



- (51) International Patent Classification:
C09J 175/16 (2006.01) C09J 7/00 (2006.01)
- (21) International Application Number:
PCT/US2013/035357
- (22) International Filing Date:
5 April 2013 (05.04.2013)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
2012-086811 5 April 2012 (05.04.2012) JP
- (71) Applicant: 3M INNOVATIVE PROPERTIES COMPANY [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).
- (72) Inventors; and
- (71) Applicants : KOBAYASHI, Hiroyuki [JP/JP]; 33-1, Tamagawadai 2-chome, Setagaya-ku, Tokyo 158-8583 (JP). FUJITA, Jun [JP/JP]; 33-1, Tamagawadai 2-chome, Setagaya-ku, Tokyo 158-8583 (JP). KASAHARA, Takahiro [JP/JP]; 33-1, Tamagawadai 2-chome, Setagaya-ku, Tokyo 158-8583 (JP).
- (74) Agents: EHRICH, Dena M. et al.; 3M Center, Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

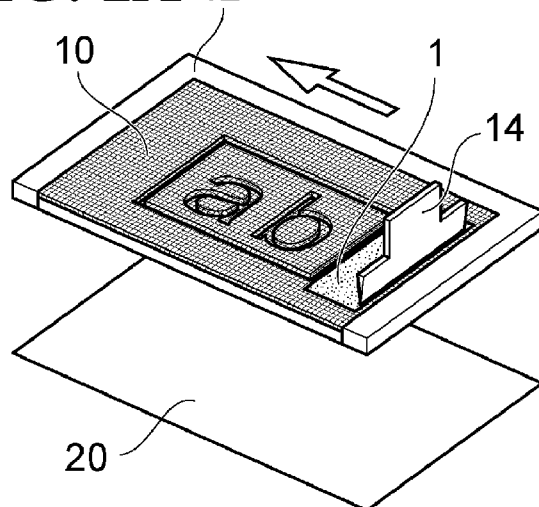
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: RADIATION-CURED ADHESIVE COMPOSITION AND LAMINATE USING THE SAME

FIG. 1A 12



(57) Abstract: There is provided a radiation-cured adhesive composition that is excellent in suitability for screen printing and exhibits high adhesiveness after curing. There is also provided a radiation-cured adhesive composition containing from 10 to 70 wt.% of an ethylenically unsaturated monomer not containing an aromatic ring, from 1 to 10 wt.% of a photopolymerization initiator, and from 10 to 55 wt.% of a cross linking agent; the radiation-cured adhesive composition containing from 10 to 45 wt.% of an alkyl (meth)acrylate having from 8 to 18 carbon atoms in the alkyl group as the ethylenically unsaturated monomer not containing an aromatic ring, and containing from 10 to 50 wt.% of a urethane poly(meth)acrylate having a weight average molecular weight of from 20,000 to 100,000 as the cross linking agent.

RADIATION-CURED ADHESIVE COMPOSITION AND LAMINATE USING THE SAME

5

BACKGROUND

Technical Field

[0001]

The present invention relates to a radiation-cured adhesive composition and a laminate using the same.

10

Background

[0002]

There are known various kinds of compositions that exhibit curability when irradiated with ultraviolet or other radiation. Adhesive tapes, adhesive sheets, and the like, are formed by applying such compositions onto substrates in a state not yet being cured by radiation and then irradiating with radiation.

15

Examples of compositions used in such a field include those disclosed in Japanese Unexamined Patent Application Publication No. H4-183770, Japanese Unexamined Patent Application Publication No. 2004-143223, Japanese Unexamined Patent Application Publication No. 2004-323796, Japanese Unexamined Patent Application Publication No. S61-209281, and Japanese Unexamined Patent Application Publication No. H11-246612.

20

[0003]

Meanwhile, although adhesive compositions (for example, solvent-based adhesives or water-based adhesives) are applied onto substrates by roll coating, dispenser, screen-printing, or other application means, a fine pattern is not easy to apply because the contained adhesive is a polymer and is also adhesive. Accordingly, in the case when an adhesive layer having a specific shape is to be formed on

25

a substrate, the common practice is to punch out and process the adhesive film.

[0004]

That is, a method is adopted, in which an adhesive laminated with two sheets of film is punched out and processed into a desired shape and the adhesive is affixed to an adherend after discarding the unwanted portion and after processing. However, with this method, the portions not needed for affixing

30

come to be discarded in large quantities, and not only does this lead to discarding of adhesive, but also there is a concern of the environmental load of increased waste.

[0006]

The above-described composition, which becomes an adhesive by irradiation with radiation, is definitely superior, because a problem of production of volatile materials (organic solvents, and the like) during adhesion processing is less likely to occur compared with solvent-based adhesives, and the amount of heat, and the like, used for processing is reduced compared with water-based adhesives (emulsion-based, and the like), in which the water, having large specific heat capacity, must be volatilized.

35

[0007]

However, no composition is known, among such radiation-cured adhesive compositions, that is

capable of fine patterning on the same level as those conventionally fabricated by die cutting and that at the same time exhibits high adhesiveness to all kinds of adherends including metal, plastic, and the like.

SUMMARY

[0008]

In a first aspect of the present invention, a radiation-cured adhesive composition can be obtained, containing from 10 to 70 wt.% of an ethylenically unsaturated monomer not containing an aromatic ring, from 1 to 10 wt.% of a photopolymerization initiator, and from 10 to 55 wt.% of a crosslinking agent; the radiation-cured adhesive composition containing from 10 to 45 wt.% of an alkyl (meth)acrylate having from 8 to 18 carbon atoms in the alkyl group as the ethylenically unsaturated monomer not containing an aromatic ring, and containing from 10 to 50 wt.% of a urethane poly(meth)acrylate having a weight average molecular weight of from 20,000 to 100,000 as the crosslinking agent.

[0009]

The radiation-cured adhesive composition of the present invention exhibits excellent adhesiveness on a wide range of adherends including stainless steel, ABS, and the like because specific components are combined in prescribed quantities. Shape processing furthermore is easy even with fine shapes because stringiness is not likely to be produced during application on an adherend by screen-printing. Also, the composition can be leveled easily after application, and therefore, for example, the adhesive layer is not likely to be formed in a swollen condition, and a desired fine shape can be obtained assuredly. Also, even if air is briefly taken in, there is a tendency for the bubbles to clear naturally, and therefore the formation of cavities in the adhesive layer and the production of roughness on the surface is prevented.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010]

FIG. 1A is a perspective view illustrating a radiation-cured adhesive composition in an uncured state that is laid on a mesh, with a squeegee and a scraper having been arranged thereon;

FIG. 1B is a perspective view illustrating the radiation-cured adhesive composition being spread by the scraper on the mesh and an adherend being brought into proximity with the bottom face of the mesh;

FIG. 1C is a perspective view illustrating the radiation-cured adhesive composition being printed on the adherend by the squeegee;

FIG. 1D is a perspective view illustrating the state on completion of the printing;

FIG. 1E is a perspective view illustrating the radiation-cured adhesive composition having been transferred onto the adherend; and

FIG. 1F is a perspective view illustrating the adhesive having a desired shape as formed on the adherend.

FIG. 2A is a perspective view of the end portion of an adhesive having been drawn out from a roll-form adhesive film; and

FIG. 2B is a perspective view illustrating the appearance when cut by a die cutter.

DETAILED DESCRIPTION

[0011]

Embodiments of the present disclosure are described in further detail below, but the present disclosure is not limited to just these embodiments.

[0012]

The presently disclosed radiation-cured adhesive composition contains an ethylenically unsaturated monomer not containing an aromatic ring, a polymerization inhibitor, and a crosslinking agent as necessary components, and contains an alkyl (meth)acrylate having from 8 to 18 carbon atoms in the alkyl group as the ethylenically unsaturated monomer not containing an aromatic ring, and a urethane poly(meth)acrylate having a weight average molecular weight of 20,000 to 100,000 as the crosslinking agent. In the present invention, the statement "(meth)acrylate" signifies acrylate or methacrylate, and the same applies in other cases as well.

[0013]

"Ethylenically unsaturated monomer not containing an aromatic ring" (hereinafter referred to as "component A") signifies an ethylenically unsaturated monomer in which a benzene ring, naphthalene ring, or other aromatic ring is not present in the molecule, and the ethylenically unsaturated bond contains a substituted or non-substituted vinyl bond. A content of component A is from 10 to 70 wt.% based on a total weight of the radiation-cured adhesive composition, and from 10 to 45 wt.% of an alkyl (meth)acrylate having from 8 to 18 carbon atoms in the alkyl group (hereinafter referred to as "component A1"), based on the total weight of the radiation-cured adhesive composition, must be contained as component A. Component A1 contributes mainly to adhesiveness after curing. Note that the number of ethylenically unsaturated groups in component A is ideally one per molecule.

[0014]

From the viewpoint of adhesiveness on metal or plastic, the content of component A is preferably from 20 to 70 wt.%, and more preferably from 30 to 60 wt.%. Also, component A1 is preferably from 10 to 45 wt.%, and more preferably from 20 to 40 wt.%. The excellence of the adhesiveness is further increased by containing component A1 to such extent. The number of carbon atoms in the alkyl group of component A1 is preferably from 8 to 16, and more preferably from 8 to 12. This alkyl group may contain branches. 8 or more carbon atoms are preferable from the viewpoint of odor.

[0015]

Examples of component A1 include n-octyl (meth)acrylate, isooctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, isodecyl (meth)acrylate, lauryl (meth)acrylate, myristyl (meth)acrylate, hexyldecyl (meth)acrylate, hexadecyl (meth)acrylate, octadecyl (meth)acrylate, isostearyl (meth)acrylate, and octyldecyl (meth)acrylate. 2-ethylhexyl acrylate and lauryl acrylate are particularly preferable as component A1.

