softening point 155°C, density 0.87 g/cm³, Eastflex PP1010PL (trade name) manufactured by Eastman Chemical Company

(B3) noncrystalline propylene/ethylene copolymer (melt viscosity at 190°C: 450 mPas, softening point 141°C, density 0.86 g/cm³, Rexentac 2304 (trade name) manufactured by Huntsman Corporation

[0094] (C) Tackifying resin

(C1) Hydrogenated alicyclic/aromatic copolymer hydrocarbon resin (softening point: 103°C, T-REZ HC103 (trade name) manufactured by JXTG Energy Corporation

(C2) Hydrogenated alicyclic hydrocarbon resin (softening point: 103°C, T-REZ

HA103 (trade name) manufactured by JXTG Energy Corporation)

(C3) Hydrogenated alicyclic hydrocarbon resin (softening point: 125°C, T-REZ

HA125 (trade name) manufactured by JXTG Energy Corporation)

[0095] (D) Wax

(D1) Fischer-Tropsch wax (melting point: 108°C, penetration 2, Sasol Wax H1 (trade name) manufactured by Sasol Corporation)

(D2) Fischer-Tropsch wax (melting point: 80°C, penetration 7, Sasol C80 (trade name) manufactured by Sasol Corporation)

(D3) Paraffin wax (Melting point: 69°C, penetration 12, Paraffin 155F (trade name) manufactured by NIPPON SEIRO CO., LTD.)

(D4) Microcrystalline wax (melting point: 84°C, penetration 12, Hi-Mic 1080 (trade name) manufactured by NIPPON SEIRO CO., LTD.)

(D5) Polyethylene wax (melting point: 109°C, penetration 7, High Wax 320P (trade name) manufactured by Mitsui Chemical Co., Ltd.)

(D6) Polypropylene wax (melting point: 140/148°C, penetration 1 or less, High Wax NP105 (trade name) manufactured by Mitsui Chemical Co., Ltd.)

[0096] (E) Plasticizer

(E1) Paraffin oil (Diana Fresia S32 (trade name) manufactured by Idemitsu Kosan Co., Ltd.)

(E2) Naphthenic oil (SUNPURE N90 (trade name) manufactured by Nippon Sun Oil Co., Ltd.)

[0097] (F) Antioxidant

(F1) Phenol-based antioxidant (Adekastab AO60 (trade name) manufactured by ADEKA CORPORATION)

(F2) Phosphorous-based antioxidant (JP650 (trade name) manufactured by JOHOKU CHEMICAL CO., LTD.)

(F3) Sulfur-based antioxidant (Sumilyzer TPS (trade name) manufactured by Sumitomo Chemical Company, Limited)

[0098] These components were melted and mixed in the ratios shown in Tables 1 and 3 at about 155°C for about one hour using a universal stirrer to produce hot-melt adhesives of Examples and Comparative Examples. These hot-melt adhesives were evaluated for melt viscosity, “maximum static friction coefficient” on cardboard, tilt angle measurement (non-slip performance) and damage to cardboard substrate. Peelability from an olefin substrate, exudation, and thread formation were evaluated to confirm workability. The evaluation results are shown in Tables 2 and 4.

[0099] To a K liner cardboard, a hot-melt adhesive melted at 180°C was applied in a 3 cm long bead shape and an application amount of 3 g/m. Sixty seconds after the application, the cardboard was aged in a thermostatic chamber at 50°C, 23°C, or 0°C.

After another 30 seconds, another K-liner cardboard with a 3 kg weight was superposed on the hot-melt adhesive to prepare a sample, and the sample was fixed to a tiltable platform.

[0100] After 150 seconds under load, the platform was tilted by 5° after elapse of every one second, and the angle when the sample (superposed cardboards) on the platform slipped down was measured, and the material breakage state of the cardboard was observed. The evaluation criteria are as follows.

[0101] ◎: The tilt angle is 45° or more and there is no material breakage.

○: The tilt angle is 35° or more and less than 45°, and there is no material breakage.

×: The tilt angle is less than 35°, or material breakage.

