

DESCRIPTION

[Title of invention]

NONE-CROSSLINKABLE ADHESIVE COMPOSITION AND ADHESIVE SHEET

5

[Technical Field]

[0001]

10 The present invention relates to an adhesive sheet attached to optical members such as a polarizing plate and a liquid crystal panel, a glass substrate for display, etc. and electronic parts such as a semiconductor wafer, a semiconductor package, etc. to be used to protect these members and parts from being scratched, damaged and contaminated when conveying and processing these members and parts.

15

[Background Art]

[0002]

20 It is commonly performed to attach adhesive sheets to optical members and electronic parts in order to protect these members and parts from being scratched, damaged and contaminated when conveying and processing these members and parts. In these optical members and electronic parts, each acting as an adherend, there are such various surface conditions as to vary from smooth ones to rough ones, and nevertheless the adhesive sheet must be attached properly to these surfaces. At the end of conveying and processing works thereof, however, this adhesive sheet must unstick without leaving any adhesive agent on the adherend.

25

[0003]

30 As a surface protection sheet for a wide variety of members, a surface protection sheet excellent in resistance to time-dependent adhesive force degradation is reported (see the patent document 1). The surface protection sheet described in the patent document 1, however, has a problem that its adhesive agent is hard and therefore it is impossible to achieve a proper adhesion condition to a rough-surfaced adherend.

[0004]

35 Further, as an adhesive sheet used at the time of processing a silicon wafer, an adhesive sheet with an excellent pickup property is reported (see the patent document 2). This adhesive sheet described in the patent document 2, however, contains low-molecular components, and hence such troubles occur that chips unstick from the adhesive sheet during dicing the silicon wafer and fly apart, and contaminating objects attributable to the adhesive agent remain on the silicon

wafer in some cases.

[Citation List]

[Patent Literature]

[0005]

5 [Patent Literature 1] Japanese unexamined patent application publication
No. 2010-42580

[Patent Literature 2] Japanese unexamined patent application publication
No. 2008-60434

10 [Summary]

[Technical Problem]

[0006]

15 The present disclosure has been made to solve the above-mentioned
conventional problems and therefore it is an object of the embodiments disclosed
herein to provide an adhesive sheet which can stick properly to both smooth
surfaces and rough surfaces of optical members, electronic parts, etc. with its
adhesiveness unchanged thereto and whose adhesive agent does not remain on an
adherend at the time of being unstuck therefrom.

20 [Solution to Problem]

[0007]

The following embodiments are provided to achieve the above-mentioned
purpose.

25 (1) A non-crosslinkable adhesive composition having a weight average molecular
weight ranging from 700,000 to 2,000,000, a molecular weight distribution less
than or equal to 5; and a (meth)acrylic acid ester copolymer containing no
functional group reacting with isocyanate-based curing agent or epoxy-based
curing agent included as a main component.

30 (2) The non-crosslinkable adhesive composition, described in (1), characterized in
that the above-mentioned functional group reacting with the isocyanate-based
curing agent or the epoxy-based curing agent is a carboxyl group or a hydroxyl
group.

35 (3) An adhesive sheet in which the non-crosslinkable adhesive composition
described in (1) or (2) is stacked on at least one surface of a base material film
and whose adhesive force (A1) to an adherend with surface roughness $R_z=5\mu\text{m}$
and adhesive force (A2) to an adherend with surface roughness $R_z=0.5\mu\text{m}$
satisfy the following relationship.

$$A1/A2=0.8 \text{ to } 1.2$$

[0007a]

In an aspect, there is provided a non-crosslinkable adhesive composition comprising:

a weight average molecular weight ranging from 700,000 to 2,000,000, and

a molecular weight distribution ranging from 2.5 to 4,

wherein a (meth)acrylic acid ester copolymer not containing a carboxylic group or a hydroxyl group that are a functional group reacting with an isocyanate-based curing agent, and an isocyanate curing agent are at least included.

[0007b]

In another aspect, there is provided an adhesive sheet in which the non-crosslinkable adhesive composition as defined above is stacked on at least one surface of a base material film, wherein adhesive force (A1) to a SUS 304 steel plate (1.5mm to 2.0mm thick) ground so that its surface roughness Rz becomes $5\mu\text{m}$ and adhesive force (A2) to a SUS 304 steel plate (1.5mm to 2.0mm thick) ground so that its surface roughness Rz becomes $0.5\mu\text{m}$ satisfy the following relationship: $A1/A2=0.8$ to 1.2 .

[Advantageous Effect]

[0008]

By using the adhesive sheet according to the present disclosure, the adhesiveness of the adhesive sheet becomes unchanged regardless of a degree of the surface roughness of an adherend and the adhesive sheet becomes able to unstick without leaving the adhesive agent on the adherend.