[0016]

At least one kind of monomer selected from a group including an alkyl (meth)acrylate other than

those having 8 to 18 carbon atoms in the alkyl group (hereinafter referred to as "component A2"), an alkoxyalkyl (meth)acrylate (hereinafter referred to as "component A3"), a (meth)acrylate containing a carboxylic acid (hereinafter referred to as "component A4"), and an ethylenically unsaturated monomer containing an amide group (hereinafter referred to as "component A5") may be contained as component A.

[0017]

Examples of component A2 include butyl (meth)acrylate, hexyl (meth)acrylate, and other alkyl (meth)acrylates having 4 to 6 carbon atoms in the alkyl group, behenyl (meth)acrylate and other alkyl (meth)acrylates having 20 to 22 carbon atoms in the alkyl group, and cyclohexyl (meth)acrylate, isobornyl (meth)acrylate, and other alicyclic (meth)acrylates. Examples of component A3 include polyalkylene glycol mono(meth)acrylate and polyalkylene glycol monoalkyl ether (meth)acrylate. The adhesive strength can often be improved by adjusting the glass transition temperature and storage modulus of the adhesive after curing by suitably using these monomers. Examples of component A4 include (meth)acrylic acid, acrylate dimers, omega-carboxy-polycaprolactone mono(meth)acrylate, and 2-(meth)acryloyloxyethyl phthalate, 2-(meth)acryloyloxyethyl hexahydrophthalate, 2-(meth)acryloyloxyethyl succinate, and other adducts of hydroxyl-containing (meth)acrylates acid anhydrides. Particularly preferable as component A4 are omega-carboxy-polycaprolactone mono(meth)acrylate and 2-(meth)acryloyloxyethyl phthalate or 2-(meth)acryloyloxyethyl hexahydrophthalate. The adhesive strength can be markedly improved on adherends of stainless steel, other metals, plastic, or the like, by adding these components.

[0018]

Monomers containing amide groups are ideal as component A5. The cohesive force of the adhesive is improved by adding these components, and the effect of improving the adhesive strength on adherends of stainless steel, other metals, glass, or the like, is great particularly in the case when combined with the abovementioned acid-group-containing monomers. At least one kind of monomer selected from a group including (meth)acrylamide, N-substituted (meth)acrylamide, N,N-substituted (meth)acrylamide, aminoalkyl (meth)acrylamide, N-substituted aminoalkyl (meth)acrylamide, and N,N-substituted aminoalkyl (meth)acrylamides is preferable as component A5. Specific examples include N-methylol (meth)acrylamide, N-methoxymethyl N-methylol (meth)acrylamide, N-ethoxymethyl N-methylol (meth)acrylamide, N-n-butoxymethyl N-methylol (meth)acrylamide, N-iso-butoxymethyl N-methylol (meth)acrylamide, N,N-dimethyl N-methylol (meth)acrylamide, N,N-diethyl N-methylol (meth)acrylamide, N-t-butyl N-methylol (meth)acrylamide, N-isopropyl N-methylol (meth)acrylamide, N-t-octyl N-methylol (meth)acrylamide, N,N-dimethylaminoethyl N-methylol (meth)acrylamide, N,N-dimethylaminopropyl N-methylol (meth)acrylamide, diacetone acrylamide, and other substituted acrylamides, and N-vinylpyrrolidone, N-vinylcaprolactam, and other vinyl monomers. Dimethylaminopropyl methacrylamide (DMPMA) is preferable among these.

[0019]

The radiation-cured adhesive composition can contain from 10 to 40 wt.% of an ethylenically unsaturated monomer containing an aromatic ring (hereinafter referred to as "B"), based on the total

weight of the radiation-cured adhesive composition. Component B is an ethylenically unsaturated monomer having a benzene ring, naphthalene ring, or other aromatic ring in the molecule, and contributes mainly to cohesive force to improve adhesive strength. In the case when using component B, the boiling point of component A is preferably less than that of component B (that is, the boiling point of component B is at or above the boiling point of component A).

[0020]

A content of component B is preferably from 10 to 40 wt.%, and more preferably from 10 to 30 wt.%, from the fact that the effects above can be improved. At least one kind of monomer selected from a group including alkylene glycol mono(alkylaryl) ether mono(meth)acrylate, polyalkylene glycol mono(alkylaryl) ether mono(meth)acrylate, alkylene glycol monoaryl ether mono(meth)acrylate, and polyalkylene glycol monoaryl ether mono(meth)acrylate can be used as component B.

[0021]

An example of an alkylene glycol mono(alkylaryl) ether mono(meth)acrylate (this signifies a (meth)acrylate ester of a mono(alkylaryl) ether of alkylene glycol, and is referred to also as "oxyalkylene alkylaryl ether (meth)acrylate," "alkylaryl alcohol alkylene oxide-modified (meth)acrylate," and the like) is ethylene glycol mono(alkylphenyl) ether mono(meth)acrylate, and the number of carbon atoms in the alkyl portion of the alkylphenyl group is preferably from 1 to 12, and more preferably from 6 to 12. An example of an alkylene glycol mono(alkylaryl) ether mono(meth)acrylate is nonylphenyloxyethylene acrylate (e.g., Aronix M111, Toagosei Co., Ltd.).

[0022]

An example of a polyalkylene glycol mono(alkylaryl) ether mono(meth)acrylate (this signifies a (meth)acrylate ester of a mono(alkylaryl) ether of polyalkylene glycol, and is referred to also as "polyoxyalkylene alkylaryl ether (meth)acrylate," "alkylaryl alcohol polyalkylene oxide-modified (meth)acrylate," and the like) is polyethylene glycol mono(alkylphenyl) ether mono(meth)acrylate, and the number of carbon atoms in the alkyl portion of the alkylphenyl group is preferably from 1 to 12, and more preferably from 6 to 12. An example of a polyalkylene glycol mono(alkylaryl) ether mono(meth)acrylate is nonylphenoxytetraethylene glycol acrylate (e.g., Aronix M113, Toagosei Co., Ltd.).

[0023]

An example of an alkylene glycol monoaryl ether mono(meth)acrylate (this signifies a (meth)acrylate ester of a monoaryl ether of alkylene glycol, and is referred to also as "oxyalkylene aryl ether (meth)acrylate," "aryl alcohol alkylene oxide-modified (meth)acrylate," and the like) is ethylene glycol monophenyl ether mono(meth)acrylate.

[0024]

An example of a polyalkylene glycol monoaryl ether mono(meth)acrylate (this signifies a (meth)acrylate ester of a monoaryl ether of polyalkylene glycol, and is referred to also as "polyoxyalkylene aryl ether (meth)acrylate," "aryl alcohol polyalkylene oxide-modified (meth)acrylate," and the like) is polyethylene glycol monophenyl ether mono(meth)acrylate. Examples of polyalkylene glycol monoaryl ether mono(meth)acrylates include phenoxyethoxyethyl acrylate (e.g., Aronix M101A,

Toagosei Co., Ltd.) and tetraalkylene glycol monophenyl ether monoacrylate (e.g., Aronix M102, Toagosei Co., Ltd.).

[0025]

An example of an aryloxyalkyl mono(meth)acrylate is phenoxyethyl acrylate (e.g., Biscoat #192, Osaka Organic Chemical Industry). Alkylene glycol mono(alkylaryl) ether mono(meth)acrylate is preferable, and nonylphenyloxyethylene acrylate is particularly preferable, from the fact that the surface energy is lowered.

[0026]

A photopolymerization initiator (hereinafter referred to as "component C"), which is a component of the radiation-cured adhesive composition, is a substance that can bring about radical polymerization, cationic polymerization, or the like, on being irradiated with ultraviolet or other radiation, and is used for initiating a reaction with components A and B described above and a crosslinking agent to be described later. Component C is contained at from 1 to 10 wt.% based on the total weight of the radiation-cured adhesive composition. The content is preferably from 0.5 to 8 wt.%, and more preferably from 1 to 5 wt.%.

[0027]

Component C is preferably a photo-radical initiator, and specific examples include 1-hydroxy-cyclohexyl-phenylketone, 2-hydroxy-2-methyl-1-phenyl-1-propanone, 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone, 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-benzyl]phenyl}-2-methyl-propane-1-one (e.g., Irgacure 127, Ciba Specialty Chemicals), and other alpha-hydroxyketones; methyl benzoylformate and other phenylglyoxylates; alpha,alpha-dimethoxy-alpha-phenylacetophenone (e.g., Irgacure 651, Ciba Specialty Chemicals) and other benzyl dimethyl ketals; 2-benzyl-2-(dimethylamino)-1-[4-(4-morphorinyl)phenyl]-1-butanone, 2-methyl-1-[4-(methylthio)phenyl]-2-(4-morphorinyl)-1-propanone, and other alpha-aminoketones; diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide (e.g., Darocur TAF, Ciba Specialty Chemicals) and other monoacyl phosphines; bis (2,4,6-trimethylbenzoyl) phenyl phosphine oxide (e.g., Irgacure 819, Ciba Specialty Chemicals) and other bis acyl phosphines; phosphine oxide; bis (eta5-2,4-cyclopentadiene-1-yl) bis [2,6-difluoro-3-(1-H-propyl-1-yl)phenyl] titanium and other metallocenes; benzoin ethyl ether, benzoin isopropyl ether, anisoin methyl ether, and other benzoin ether-based compounds; benzyl dimethyl ketal and other ketal-based compounds; 1-phenone-1,1-propanedione-2-(o-ethoxycarbonyl)oxim and other photoactive oxim-based compounds; benzophenone, benzoyl benzoic acid, 3,3'-dimethyl-4-methoxybenzophenone, and other benzophenone-based compounds; thioxanthone, 2-chloro thioxanthone, 2-methyl thioxanthone, 2,4-dimethyl thioxanthone, isopropyl thioxanthone, 2,4-dichloro thioxanthone, 2,4-diethyl thioxanthone, 2,4-diisopropyl thioxanthone, and other thioxanthone-based compounds; camphor quinone; 2-ethyl anthraquinone, 2-isopropyl anthraquinone, and the like. These compounds may be used singly or in mixtures of pluralities. A phosphorus-containing initiator is preferable from the viewpoint of speed of curing. Particularly in the case when curing in air, the combination of a phosphorus-containing initiator and 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-benzyl]phenyl}-2-methyl-propane-1-one is preferable from the perspective of curability.