[0102] <Substrate Damage Measurement>

To a K liner cardboard, a hot-melt adhesive melted at 180°C was applied in a 3 cm long bead shape and an application amount of 3 g/m. After the hot-melt adhesive has been completely solidified, another cardboard was superposed thereon, a weight of 3 kg was placed on the superposed cardboards, which was left to stand in a thermostatic chamber at 50°C, 23°C, or 0°C for 24 hours. Thereafter, the superposed cardboards in the thermostatic chamber at each temperature were peeled off by hand, and substrate damage was evaluated by confirming the cardboard condition. The evaluation criteria for the substrate damage of cardboard are as follows.

[0103] ◎: No damage

○: Slightly fluffy

×: Damaged

[0104] <Peelability from Olefin Substrate>

To a K liner cardboard, a hot-melt adhesive melted at 180°C was applied in a 3 cm long bead shape, and an application amount of 3 g/m. After the hot-melt adhesive has been completely solidified, a polypropylene plate was superposed on the hot-melt adhesive on the cardboard surface, and a laminate of these served as a sample. A weight of 3 kg was placed on the sample, which was left to stand under load in a thermostatic chamber at 50°C, 23°C, or 0°C for 24 hours.

[0105] Thereafter, the polypropylene plate was peeled off from the cardboard by hand in the thermostatic chamber at each temperature, and it was confirmed whether or not interfacial peeling of the hot-melt adhesive from the polypropylene plate occurred. The evaluation criteria are as follows.

[0106] ◎: Interfacial peeling

○: Slight material breakage was observed in hot-melt adhesive.

×: Material breakage of cardboard substrate was observed.

[0107] <Exudation>

To a K liner cardboard, a hot-melt adhesive melted at 180°C was applied in a 3 cm

long bead shape, and an application amount of 3 g/m. After the hot-melt adhesive has been completely solidified, another cardboard was superposed thereon, a weight of 3 kg was placed on the superposed cardboards, which was left to stand under load in a thermostatic chamber at 50°C for 24 hours. Thereafter, the superposed cardboards in the thermostatic chamber were peeled off by hand, and the exuding condition on the cardboard was evaluated. The evaluation criteria for the exuding condition are as follows.

- [0108] ⊙: No exudation
 ○: Slightly exuded
 ×: Exuded

[0109] <Thread Forming Properties>

A hot-melt adhesive was vertically applied intermittently to an adherend at a distance of 20 cm from a tip of a hot melt gun. The state of fallen materials between the hot melt gun and the adherend was visually observed to evaluate thread forming properties. Measurement conditions are as follows.

- [0110] Temperature setting: Temperature inside of a tank, temperature inside of a hose, and temperature inside of a nozzle are all at 180°C

 Nozzle diameter: 14/1000 inches

 Nozzle: 1 orifice (number of discharge ports: 1)

 Discharge pressure: 0.3 MPa

 Number of discharged shots: 180 shots/1 minute

- [0111] The evaluation criteria are as follows:

 ⊙: The shape of fallen materials is granular.
 ○: The shape of fallen materials is thread form, but the amount of thread-form materials is small.
 ×: The shape of fallen materials is thread form, and the amount of thread-form materials is also large.

- [0112]

[illegible]

[0113] [Table 2]

		Example							
		1	2	3	4	5	6	7	8
Performance test results	Non-slip performance (tilt angle)	50°C	◎	◎	◎	◎	◎	◎	◎
		23°C	◎	◎	◎	◎	◎	◎	◎
		0°C	◎	○	◎	○	○	○	◎
Substrate damage		50°C	◎	◎	◎	○	◎	◎	○
		23°C	◎	◎	◎	◎	◎	◎	◎
		0°C	◎	◎	◎	◎	◎	◎	◎
Peelability from olefin substrate		50°C	◎	◎	◎	○	◎	◎	◎
		23°C	◎	◎	◎	◎	◎	◎	◎
		0°C	◎	◎	◎	◎	◎	◎	◎
Exudation		50°C	◎	◎	◎	○	◎	◎	◎
Thread forming properties			○	○	○	○	○	○	○

[illegible]

[0115] [Table 4]