[Brief Description of Drawings]

[0009]

Fig. 1 is a cross-sectional view showing an adhesive sheet 1 according to present embodiments.

[Description of Embodiments]

[0010]

Hereunder is a detailed description on embodiments of the present invention based on the drawings.

Fig. 1 is a cross-sectional view showing an adhesive sheet 1 according to the present embodiments. The adhesive sheet 1 includes a base material film 3, a non-crosslinkable adhesive composition layer 5 provided on the base material film 3. A structure of each layer is described below.

[0011]

<Base Material Film>

The base material film is not particularly limited and any one can be arbitrarily selected from heretofore known resin films to be able to use. Specifically, the following materials can be cited for use: for example, polyethylene, 5 polypropylene; ethylene-polypropylene copolymer; and polyolefin like polybutene; ethylene-vinyl acetate copolymer, ethylene copolymer like ethylene(meth)acrylic acid copolymer and ethylene (meth)acrylic acid ester copolymer; engineering plastic such as polyethylene terephthalate, polybutylene terephthalate, polycarbonate, polymethacrylic acid methyl; soft polyvinyl chloride; half hard 10 polyvinyl chloride; polyester; polyurethane; polyamide; polyimide; and a high-polymer material such as natural rubber and synthetic rubber. Further, a film produced by mixing or multi-layering two or more materials selected from the above group may be used as the base material film. Any of materials can be arbitrarily selected from the above group depending on its adherence property to 15 the adhesive composition.

[0012]

The thickness of the above-mentioned base material film is not particularly limited and can be arbitrarily determined according to a purpose of use. Generally, the thickness is 30 to 500 μ m and preferably 50 to 200 μ m.

[0013]

5 <None-crosslinkable Adhesive Composition>

The none-crosslinkable adhesive composition stacked on the surface of the base material film ranges from 700,000 to 2,000,000 in weight average molecular weight and is 5 or less in molecular weight distribution, and includes, as a main component, a (meth)acrylic acid ester copolymer containing no functional group reacting with an isocyanate-based curing agent or an epoxy-based curing agent. In addition, "(meth)acryl" means acryl and/or methacryl. Further, "main component" means that a ratio of (meth)acrylic acid ester copolymer in the none-crosslinkable adhesive composition is 50 to 100% by mass and the ratio is preferably 80 to 100% by mass.

15 [0014]

As a monomer component for constituting the (meth)acrylic acid ester copolymer according to the present embodiment, the following components are cited for use: for example, (meth)acrylic acid alkyl ester such as (meth)acrylic acid methyl, (meth)acrylic acid ethyl, (meth)acrylic acid propyl, (meth)acrylic acid isopropyl, (meth)acrylic acid butyl, (meth)acrylic acid isobutyl, (meth)acrylic acid s-butyl, (meth)acrylic acid t-butyl, (meth)acrylic acid pentyl, (meth)acrylic acid hexyl, (meth)acrylic acid heptyl, (meth)acrylic acid octyl, (meth)acrylic acid isooctyl, (meth)acrylic acid 2-ethylhexyl, (meth)acrylic acid nonyl, (meth)acrylic acid isononyl, (meth)acrylic acid decyl, (meth)acrylic acid isodecyl, (meth)acrylic acid undecyl, (meth)acrylic acid dodecyl, (meth)acrylic acid tridecyl, (meth)acrylic acid tetradecyl, (meth)acrylic acid pentadecyl, (meth)acrylic acid hexadecyl, (meth)acrylic acid heptadecyl, and (meth)acrylic acid octadecyl; and (meth)acrylic acid cycloalkyl ester such as (meth)acrylic acid cyclohexyl, etc.; (meth)acrylic acid allyl ester such as (meth)acrylic acid phenyl, etc.; (meth)acrylic acid alkoxy alkyl such as (meth)acrylic acid methoxy ethyl and (meth)acrylic acid ethoxy ethyl; and a nitrile-based monomer such as acrylonitrile and methacrylonitrile. The (meta)acrylic acid ester can be singularly used, or two or more ones are combined to be able to use.

[0015]

35 The (meth)acrylic acid ester copolymer according to the present embodiment contains no functional group reacting with the isocyanate-based curing agent or the epoxy-based curing agent, and therefore can be polymerized without using a carboxyl group-containing monomer such as the (meth)acrylic acid,

etc., and a hydroxyl group-containing monomer such as (meth)acrylic acid-2-hydroxyethyl, (meth)acrylic acid-2-hydroxypropyl, (meth)acrylic acid-4-hydroxybutyl, (meth)acrylic acid-6-hydroxyhexyl, (meth)acrylic acid-8-hydroxyoctyl, (meth)acrylic acid-10-hydroxydecyl, and (meth)acrylic acid-12-hydroxylauryl. That is, this means that the (meta)acrylic acid ester copolymer according to the present embodiment is 0.1mgKOH/g or less in acid value (see JIS K0070 Neutralizing Titration Method), and is 0.1mgKOH/g or less in hydroxyl value (see JIS K0070 Neutralizing Titration Method).