[0028]

A crosslinking agent (hereinafter referred to as "component D"), which is a component of the radiation-cured adhesive composition, is a compound for reacting with components A and B described above to form a crosslinked structure and for adjusting the composition to a suitable viscosity. A compound having a plurality of ethylenically unsaturated bonds can be used as component D, and a poly(meth)acrylate compound is preferable as that compound. The poly(meth)acrylate compound should have from 1.1 to 6 (meth)acryloyl groups, more preferably from 1.1 to 4, and even more preferably from 1.1 to 2. A content of component D is from 10 to 55 wt.%, and preferably from 10 to 50 wt.%, based on the total weight of the radiation-cured adhesive composition.

[0029]

Component D contains from 10 to 50 wt.% of a urethane poly(meth)acrylate (hereinafter referred to as "component D1") having a weight average molecular weight from 20,000 to 100,000, based on the total weight of the radiation-cured adhesive composition. The content of component D1 is preferably from 20 to 45 wt.%, and more preferably from 20 to 40 wt.%. Also, the weight average molecular weight (here, the value calculated by gel permeation chromatography (GPC) based on styrene) is more preferably from 20,000 to 90,000, and even more preferably from 35,000 to 85,000. The urethane portion of component D1 may be a polyester urethane, a polyether urethane, or a polyester-ether urethane. The isocyanate forming the urethane may be an aliphatic isocyanate, an alicyclic isocyanate, or an aromatic isocyanate, and the number of isocyanate groups per molecule should be 2). Component D1 may also be a mixture of a multifunctional compound and a monofunctional compound. Specifically, a bifunctional compound and a monofunctional compound may be mixed to form, for example, a 1.5-functional compound.

[0030]

Examples of components D other than component D1 include 2-hydroxy-3-acryloyloxypropyl methacrylate, polyethylene glycol di(meth)acrylate, propoxylated ethoxylated bisphenol A di(meth)acrylate, ethoxylated bisphenol A di(meth)acrylate, 9,9-bis[4-(2-acryloyloxyethoxy)phenyl]fluorene, propoxylated bisphenol A di(meth)acrylate, 1,6-hexanediol A di(meth)acrylate, dipropylene glycol di(meth)acrylate, ethoxylated isocyanuric acid tri(meth)acrylate, pentaerythritol tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, and the like. The content of these components may be less than that of component D1, and the content may be 0. That is, component D may also contain only component D1.

[0031]

The radiation-cured adhesive composition can contain an inorganic or organic thixotropic agent (hereinafter referred to as "component E"). Examples of inorganic thixotropic agents of component E include clay (for example, bentonite) having a particle size of less than 0.1 μm , silica, alumina, titania, zirconia, calcium carbonate, mica, smectite, and surface-treated materials thereof. Examples of organic thixotropic agents of component E include fatty acids, hydroxy fatty acids, fatty acid amines, fatty acid amides, or other aliphatic amide compounds, hydrogenated castor oil, fatty acid metal soaps, sorbitan fatty acid ester derivatives, sorbit fatty acid ester derivatives, alkylene glycol fatty acid esters, fatty acid

glycerin esters, dibenzylidene sorbitol derivatives, modified acrylic polymers and copolymers, polyhydroxycarboxylic acid amines and amides, polyvinyl alcohols, and vinyl polymers (vinyl methyl ether/maleic anhydride). A typical content of component E is from 0.1 to 5 wt.% based on the total weight of the radiation-cured adhesive composition. A thixotropic agent containing inorganic micropowder is preferable as component E.

[0032]

The radiation-cured adhesive composition preferably further contains a leveling agent (hereinafter referred to as "component F"). Examples of component F include silicone oligomers, aliphatic oils, acrylic oligomers, polyester oligomers, and liquid synthetic rubber, and BYK-Chemie Japan DISPERBYK series, Evonik TEGO Airex series, Kusumoto Chemicals Disparlon series, Air Products Japan Surfynol series, and other commercially available leveling agents can be used. An ideal content is from 0.01 to 10 wt.%, and more preferably from 0.05 to 2 wt.%, based on the total weight of the radiation-cured adhesive composition.

[0033]

The radiation-cured adhesive composition may further contain a tackifying resin (hereinafter referred to as "component G"). The tackifying agent of component G is not particularly limited provided that the adhesiveness of the adhesive composition of the present invention can be improved, and examples include rosin-based resins, coumarone-indene-based resins, terpene-based resins, C5-based petroleum resins, C9-based petroleum resins, styrene-based copolymers, alkylphenol resins, xylene resins, hydrated and modified resins thereof, and the like. In particular, favorable results can be obtained, from the viewpoint of compatibility with the adhesive composition, when using hydrated rosin resins, terpene resins, terpene phenol resins, and alkylphenol-modified xylene resins.

[0034]

The rosin resins used in the present disclosure can be commercially available rosins, hydrogenated rosins, or derivatives thereof. Examples include "Tamanol" series rosin-modified phenol resins; "Ester Gum" series, "Pensel" series, and "Super Ester" series rosin ester resins, and "Pinecrystal" rosin derivative (all manufactured by Arakawa Chemical); "Hariphenol" series rosin-modified phenol resins; "Hariester" series and "Neotall" series rosin ester resins (manufactured by Harima Chemicals), and the like. The terpene-based resins used in the present invention can be commercially available terpene resins or derivatives thereof. Examples include YS resin TO series, TR series, YS Polystar T series, 2000 series, U series, S series, N series, Mighty Ace GG series, and K series (all manufactured by Yasuhara Chemical). The xylene resins used in the present invention can be commercially available xylene resins and derivatives thereof. Nikanol (manufactured by Fudow Co., Ltd.), and the like, can be used. The softening point of component G is preferably from 60 to 150°C, and more preferably from 80 to 130°C, from the perspective of balance of properties and performance after curing. A content of component G is preferably from 10 to 30 wt.%, and more preferably from 10 to 20 wt.%, of the total quantity of the radiation-cured adhesive composition, from the perspective of the balance of properties and performance after curing.

[0035]

The radiation-cured adhesive composition described above can be cured in the presence of oxygen or in the presence of an inert gas to be used as an adhesive. In the case when cured in the presence of oxygen, the curing is preferably done by UVA and/or UVB irradiation, and the intensity is ideally from 100 to 1500 mW/cm². In the case when cured in the presence of an inert gas, a polymerization modifier is preferably included in the radiation-cured adhesive composition, and curing should be done with UV irradiation of an intensity of 20 mW/cm² or higher. The polymerization modifier is preferably a polymerization modifier by radical reaction, and specific examples include alpha-methylstyrene, alpha-methylstyrene dimers, and compounds having thiol groups. An alpha-methylstyrene dimer is particularly preferable from the perspective of odor.

[0036]

The radiation-cured adhesive composition can be obtained by mixing each component described above with the condition that light capable of bringing about a curing reaction is not introduced to the contained curing agent, and all additives that are commonly used in the field can be added in ranges that do not impede the effect of the present invention. For example, antioxidants, photostabilizers, dyes, pigments, fragrances, and the like, can be added.

[0037]

FIG. 1 is a perspective view typically illustrating states in which an adhesive having a desired shape is formed on a substrate by screen-printing using a radiation-cured adhesive composition. FIG. 1A is a perspective view illustrating a radiation-cured adhesive composition 1 in an uncured state that is laid on a mesh including a mesh body 10 for a square frame forming the letters "ab" to be screen printed and a holder 12 for holding the same, with a squeegee 14 having been arranged thereon. An adherend 20 is present at a distance from the mesh. FIG. 1B is a perspective view illustrating the radiation-cured adhesive composition 1 being spread by the squeegee 14 on the mesh and the adherend 20 being brought into proximity with the bottom face of the mesh. FIG. 1C is a perspective view illustrating the radiation-cured adhesive composition 1 being printed on the adherend 20 by wiping off with the squeegee 14 while pressing the mesh against the adherend 20. FIG. 1D is a perspective view illustrating the state on completion of the printing; and FIG. 1E is a perspective view illustrating the adherend 20, which has been removed from the mesh, and with the square frame and the letters "ab" having been transferred onto the adherend 20. FIG. 1F is a perspective view illustrating the adhesive 2 having a desired shape as formed on the adherend 20 by irradiating the radiation-cured adhesive composition 1 with ultraviolet radiation from a UV irradiation machine 30. A laminate having a patterned adhesive composition (radiation-cured adhesive composition 2 after curing) on a substrate (adherend 20) can be obtained thereby.

[0038]

The radiation-cured adhesive composition can be shape processed easily because occurrence of stringiness during plate removal in screen-printing (stringiness in the state in FIG. 1E) is not likely to occur, and there is no situation in which the adhesive layer is cured in a swollen condition, because the radiation-cured adhesive composition can be leveled easily after application. Additionally, even if air is briefly taken in, bubbles will clear naturally. The adhesive after curing exhibits excellent adhesiveness on a wide range of adherends including stainless steel, ABS, or the like. FIG. 2 illustrates the formation of an

adhesive layer by conventional die cutting. FIG. 2A is a perspective view illustrating the end portion of an adhesive 50 having been drawn out from a roll-form adhesive film. FIG. 2B is a perspective view illustrating the appearance when cut by a die cutter, and the adhesive divided into adhesive 50a to be affixed to an adherend and adhesive 50b to be discarded. FIG. 2C is a perspective view illustrating the adhesive 50a for affixing having been affixed to the adherend 20. Thus, with the method by conventional die cutting, the adhesive 50b to be discarded is inevitably produced, but with the present invention, there is no such waste, and the load on the environment has been fully considered.