Performance test results	Example			Comparative Example				
	9	10	11	1	2	3	4	5
Non-slip performance (tilt angle)	50°C	◎	◎	○	×	◎	○	○
	23°C	◎	◎	◎	◎	○	×	◎
	0°C	○	◎	◎	◎	×	×	◎
Substrate damage	50°C	○	◎	○	×	◎	○	×
	23°C	◎	◎	◎	◎	◎	×	×
	0°C	◎	◎	◎	◎	○	×	×
Peelability from olefin substrate	50°C	○	◎	○	×	◎	○	×
	23°C	◎	◎	◎	×	◎	×	×
	0°C	◎	◎	◎	○	○	×	×
Exudation	◎	◎	◎	×	×	×	×	×
Thread forming properties	○	○	○	×	○	○	×	○

- [0116] As shown in Tables 2 and 4, the hot-melt adhesives of Examples 1 to 11 are excellent in non-slip performance, prevent damage to the cardboard substrate, and the cardboard can be easily peeled off from the olefin substrate. Therefore, the worker can unpack cardboard boxes and carry them easily.
- [0117] Furthermore, the hot-melt adhesives of the examples have almost no thread formation even when jetted from a hot melt gun, and do not exude to the cardboard.
- [0118] On the other hand, the hot-melt adhesives of Comparative Examples 1 to 5 are significantly inferior in any one of the non-slip performance, substrate damage, and peelability from the olefin substrate.
- [0119] Since the hot-melt adhesives of Comparative Examples 1, 2 do not contain the component (A1), the non-slip performance at 50°C is low, and damaged the cardboard substrate at 0°C.
- [0120] Since the hot-melt adhesive of Comparative Example 3 does not contain the component (B), the non-slip performance at 0 to 23°C is degraded.
- [0121] The hot-melt adhesive of Comparative Example 4 does not contain the tackifying resin (C), and the hot-melt adhesive of Comparative Example 5 does not contain the wax (D). The hot-melt adhesives of Comparative Examples 4 and 5 are inferior in all performances and do not function as the hot-melt adhesive.

Industrial Applicability

- [0122] The present invention provides a hot-melt adhesive. The hot-melt adhesive of the present invention is useful as an adhesive for cardboard, prevents stacked cardboard boxes from collapsing, prevents the cardboard substrate from being damaged, and the cardboard boxes can be easily peeled off from the pallet.

Claims

- [Claim 1] A hot-melt adhesive comprising a crystalline olefin polymer (A), a non-crystalline olefin polymer (B), a tackifying resin (C) and a wax (D), wherein
the crystalline olefin polymer (A) comprises a metallocene-type propylene/ethylene copolymer (A1) having an ethylene content of 5 to 10% by weight.
- [Claim 2] The hot-melt adhesive according to claim 1, wherein the metallocene-type propylene/ethylene copolymer (A1) has a density of 0.87 to 0.95 g/cm³, a melt viscosity at 190°C of 1000 to 2000 mPas.
- [Claim 3] The hot-melt adhesive according to claim 1 or 2, wherein the non-crystalline olefin polymer (B) comprises a propylene/ethylene/butene copolymer (B1).
- [Claim 4] The hot-melt adhesive according to any one of claims 1 to 3, wherein 10 to 70 parts by weight of (A1) are contained, based on 100 parts by weight in total of (A) to (D).
- [Claim 5] The hot-melt adhesive according to any one of claims 1 to 4, wherein 2 to 20 parts by weight of (B1) are contained, based on 100 parts by weight in total of (A) to (D).
- [Claim 6] A cardboard having a coating of the hot-melt adhesive according to any one of claims 1 to 5, which has been bonded and solidified at its coated portion.

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2019/048071

A. CLASSIFICATION OF SUBJECT MATTER
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ADD.

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09J C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2016 155916 A (HENKEL JAPAN LTD) 1 September 2016 (2016-09-01) example 8; table 3 paragraphs [0001], [0083], [0084] -----	1-6
X	US 2016/130480 A1 (KAUFFMAN THOMAS F [US] ET AL) 12 May 2016 (2016-05-12) example 14; table 4 paragraphs [0089], [0097] -----	1-6
X	US 2018/002578 A1 (KAUFFMAN THOMAS F [US] ET AL) 4 January 2018 (2018-01-04) examples E16-E22, E26, E27, E30, E31; tables 7, 9, 10 paragraphs [0059], [0061] -----	1-6



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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