[0016]

As the isocyanate curing agent, the following materials are cited for use: for example, an isocyanate monomer; such as tolylenediisocyanate, chlorophenylenediisocyanate, hexamethylene diisocyanate, tetramethylenediisocyanate, isophoronediiisocyanate, xylylenediisocyanate, diphenylmethane diisocyanate, and hydrogenated diphenylmethane diisocyanate; and an adduct-based isocyanate compound produced by adding an isocyanate monomer to trimethylolpropane, etc.; and an isocyanurate compound, and a burrete-type compound, and further an urethane prepolymer-type isocyanate produced by applying an addition reaction to heretofore known polyetherpolyol and polyesterpolyol, acrylicpolyol, and polybutadienepolyol, and polyisoplanepolyol.

[0017]

As the epoxy-based curing agent, the following materials are cited for use: for example, ethylene glycol diglycidyl ether; polyethylene glycol diglycidyl ether; glycerin diglycidyl ether; glycerin tridiglycidyl ether; 1, 6-hexysanedior diglycidyl ether; trimethyl propane triglycidyl ether; diglycidyl aniline; N, N, N, N'-tetraglycidyl-m-xylylene diamine; 1, 3-Bis(N, N-diglycidyl aminemethyl); cyclohexane; N, N, N, N'-tetraglycidyl aminopheny methane; triglycidyl isocyanurate; m-N, N-diglycidyl aminophenylglycidyl ether; N, N-diglycidyltoluidine; and N, N-diglycidylaniline.

[0018]

The (meth)acrylic acid ester copolymer according to the present embodiment ranges from 700,000 to 2,000,000 and more preferably ranges from 1,000,000 to 1,500,000 in weight average molecular weight (Mw). When the weight average molecular weight is under 700,000, an adhesive agent remains on an adherend in some cases at the time of unsticking the adhesive sheet 1, while when the weight average molecular weight exceeds 2,000,000 the adhesiveness of the adhesive sheet 1 remarkably lowers in relation to a rough-surfaced adherend, and thus the adhesiveness changes depending on the surface roughness of the adherend.

[0019]

Further, the (meth)acrylic acid ester copolymer according to the present embodiment is 5 or less and desirably ranges from 2.5 to 4 in molecular weight distribution. Here, the molecular weight distribution means a value obtained by dividing the weight average molecular weight (Mw) by a number average molecular weight (Mn). When the molecular weight distribution exceeds 5, the contribution of low-molecular components to the adhesiveness increases to cause the adhesive agent to remain on the adherend in some cases and further the adhesiveness changes depending on the surface roughness of the adherend. Though the molecular weight distribution can be reduced by a polymerization method, a polymerization condition and refinement of polymers, the production cost rises. Hence, the molecular weight distribution is preferably 2.5 or more in consideration of the cost rise. In addition, the weight average molecular weight (Mw) and the number average molecular weight (Mn) are expressed in terms of polystyrene measured by the gel permeation chromatography (GPC).

[0020]

A method for manufacturing the (meth)acrylic acid ester copolymer according to the present embodiment can be realized by the heretofore known methods. For example, a radical polymerization method such as a solution polymerization method, a suspension polymerization method, a block polymerization method, a precipitation polymerization method, and an emulsion polymerization method can be arbitrarily selected. Among these polymerization methods, the emulsion polymerization method is more desirable since a polymer which is high in molecular weight and is narrow in molecular weight distribution can be manufactured. As a radical polymerization initiator, various types of heretofore known ones such as azo-based and hydrogen peroxide-based ones can be used.

[0021]

Along with the (meth)acrylic acid ester copolymer acting as the main component of the non-crosslinkable adhesive composition, an arbitrary and appropriate additive agent may be contained without departing from the purpose of the present invention. The following agents are cited: for example, an ultraviolet curable resin, a photopolymerization initiator, an ultraviolet absorber, a tackifier, a curing agent, a plasticizer, an antioxidant, an antistatic, a polymerization inhibitor, a silane coupling agent, and an organic or inorganic filler.

[0022]

The above ultraviolet curable resin is used when curing the non-crosslinkable adhesive composition by radiating ultraviolet rays thereto to

make it easy to unstick the non-crosslinkable adhesive composition. The ultraviolet curable resin is not particularly limited and the following materials are cited for use: for example, urethane (meth)acrylate, epoxy (meth)acrylate, polyester (meth)acrylate, and polyether (meth)acrylate.