Following are non-limiting, exemplary embodiments and combinations of embodiments for the present disclosure:

Embodiment 1. A radiation-cured adhesive composition comprising: from 10 to 70 wt.% of an ethylenically unsaturated monomer not containing an aromatic ring; from 1 to 10 wt.% of a photopolymerization initiator; and from 10 to 55 wt.% of a crosslinking agent;

the radiation-cured adhesive composition comprising from 10 to 45 wt.% of an alkyl (meth)acrylate having from 8 to 18 carbon atoms in the alkyl group as the ethylenically unsaturated monomer not containing an aromatic ring, and from 10 to 50 wt.% of a urethane poly(meth)acrylate having a weight average molecular weight of 20,000 to 100,000 as the crosslinking agent

Embodiment 2. The radiation-cured adhesive composition according to Embodiment 1, further comprising from 10 to 40 wt.% of an ethylenically unsaturated monomer containing an aromatic ring.

Embodiment 3. The radiation-cured adhesive composition according to Embodiment 1 or 2, wherein the ethylenically unsaturated monomer not containing an aromatic ring is a monomer having a boiling point at or above that of the ethylenically unsaturated monomer containing an aromatic ring.

Embodiment 4. The radiation-cured adhesive composition according to any one of Embodiments 1 to 3, wherein at least one kind of monomer selected from a group including an alkyl (meth)acrylate other than one having from 8 to 18 carbon atoms in the alkyl group, an alkoxyalkyl (meth)acrylate, a (meth)acrylate containing a carboxylic acid, and an ethylenically unsaturated monomer containing an amide group is contained as the ethylenically unsaturated monomer not containing an aromatic ring .

Embodiment 5. The radiation-cured adhesive composition according to any one of Embodiments 1 to 4, wherein the urethane poly(meth)acrylate is a mixture of a urethane di(meth)acrylate and a urethane mono(meth)acrylate, or a urethane di(meth)acrylate, and the weight average molecular weight is from 35,000 to 850,000.

Embodiment 6. The radiation-cured adhesive composition according to any one of Embodiments 2 to 5, wherein the ethylenically unsaturated monomer containing an aromatic ring is at least one kind selected

from a group including alkylene glycol mono(alkylaryl) ether mono(meth)acrylate, polyalkylene glycol mono(alkylaryl) ether mono(meth)acrylate, alkylene glycol monoaryl ether mono(meth)acrylate, polyalkylene glycol monoaryl ether mono(meth)acrylate, and aryloxyalkyl mono(meth)acrylate.

5 Embodiment 7. The radiation-cured adhesive composition according to any one of Embodiments 4 to 6, wherein the ethylenically unsaturated monomer containing an amide group is at least one kind selected from a group including (meth)acrylamide, N-substituted (meth)acrylamide, N,N-substituted (meth)acrylamide, aminoalkyl (meth)acrylamide, N-substituted aminoalkyl (meth)acrylamide, and N,N-substituted aminoalkyl (meth)acrylamide.

10

Embodiment 8. The radiation-cured adhesive composition according to any one of Embodiments 1 to 7, further comprising an inorganic or organic thixotropic agent.

15

Embodiment 9. The radiation-cured adhesive composition according to Embodiments 1 to 8, further comprising a leveling agent.

Embodiment 10. The radiation-cured adhesive composition according to any one of Embodiments 1 to 9, wherein curing is performed by UV irradiation in the presence of oxygen.

20

Embodiment 11. The radiation-cured adhesive composition according to any one of Embodiments 1 to 9, further comprising a polymerization modifier, and wherein curing is performed by UV irradiation at a strength of 20 mW/cm² or higher in the presence of an inert gas.

25

Embodiment 12. The radiation-cured adhesive composition according to any one of Embodiments 1 to 11, wherein a peeling strength on stainless steel and ABS after curing is 4 N/cm or higher.

Embodiment 13. An adhesive obtained by curing a radiation-cured adhesive according to any one of Embodiments 1 to 12.

30

Embodiment 14. A laminate, having a layer containing an adhesive according to Embodiment 13 patterned by screen printing on a substrate.

[Examples]

[0039]

35

The present disclosure is described more specifically below based on working examples and comparative examples, but the present disclosure is not limited to the working examples below.

[0040]

First, the names, chemical species, manufacturers, and categories (names in the present specification) of the materials used in the examples and working examples below are summarized in

Table 1.

[Table 1]

Trade Name	Chemical species	Manufacturer	Categories
Aronix M111	Nonylphenoxyethylene acrylate	Toagosei Co., Ltd.	Ethylenically unsaturated monomer containing an aromatic ring
Aronix M113	Nonylphenoxytetraethylene glycol acrylate	Toagosei Co., Ltd.	Ethylenically unsaturated monomer containing an aromatic ring
Viscoat #192	Phenoxyethyl Acrylate	Osaka Organic Chemical Industry	Ethylenically unsaturated monomer containing an aromatic ring
Aronix M101A	Phenoxyethoxyethyl acrylate	Toagosei Co., Ltd.	Ethylenically unsaturated monomer containing an aromatic ring
Viscoat #MTG	Methoxy triethylene glycol acrylate	Osaka Organic Chemical Industry	Ethylenically unsaturated monomer not containing an aromatic ring
2EHA	2-ethylhexyl acrylate	Nippon Shokubai Co, Ltd.	Alkyl (meth) acrylates having 8-18 carbon atoms in the alkyl group
LA	Lauryl acrylate	NOF Corporation	Alkyl(meth)acrylates having 8-18 carbon atoms in the alkyl group
MEA	Methoxyethyl acrylate	Nippon Shokubai Co, Ltd.	Alkoxyalkyl(meth)acrylate
Aronix M5300	Caprolactone acrylate	Toagosei Co., Ltd.	(Meth)acrylate containing carboxylic acid
Acrylester HH	Hexahydrophthalic acid 2-methacryloxy ethyl	Mitsubishi Rayon Co, Ltd.	(Meth)acrylate containing a carboxylic acid
DMAPMAM	N,N-Dimethylaminopropyl methacrylamide	MRC Unitec Co, Ltd.	Ethylenically unsaturated monomer containing an amide group
Darocur TPO	Diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide	Ciba Specialty Chemical Co, Ltd.	Photopolymerization initiator
Irgacure 819	bis (2,4,6-trimethylbenzoyl) phenyl phosphine oxide	Ciba Specialty Chemical Co, Ltd.	Photopolymerization initiator
Irgacure 127	2-hydroxy-1-2-{4-[4-(2-hydroxy-2-methylpropionyl)-benzyl]phenyl}-2-methyl-propane-1-one	Ciba Specialty Chemical Co, Ltd.	Photopolymerization initiator
Irgacure 651	Alpha, alpha-dimethoxy-alpha phenylacetophenone	Ciba Specialty Chemical Co, Ltd.	Photopolymerization initiator
KHP22J	Polyester urethane diacrylate(Mw46000, bifunctional)	Negami Chemical Industrial Co., Ltd.	Urethane poly(meth)acrylate having weight average molecular weight 20000-100000
KHP22J(1.5)	Polyester urethane diacrylate, polyester urethane monoacrylate mixture(Mw46000, 1.5 functional)	Negami Chemical Industrial Co., Ltd.	Urethane poly(meth)acrylate having weight average molecular weight 20000-100000

KHP22M	Polyester urethane dimethacrylate (Mw46000, bifunctional)	Negami Chemical Industrial Co., Ltd.	Urethane poly(meth)acrylate having weight average molecular weight 20000-100000
UN7700	Polyester urethane diacrylate (Mw20000, bifunctional)	Negami Chemical Industrial Co., Ltd.	Urethane poly(meth)acrylate having weight average molecular weight 20000-100000
UV3700	Polyester urethane diacrylate (Mw36000, bifunctional)	Negami Chemical Industrial Co., Ltd.	Urethane poly(meth)acrylate having weight average molecular weight 20000-100000
SSFX-1	Polyester urethane diacrylate(Mw46000, bifunctional)	Negami Chemical Industrial Co., Ltd.	Urethane poly(meth)acrylate having weight average molecular weight 20000-100000
A200	Fumed silica	Nippon Aerosil Co., Ltd.	Thixotropic agent containing inorganic micropowder
R972	Hydrophobic treated fumed silica	Nippon Aerosil Co., Ltd.	Thixotropic agent containing inorganic micropowder
HP100	Xylene phenol resin	Fudow Co., Ltd.	Tackifier
TO125	Terpene resin	Yasuhara Chemical Co., Ltd.	Tackifier
TO115	Terpene resin	Yasuhara Chemical Co., Ltd.	Tackifier
A125	Rosin ester	Arakawa Chemical Industries, Ltd.	Tackifier
T125	Rosin ester	Arakawa Chemical Industries, Ltd.	Tackifier
KE311	Rosin ester	Arakawa Chemical Industries, Ltd.	Tackifier
HP100	Xylene phenol resin	Fudow Co., Ltd.	Tackifier
AMSD	Alpha-methylstyrene dimer	Goi Chemical Co., Ltd.	Polymerization modifier
aMSt	Alpha-methylstyrene	Wako Pure Chemical Industries, Ltd.	Polymerization modifier
KP323	Silicone oligomers	Shin-etsu Chemical Co., Ltd.	Leveling agent

[0041]

[Working examples 1 to 3]

The compositions having the compositions listed in Table 2 below were mixed in UV-cut plastic bottles. The composition was applied by doctor blade to a thickness of 50 μm on a silicone-treated transparent polyester film, and was cured by passing three times through a Fusion FS300 curing oven (H bulb, 15 m/minute, 200 $\text{mJ}/\text{cm}^2/\text{pass}$) in an oxygen atmosphere. Sufficient curing was possible thereby. Curing was then further performed seven times in an oxygen atmosphere. The total dosage of irradiation was 2000 mJ/cm^2 . The adhesive composition (pressure-sensitive adhesive) on the PET film obtained thereby was laminated with another silicone-treated PET film.

[Table 2]

Trade Name	Embodiment 1	Embodiment 2	Embodiment 3
2EHA	10	10	10
LA	46	46	46
Acrylester HH	5	5	5
Darocur TPO	1.0	1.0	1.0
Irgacure 127	3.0	3.0	3.0
SSFX-1	39.0	39.0	39.0
R972	1.0	1.0	1.0
TO125	25.0	-	-
TO115	-	25.0	-
HP100	-	-	25.0

[0042]

(Method of measurement of peeling strength)

The peeling strength (peeling adhesive strength) was measured by a method based on JIS Z 0237. The details are as follows. The adhesive sheet obtained above was cut by cutter into 25×70 mm pieces. Also, a release film was peeled from the cured surface, and the adhesive sheet was affixed to a polyester film (S-25, Unitika), which had been cut into a 30×150 mm piece having a thickness of 25 μm. A remaining release film was removed from the adhesive sheet, and then the adhesive sheet was affixed using a rubber roller having a weight of 2 kg to an ABS plate (manufactured by Nihon Tact Co., Ltd.) having a thickness of 2 mm, a polypropylene (PP) plate (manufactured by Nihon Tact Co., Ltd.) having a thickness of 2 mm, or a stainless steel plate (manufactured by Nihon Tact Co., Ltd.) having a thickness of 1 mm, which had been immersed in isopropyl alcohol (IPA) and wiped with a cloth. After setting aside for 20 minutes at room temperature, a tension at a peeling speed of 300 mm/minute was applied to the polyester film by tension tester (AG-IS, Shimadzu), and the 180° peeling strength of the adhesive sheet was measured.

[0043]

(Method of measurement of static shear strength)

A release film was peeled from the adhesive sheet obtained above, the adhesive sheet was affixed to a polyester film (S-25, Unitika) having a thickness of 25 μm, and the sheet was cut by cutter into a 25×100 mm piece. A remaining release film was removed from the adhesive sheet, and then the adhesive sheet was affixed using a rubber roller having a weight of 2 kg to a stainless steel plate (manufactured by Nihon Tact Co., Ltd.) having a thickness of 1.0 mm, which had been washed with isopropyl alcohol (IPA) or methyl ethyl ketone (MEK), so as to cover a range of 25 mm × 25 mm of the plate. The sample was suspended together with a 500 g weight in a 70°C chamber. The time until separation and dropping (drop off) and the extent of shifting were measured after 24 hours.

[0044]

(Method of measurement of suitability for screen-printing)

The suitability for screen-printing of the radiation-cured adhesive compositions obtained in the comparative examples was evaluated using a screen printer (SERIA, HK320). A screen-printing plate

was applied in a pattern on a polyester film (S-100, Unitika Ltd.) having a thickness of 100 μm using a patterned polyester mesh plate (Tetron #120 mesh, 54 μm line width, 55% aperture, Tokai Shoji Co., Ltd.), and the stringiness when removing from the polyester film and the leveling and bubble clearing of the printed object were observed. Those having very good stringiness, leveling, and bubble clearing were evaluated as excellent, those having good stringiness, leveling, and bubble clearing were evaluated as good, those having no stringiness but having a somewhat disorderly printed surface were evaluated as passable, and those having occurrence of stringiness during plate removal were evaluated as failed.

[0045]

The content (%) of each component and the measurement results are listed in Table 3 below. In the table, CF signifies cohesive failure, AF signifies adhesive failure, and Shocky signifies that the state of peeling is not uniform, which is a state in which high strength and low strength appear alternately.

[Table 3]

Trade Name	Embodiment 1	Embodiment 2	Embodiment 3
2EHA	7.7%	7.7%	7.7%
LA	35.4%	35.4%	35.4%
Acrylester HH	3.8%	3.8%	3.8%
Darocur TPO	0.8%	0.8%	0.8%
Irgacure 127	2.3%	2.3%	2.3%
SSFEX-1	30.0%	30.0%	30.0%
R972	0.8%	0.8%	0.8%
TO125	19.2%	0.0%	0.0%
TO115	0.0%	19.2%	0.0%
HP100	0.0%	0.0%	19.2%
SUS Detachment Strength (N/cm)	6.3	7.6	7.7
Failure Mode	CF	CF	AF
ABS Detachment strength (N/cm)	7.6	6.0	8.1
Failure Mode	AF	AF	Shocky
PP Detachment Strength (N/Cm)	4.1	4.5	0.0
Failure Mode	AF	AF	Shocky
Drop-off (min)	>1440	35.0	>1440
Slippage(mm)	0.2	-	0
Screen-printing Suitability	Favorable	Favorable	Favorable

[0046]

[Working examples 4 to 10]

Compositions having the compositions listed in Tables 4 and 5 below were created in the same manner as above, and the same kinds of measurements as above were performed. The content (%) of each component and the measurement results are listed in Tables 6 and 7 below.

[Table 4]

Trade Name	Embodiment 4	Embodiment 5	Embodiment 6	Embodiment 7	Embodiment 8	Embodiment 9	Embodiment 10
Aronix M111	25	25	25	25	25	25	25

LA	34	34	34	34	34	34	34
Acrylester HH	5	5	5	5	5	5	5
Darocur TPO	1.0	1.0	1.0	0.0	0.0	-	-
Irgacure 819	-	-	-	2.0	2.0	2.0	2.0
Irgacure 127	3.0	3.0	3.0	-	-	-	-
Irgacure 651	-	-	-	2.0	2.0	2.0	2.0
SSFX-1	39.0	39.0	39.0	36.0	36.0	36.0	36.0
R972	1.0	1.0	1.0	2.0	2.0	2.0	2.0
TO125	25.0	0.0	-	20.0	25.0	-	-
TO115	-	25.0	-	-	-	25.0	-
A125	-	-	-	-	-	-	25.0
HP100	-	-	25.0	-	-	-	-

[0047]

[Table 5]

Trade Name	Embodi ment 11	Embodi ment 12	Embodi ment 13	Embodi ment 14	Embodi ment 15	Embodi ment 16	Embodi ment 17
Aronix M111	25	25	25	25	25	25	25
LA	34	34	34	34	34	34	34
Acrylester HH	5	5	5	5	5	5	5
Darocur TPO	-	-	-	-	-	2.0	2.0
Irgacure 819	2.0	2.0	2.0	2.0	2.0	-	-
Irgacure 127	2.0	2.0	2.0	2.0	2.0	2.0	2.0
SSFX-1	36.0	36.0	36.0	36.0	36.0	36.0	36.0
R972	-	1.0	-	-	-	1.0	1.0
TO125	20.0	-	-	-	-		
TO115		20.0	-	-	-	20.0	25.0
A125			20.0	-	-	-	-
T125	-	-	-	20.0	-	-	-
KE311	-	-	-	-	20.0	-	-

5

[0048]

[Table 6]

Trade Name	Embodi ment 4	Embodi ment 5	Embodi ment 6	Embodi ment 7	Embodi ment 8	Embodi ment 9	Embodi ment 10
Aronix M111	18.8%	18.8%	18.8%	19.8%	19.1%	19.1%	19.1%
LA	25.6%	25.6%	25.6%	27.0%	26.0%	26.0%	26.0%
Acrylester HH	3.8%	3.8%	3.8%	4.0%	3.8%	3.8%	3.8%
Darocur TPO	0.8%	0.8%	0.8%	0.0%	0.0%	0.0%	0.0%
Irgacure 819	0.0%	0.0%	0.0%	1.6%	1.5%	1.5%	1.5%
Irgacure 127	2.3%	2.3%	2.3%	0.0%	0.0%	0.0%	0.0%
Irgacure 651	0.0%	0.0%	0.0%	1.6%	1.5%	1.5%	1.5%
SSFX-1	29.3%	29.3%	29.3%	28.6%	27.5%	27.5%	27.5%
R972	0.8%	0.8%	0.8%	1.6%	1.5%	1.5%	1.5%
HP100	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

TO125	18.8%	0.0%	0.0%	15.9%	19.1%	0.0%	0.0%
TO115	0.0%	18.8%	0.0%	0.0%	0.0%	19.1%	0.0%
A125	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	19.1%
HP100	0.0%	0.0%	18.8%	0.0%	0.0%	0.0%	0.0%
SUS Detachment Strength (N/cm)	6.2	6.7	4.6	8.2	7.6	7.2	7.4
Failure Mode	AF	AF	AF	AF	AF	AF	AF
ABS Detachment Strength (N/cm)	5.1	5.1	4.4	-	-	-	-
Failure Mode	AF	AF	AF	-	-	-	-
PP Detachment strength (N/cm)	4.2	3.8	3.0	6.0	6.3	3.1	3.0
Failure Mode	AF	AF	AF	AF	AF	Shocky	Shocky
Drop-off (min)	>1440	>1440	>1440	>1440	938.0	85.0	>1440
Slippage (mm)	0	0	0	0	-	-	2
Screen-printing Suitability	Favorable	Favorable	Favorable	Favorable	Favorable	Favorable	Favorable

[0049]

[Table 7]

Trade Name	Embodiment 11	Embodiment 12	Embodiment 13	Embodiment 14	Embodiment 15	Embodiment 16	Embodiment 17
Aronix M111	20.2%	20.0%	20.2%	20.2%	20.2%	20.0%	19.2%
LA	27.4%	27.2%	27.4%	27.4%	27.4%	27.2%	26.2%
Acrylester HH	4.0%	4.0%	4.0%	4.0%	4.0%	4.0%	3.8%
Darocur TPO	0.0%	0.0%	0.0%	0.0%	0.0%	1.6%	1.5%
Irgacure 819	1.6%	1.6%	1.6%	1.6%	1.6%	0.0%	0.0%
Irgacure 127	1.6%	1.6%	1.6%	1.6%	1.6%	1.6%	1.5%
SSFX-1	29.0%	28.8%	29.0%	29.0%	29.0%	28.8%	27.7%
R972	0.0%	0.8%	0.0%	0.0%	0.0%	0.8%	0.8%
TO125	16.1%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
TO115	0.0%	16.0%	0.0%	0.0%	0.0%	16.0%	19.2%
A125	0.0%	0.0%	16.1%	0.0%	0.0%	0.0%	0.0%
T125	0.0%	0.0%	0.0%	16.1%	0.0%	0.0%	0.0%
KE311	0.0%	0.0%	0.0%	0.0%	16.1%	0.0%	0.0%
SUS Detachment Strength (N/cm)	5.6	5.4	6.2	6.1	4.8	6.2	5.4
Failure Mode	AF	AF	AF	AF	AF	AF	AF
PP Detachment Strength (N/cm)	4.8	4.9	5.3	5.1	4.0	5.2	5.4
Failure Mode	AF	AF	AF	AF	AF	AF	AF
Drop-off (min)	>1440	336.0	197.0	616.0	562.0	>1440	-
Slippage (mm)	3	-	-	-	-	0.5	-
Screen-printing Suitability	Acceptable	Favorable	Acceptable	Acceptable	Acceptable	Favorable	Favorable

[Working examples 18 to 23]

Compositions having the compositions listed in Table 8 below were created in the same manner as above, the same kinds of measurements as above were performed. The content (%) of each component and the measurement results are listed in Table 9 below.

5 [Table 8]

Trade Name	Embodi ment 18	Embodi ment 19	Embodi ment 20	Embodi ment 21	Embodi ment 22	Embodi ment 23
Aronix M111	104	-	-	-	104	104
Aronix M113	-	-	104	-	-	-
Viscoat #192	-	-	-	104	-	-
Aronix M101A	-	104	-	-	-	-
2EHA	108	108	108	108	108	108
Aronix M5300	104	104	104	104	104	104
DMAPMAm	6.3	6.3	6.3	6.3	6.3	6.3
Darocur TPO	4.2	4.2	4.2	4.2	4.2	4.2
Irgacure 127	12.5	12.5	12.5	12.5	12.5	12.5
KHP22J	100.0	100.0	100.0	100.0	-	-
UN7700	-	-	-	-	100.0	-
UV3700	-	-	-	-	-	100.0
R972	6.3	6.3	6.3	6.3	6.3	6.3
HP100	41.7	41.7	41.7	41.7	41.7	41.7

[0051]

10 [Table 9]

Trade Name	Embodi ment 18	Embodi ment 19	Embodi ment 20	Embodi ment 21	Embodi ment 22	Embodi ment 23
Aronix M111	21.4%	0.0%	0.0%	0.0%	21.4%	21.4%
Aronix M113	0.0%	0.0%	21.4%	0.0%	0.0%	0.0%
Viscoat #192	0.0%	0.0%	0.0%	21.4%	0.0%	0.0%
Aronix M101A	0.0%	21.4%	0.0%	0.0%	0.0%	0.0%
Viscoat #MTG	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2EHA	22.2%	22.2%	22.2%	22.2%	22.2%	22.2%
Aronix M5300	21.4%	21.4%	21.4%	21.4%	21.4%	21.4%

DMAPMAm	1.3%	1.3%	1.3%	1.3%	1.3%	1.3%
Darocur TPO	0.9%	0.9%	0.9%	0.9%	0.9%	0.9%
Irgacure 127	2.6%	2.6%	2.6%	2.6%	2.6%	2.6%
KHP22J	20.5%	20.5%	20.5%	20.5%	0.0%	0.0%
UN7700	0.0%	0.0%	0.0%	0.0%	20.5%	0.0%
UV3700	0.0%	0.0%	0.0%	0.0%	0.0%	20.5%
R972	1.3%	1.3%	1.3%	1.3%	1.3%	1.3%
SUS Detachment Strength (N/cm)	15.1	6.1	10.7	15.6	6.5	8.8
Failure Mode	CF	AF	CF	CF	AF	CF
ABS Detachment strength (N/cm)	11.5	5.9	9.9	13.9	6.9	11.0
Failure Mode	AF	AF	CF	CF	AF	CF
Drop-off (min)	None	None	None	None	None	None
Screen- printing Suitability	Favor- able	Favor- able	Favor- able	Favor- able	Accept- able	Favor- able

[0052]

[Working examples 24 to 34]

Compositions having the compositions listed in Table 10 below were created in the same manner as above; the same kinds of measurements as above were performed. The content (%) of each component and the measurement results are listed in Table 11 below. AF90/CF10 signifies an adhesive failure of 90% and a cohesive failure of 10%.

[Table 10]

Trade Name	Embodi ment 24	Embodi ment 25	Embodi ment 26	Embodi ment 27	Embodi ment 28	Embodi ment 29	Embodi ment 30	Embodi ment 31	Embodi ment 32	Embodi ment 33	Embodi ment 34
Aronix M111	25	25	25	25	25	35	25	35	25	40	40
2EHA	36	18	26	12	12	24	26	24	26	18	18
MEA	-	-	-	20	20	-	-	-	-	-	-
Aronix M5300	25	25	25	25	25	25	25	25	25	25	25
DMAPMam	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1	1.5
Darocur TPO	1	1	1	1	1	-	-	-	-	-	-
Irgacure 819	-	-	-	-	-	2	2	2	2	2	2
Irgacure 127	3	3	3	3	3	2	2	2	2	-	-
KHP22J	24	-	-	18	18	16	24	16	24	16	16
KHP22J(1.5)	-	27	-	-	-	-	-	-	-	-	-
KHP22M	-	-	24	-	-	-	-	-	-	-	-
A200	2	2	2	-	-	-	-	-	-	-	-
HP100	10	10	10	-	10	-	-	10	10	-	-

[0053]

[Table 11]

Trade Name	Embodi ment 24	Embodi ment 25	Embodi ment 26	Embodi ment 27	Embodi ment 28	Embodi ment 29	Embodi ment 30	Embodi ment 31	Embodi ment 32	Embodi ment 33	Embodi ment 34
Aronix M111	19.6%	22.2%	21.3%	23.7%	21.6%	33.2%	23.7%	30.3%	21.6%	39.2%	39.0%
2EHA	28.2%	16.0%	22.1%	11.4%	10.4%	22.7%	24.6%	20.8%	22.5%	17.6%	17.6%
MEA	0.0%	0.0%	0.0%	19.0%	17.3%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Aronix M5300	19.6%	22.2%	21.3%	23.7%	21.6%	23.7%	23.7%	21.6%	21.6%	24.5%	24.4%

[illegible]

[0054]

[Working examples 35 to 48]

The compositions having the compositions listed in Tables 12 and 13 below were mixed in UV-cut plastic bottles. Each composition was applied by doctor blade to a thickness of 50 μm on a silicone-treated transparent polyester film, and was cured in a UV curing oven (365 nm, UV (365) N₂purge UV irradiation device, Eye Graphics Co., Ltd.). The conditions in the curing oven were 0.5 m/s and 26 mW/cm², and the total dosage of irradiation was 1000 mJ/cm². The curing process was carried out in a nitrogen gas atmosphere (O₂ concentration < 200 ppm). The adhesive composition (pressure-sensitive adhesive) on the PET film obtained thereby was laminated with another silicone-treated PET film.

[Table 12]

Trade Name	Embodi ment 35	Embodi ment 36	Embodi ment 37	Embodi ment 38	Embodi ment 39	Embodi ment 40	Embodi ment 41	Embodi ment 42
Aronix M111	25	25	25	25	25	25	25	25
2EHA	23	23	23	23	23	23	23	23
Aronix M5300	25	25	25	25	25	25	25	25
DMAPMAm	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Darocur TPO	4	4	4	4	4	4	4	4
KHP22J(1.5)	27	27	27	27	27	27	27	27
A200	1	1	1	1	1	1	1	1
HP100	10	10	10	10	10	10	10	10
AMSD	0	0.1	0.25	0.5	0.75	1	1.25	1.5
KP323	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

[0055]

[Table 13]

Trade name	Embodi ment 43	Embodi ment 44	Embodi ment 45	Embodi ment 46	Embodi ment 47	Embodi ment 48
Aronix M111	25	25	25	25	25	40
2EHA	23	23	23	32	32	15.6
Aronix M5300	25	25	25	25	25	20
DMAPMAm	1.5	1.5	1.5	1.5	1.5	0
Darocur TPO	4	4	4	4	4	4
KHP22J	-	-	-	18	18	-
KHP22J(1.5)	27	27	27	-	-	36.4
A200	1	1	1	2	2	1
HP100	10	10	10	10	10	10
AMSD	0.25	0.25	0.25	-	-	0.3
aMSt	-	-	-	0.5	0.5	-
KP323	0.3	0.6	0.9	0.2	0.5	0.3

[0056]

The content (%) of each component and the measurement results are listed in Tables 14 and 15 below.

[Table 14]

Trade name	Embodiment 35	Embodiment 36	Embodiment 37	Embodiment 38	Embodiment 39	Embodiment 40	Embodiment 41	Embodiment 42
Aronix M111	21.4%	21.4%	21.4%	21.3%	21.3%	21.2%	21.2%	21.1%
2EHA	19.7%	19.7%	19.6%	19.6%	19.6%	19.5%	19.5%	19.4%
Aronix M5300	21.4%	21.4%	21.4%	21.3%	21.3%	21.2%	21.2%	21.1%
DMA PMAm	1.3%	1.3%	1.3%	1.3%	1.3%	1.3%	1.3%	1.3%
Darocur TPO	3.4%	3.4%	3.4%	3.4%	3.4%	3.4%	3.4%	3.4%
KHP22J(1.5)	23.1%	23.1%	23.1%	23.0%	23.0%	22.9%	22.9%	22.8%
A200	0.9%	0.9%	0.9%	0.9%	0.9%	0.8%	0.8%	0.8%
HP100	8.6%	8.6%	8.5%	8.5%	8.5%	8.5%	8.5%	8.5%
AMSD	0.0%	0.1%	0.2%	0.4%	0.6%	0.8%	1.1%	1.3%
KP323	0.3%	0.3%	0.3%	0.3%	0.3%	0.3%	0.3%	0.3%
SUS	3.85	5.74	8.12	9.42	12.25	10.29	8.92	7.86
Detachment Strength (N/cm)								
ABS	4.01	4.07	5.57	11.69	10.32	8.26	7.11	6.55
Detachment Strength (N/cm)								
Drop-off (min)	>1440	>1440	>1440	13	4	2	2	2
Slippage(mm)	0	0	0	CF	CF	CF	CF	CF
Screen-printing Suitability	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent

[0057]

[Table 15]

Trade name	Embodiment 43	Embodiment 44	Embodiment 45	Embodiment 46	Embodiment 47	Embodiment 48
Aronix M111	21.4%	21.3%	21.2%	21.2%	21.1%	29.1%
2EHA	19.6%	19.6%	19.5%	27.1%	27.0%	11.3%
Aronix M5300	21.4%	21.3%	21.2%	21.2%	21.1%	14.5%
DMAPMam	1.3%	1.3%	1.3%	1.3%	1.3%	0.0%
Darocur TPO	3.4%	3.4%	3.4%	3.4%	3.4%	2.9%
KHP22J	0.0%	0.0%	0.0%	15.2%	15.2%	0.0%
KHP22J(1.5)	23.1%	23.0%	22.9%	0.0%	0.0%	26.5%
A200	0.9%	0.9%	0.8%	1.7%	1.7%	0.7%
HP100	8.5%	8.5%	8.5%	8.5%	8.4%	7.3%
AMSD	0.2%	0.2%	0.2%	0.0%	0.0%	0.2%
aMSt	0.0%	0.0%	0.0%	0.4%	0.4%	0.0%
KP323	0.3%	0.5%	0.8%	0.2%	0.4%	0.2%
SUS Detachment Strength (N/cm)	8.12	7.02	7.18	6.23	-	6.42
Screen-printing Suitability	Excellent	Excellent	Excellent	Favorable	Excellent	Excellent

[0058]

[Comparative examples 1 to 2]

The compositions having the compositions listed in Table 16 below were mixed in UV-cut plastic bottles. Each composition was applied by doctor blade to a thickness of 50 μm on a silicone-treated transparent polyester film, and was cured in a UV curing oven (365 nm, UV (365) N₂purge UV irradiation device, Eye Graphics Co., Ltd.). The conditions in the curing oven were 0.5 m/s and 26 mW/cm², and the total dosage of irradiation was 1000 mJ/cm². The curing process was carried out in a nitrogen gas atmosphere (O₂ concentration < 200 ppm). The adhesive composition (pressure-sensitive adhesive) on the PET film obtained thereby was laminated with another silicone-treated PET film.

[Table 16]

Trade name	Comparative examples 1	Comparative examples 2
SK-C (Butyl acrylate based acrylyl syrup, Mw800,000, Soken Chemical & Engineering Co., Ltd.)	100	-
ME-3500DR (Butyl acrylate based acrylyl syrup, Mw600,000, Soken Chemical & Engineering Co., Ltd.)	-	18
2EHA	-	88.2
DMAPMam	0.2	0.8
DMA (N,N-Dimethyl acrylamide)	-	4.4

HDDMA (Hexanediol Diacrylate)	0.4	0.48
Irgacure 127	-	1.2
Irgacure 907(2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone · Ciba Specialty Chemical Co., Ltd.)	0.3	-
Irgacure 819	0.3	-
Darocur TPO	-	1.2
Kayacure DETX-S(Light sensitizing agent, Nippon Kayaku Co., Ltd.)	0.06	-
T145 (Tackifier, rosin ester, Arakawa Chemical Industries, Ltd.)	-	30
R972	-	1.44

[0059]

The suitability for screen-printing of the above adhesive compositions (pressure-sensitive adhesives) was measured in the same manner as in the working examples, at which time the suitability for screen-printing was poor in both comparative examples 1 and 2.

[0060]

1: Radiation-cured adhesive composition, 2: Radiation-cured adhesive composition after curing, 10: Mesh body, 12: Holder, 14: Squeegee, 20: Adherend, 30: UV irradiator, 50, 50a, and 50b: adhesive.

What is Claimed is:

1. A radiation-cured adhesive composition comprising: from 10 to 70 wt.% of an ethylenically unsaturated monomer not containing an aromatic ring; from 1 to 10 wt.% of a photopolymerization initiator; and from 10 to 55 wt.% of a crosslinking agent;
the radiation-cured adhesive composition comprising from 10 to 45 wt.% of an alkyl (meth)acrylate having from 8 to 18 carbon atoms in the alkyl group as the ethylenically unsaturated monomer not containing an aromatic ring, and from 10 to 50 wt.% of a urethane poly(meth)acrylate having a weight average molecular weight of 20,000 to 100,000 as the crosslinking agent
2. The radiation-cured adhesive composition according to claim 1, further comprising from 10 to 40 wt.% of an ethylenically unsaturated monomer containing an aromatic ring.
3. The radiation-cured adhesive composition according to claim 1 or 2, wherein the ethylenically unsaturated monomer not containing an aromatic ring is a monomer having a boiling point at or above that of the ethylenically unsaturated monomer containing an aromatic ring.
4. The radiation-cured adhesive composition according to any one of claims 1 to 3, wherein at least one kind of monomer selected from a group including an alkyl (meth)acrylate other than one having from 8 to 18 carbon atoms in the alkyl group, an alkoxyalkyl (meth)acrylate, a (meth)acrylate containing a carboxylic acid, and an ethylenically unsaturated monomer containing an amide group is contained as the ethylenically unsaturated monomer not containing an aromatic ring .
5. The radiation-cured adhesive composition according to any one of claims 1 to 4, wherein the urethane poly(meth)acrylate is a mixture of a urethane di(meth)acrylate and a urethane mono(meth)acrylate, or a urethane di(meth)acrylate, and the weight average molecular weight is from 35,000 to 850,000.
6. The radiation-cured adhesive composition according to any one of claims 2 to 5, wherein the ethylenically unsaturated monomer containing an aromatic ring is at least one kind selected from a group including alkylene glycol mono(alkylaryl) ether mono(meth)acrylate, polyalkylene glycol mono(alkylaryl) ether mono(meth)acrylate, alkylene glycol monoaryl ether mono(meth)acrylate, polyalkylene glycol monoaryl ether mono(meth)acrylate, and aryloxyalkyl mono(meth)acrylate.
7. The radiation-cured adhesive composition according to any one of claims 4 to 6, wherein the ethylenically unsaturated monomer containing an amide group is at least one kind selected from a group including (meth)acrylamide, N-substituted (meth)acrylamide, N,N-substituted (meth)acrylamide, aminoalkyl (meth)acrylamide, N-substituted aminoalkyl (meth)acrylamide,

and N,N-substituted aminoalkyl (meth)acrylamide.

8. The radiation-cured adhesive composition according to any one of claims 1 to 7, further comprising an inorganic or organic thixotropic agent.

9. The radiation-cured adhesive composition according to claims 1 to 8, further comprising a leveling agent.

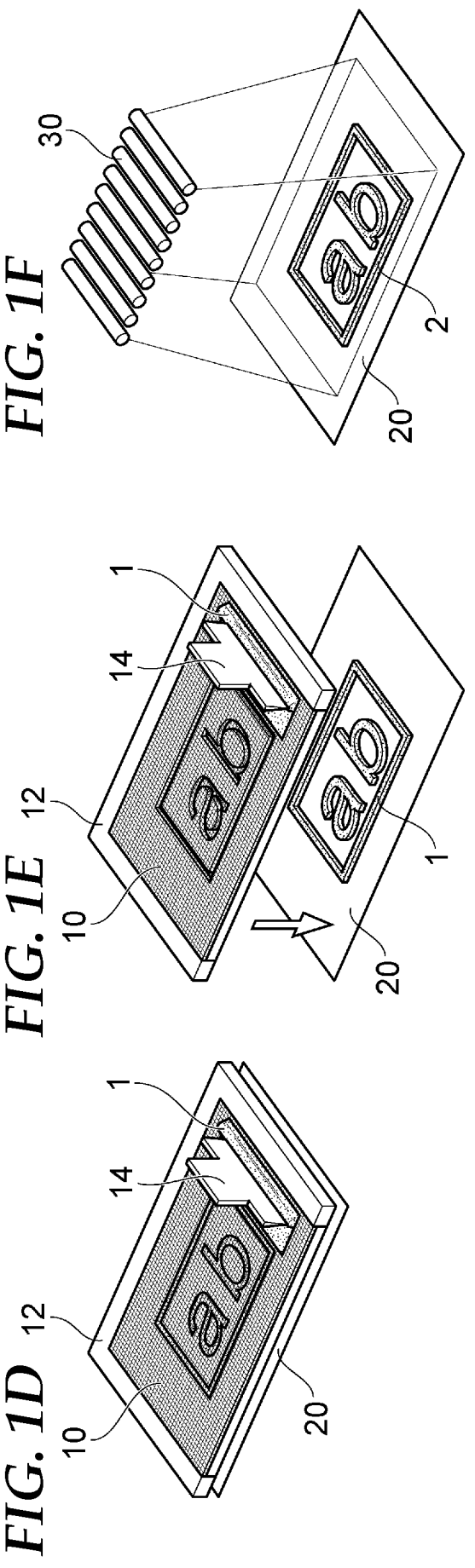
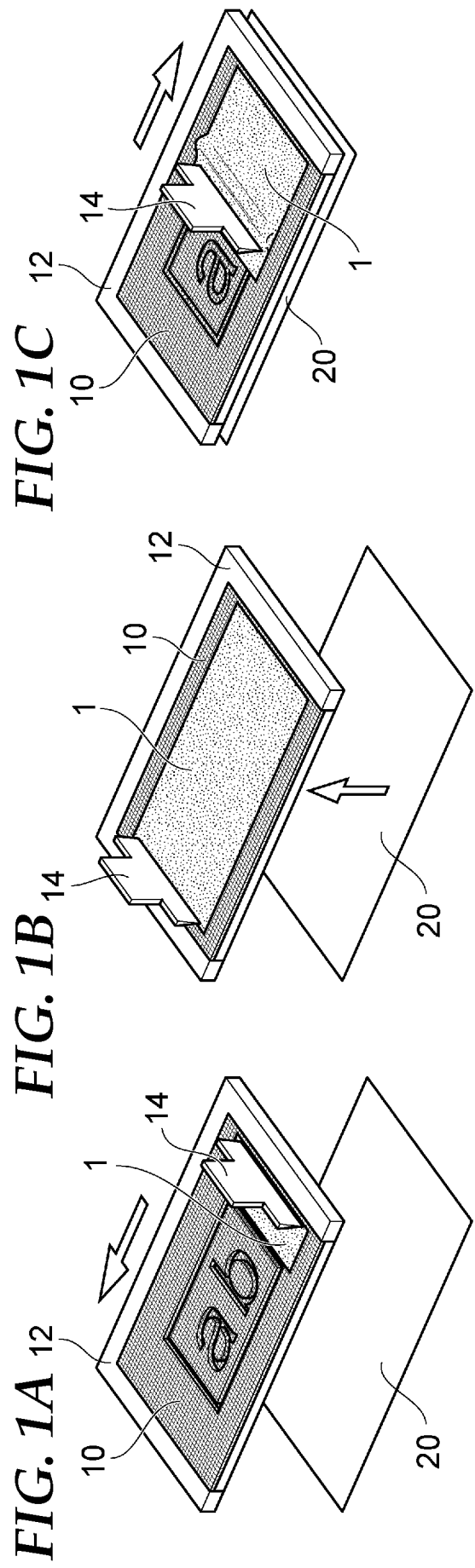
10. The radiation-cured adhesive composition according to any one of claims 1 to 9, wherein curing is performed by UV irradiation in the presence of oxygen.

11. The radiation-cured adhesive composition according to any one of claims 1 to 9, further comprising a polymerization modifier, and wherein curing is performed by UV irradiation at a strength of 20 mW/cm² or higher in the presence of an inert gas.

12. The radiation-cured adhesive composition according to any one of claims 1 to 11, wherein a peeling strength on stainless steel and ABS after curing is 4 N/cm or higher.

13. An adhesive obtained by curing a radiation-cured adhesive according to any one of claims 1 to 12.

14. A laminate, having a layer containing an adhesive according to claim 13 patterned by screen printing on a substrate.



2/2

FIG. 2A

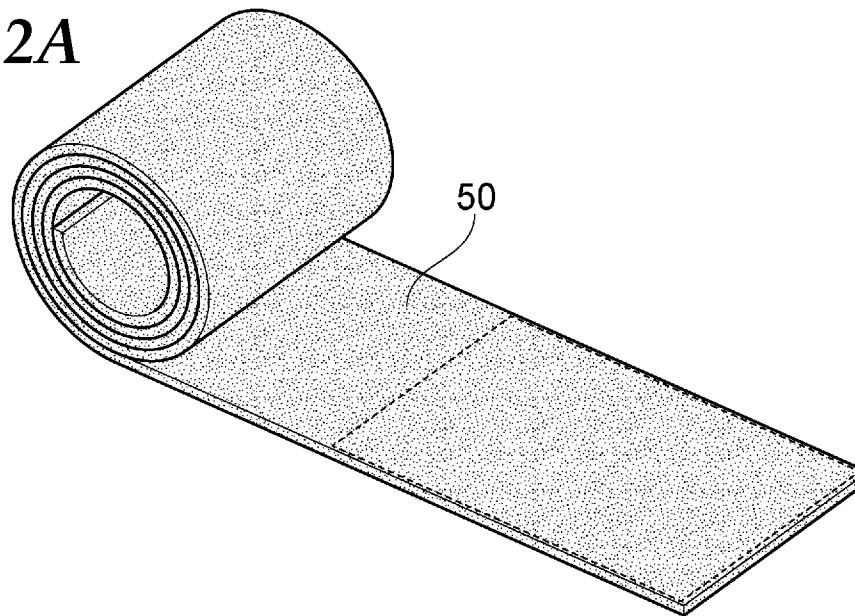


FIG. 2B

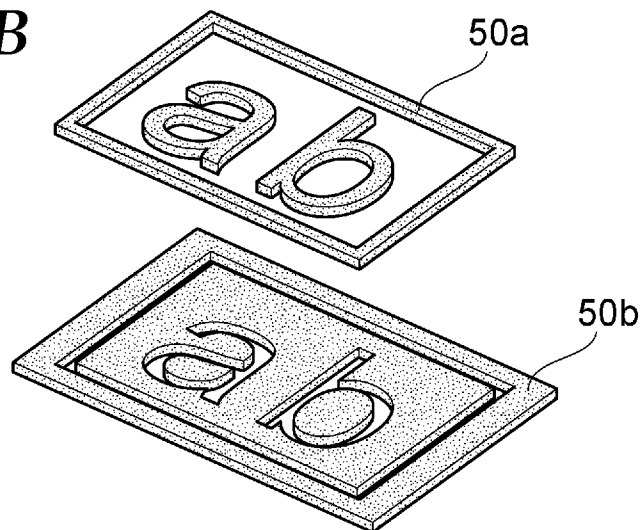
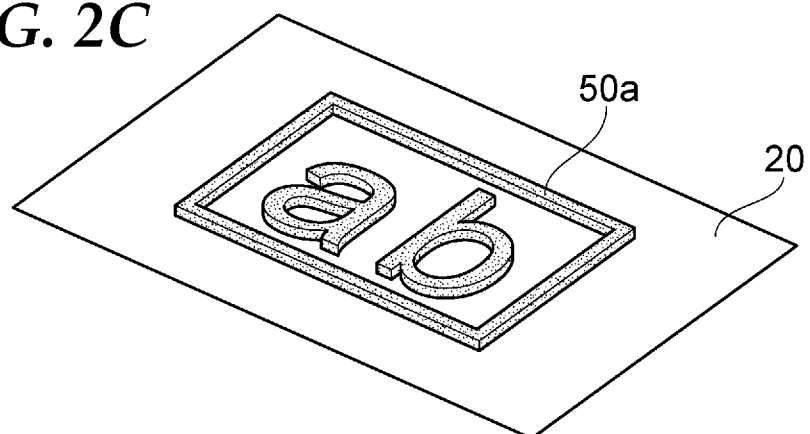


FIG. 2C



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/035357

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09J175/16 C09J7/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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

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	US 2011/070433 A1 (FUJIMOTO HIRONOBU [JP] ET AL) 24 March 2011 (2011-03-24) example 5	1-14
X	US 2006/128856 A1 (TAKAHASHI ATSUYA [JP] ET AL) 15 June 2006 (2006-06-15) claim 1; example synthesis ex.2; table 1	1-14
X	DATABASE WPI Week 199420 Thomson Scientific, London, GB; AN 1994-164188 XP002711175, & JP H06 107993 A (NIPPON KAYAKU KK) 19 April 1994 (1994-04-19) abstract	1-14
A	WO 99/50368 A1 (DSM NV [NL]) 7 October 1999 (1999-10-07)	1-14

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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

"&" document member of the same patent family

Date of the actual completion of the international search

12 August 2013

Date of mailing of the international search report

05/09/2013

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Scheuer, Sylvie

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/035357

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011070433	A1	24-03-2011	JP 5068793 B2 07-11-2012
			JP 2011068727 A 07-04-2011
			KR 20110033048 A 30-03-2011
			TW 201116581 A 16-05-2011
			US 2011070433 A1 24-03-2011

US 2006128856	A1	15-06-2006	AU 2003266675 A1 19-04-2004
			CN 1688623 A 26-10-2005
			JP 2004115757 A 15-04-2004
			KR 20050067162 A 30-06-2005
			US 2006128856 A1 15-06-2006
			WO 2004029115 A1 08-04-2004

JP H06107993	A	19-04-1994	NONE

WO 9950368	A1	07-10-1999	CN 1303422 A 11-07-2001
			EP 1082398 A1 14-03-2001
			JP 2002509977 A 02-04-2002
			TW 530187 B 01-05-2003
			WO 9950368 A1 07-10-1999