5 [0023]

In curing the non-crosslinkable adhesive composition according to the present invention by radiating ultraviolet rays thereto, the photopolymerization initiator is added. The photopolymerization initiator is not particularly limited. The following materials are cited for use: for example, isopropyl benzoin ether, isobutyl
10 benzoin ether, benzophenone, Michler's ketone, chlorothioxanthene, dodecylthioxanthene, dimethylthioxanthene, diethylthioxanthene, benzyldimethyl ketanol, α -hydroxycyclohexyl phenylketone, 2-hydroxyl methylphenyl propane, etc..

[0024]

15 Further, the non-crosslinkable adhesive composition according to the present invention is stacked on at least one surface of the base material film to be able to be used as an adhesive sheet. Then, an adhesive force (A1) of the adhesive sheet to an adherend with surface roughness $R_z=5.0\mu\text{m}$ and an adhesive force (A2) of the adhesive sheet to an adherend with surface roughness $R_z=0.5\mu\text{m}$ desirably
20 satisfy the following relationship.

$$A1/A2=0.8 \text{ to } 1.2$$

By satisfying the above formula, the adhesive sheet can obtain a proper adhesiveness irrespective of the surface roughness of the adherend.

[0025]

25 The thickness of the non-crosslinkable adhesive composition can be arbitrarily determined depending on an intended use and the adhesiveness required. Generally, the thickness is 1 to $300\mu\text{m}$ and preferably 3 to $50\mu\text{m}$.

[0026]

<Method for Manufacturing Adhesive Sheet>

30 A method for manufacturing the adhesive sheet is not particularly limited and can be selected from the heretofore known coating methods. The following methods are cited for use: for example, a roll coating method such as a reverse coating one and a gravure coating one, a spin coating one, a screen coating one, a fountain coating one, a dipping one, and a spray one. After applying a solution of
35 the non-crosslinkable adhesive composition, a non-crosslinkable adhesive composition layer with a given thickness can be obtained by volatilizing a solvent and water in a drying process. Further, the non-crosslinkable adhesive composition may be applied directly to an upper surface of the base material film, and

furthermore after applying the non-crosslinkable adhesive composition to an upper surface of a release sheet, the non-crosslinkable adhesive composition thus applied may be transcribed onto the base material film.

[0027]

5 (Effects of Present Embodiment)

By using the adhesive sheet according to the present embodiment, a proper adhesion condition can be obtained with the adhesiveness unchanged to both smooth surfaces and rough surfaces of the optical members, electronic parts, etc..

[0028]

10 Moreover, by using the adhesive sheet according to the present embodiment, the adhesive sheet can be unstuck without leaving the adhesive agent on an adherend.

[Embodiment]

[0029]

15 Next is a detailed description on embodiments and comparative examples in order to further clarify effects resulting from the present embodiments. The present invention, however, is not limited to these embodiments and comparative examples.

[0030]

20 <Embodiment 1>

[Manufacturing of Non-crosslinkable Adhesive Composition]

(1) Preparation of Acrylic Acid Ester Copolymer

Water, ethyl acrylate, butyl acrylate, acrylonitrile, and sodium lauryl sulfate as an emulsifying agent were prepared in a polymerization reactor
25 equipped with a thermometer and a stirring device. Then, depressurization, deaeration and nitrogen substitution were performed twice to remove sufficiently oxygen. Thereafter, cumene hydroperoxide and sodium formaldehyde sulfoxylate were added, and under ordinary pressure and at 30 degrees C, the emulsion polymerization was initiated to allow its reaction to continue till its polymerization
30 conversion ratio reached 95%. The emulsion polymerization solution thus obtained was fixed by a calcium chloride solution and after performing water washing and drying, the acrylic acid ester copolymer having a weight average molecular weight of 700,000 and a molecular weight distribution (Mw/Mn) of 2.5 was obtained. A monomer component of the acrylic acid ester copolymer in the
35 embodiment 1 is acrylic acid ethyl, acrylic acid butyl and acrylonitrile, and hence is described as EA/BA/AN in a Table 1.

[0031]

(2) Measurements of Weight Average Molecular Weight and Molecular Weight

Distribution

The measurements were carried out under the following conditions in CPC (Gel Permeation Chromatography).

Analyzing Device: HLC—8120GPC made by TOSOH Corporation

5 Column: G7000HXL+GMHXL+GMHXL made by TOSOH Corporation

Column Size: 7.8mmφ, 30cm long in each one and a total length=90cm long

Column Temperature: 40 degrees C

Flow Rate: 0.8ml/min.

Injection Volume: 100μl

10 Eluting Solution: Tetrahydrofuran

Detector: Differential Refractometer

Standard Sample: Polystyrene

[0032]

[Production of Adhesive Sheet]

15 The acrylic acid ester copolymers thus obtained was dissolved by ethyl acetate, and then the non-crosslinkable adhesive composition, with which 1pts. wt. of a curing agent (CORONATE L made by Nippon Polyurethane Industry Co., Ltd.) was combined based on 100 pts. wt. of the acrylic acid ester copolymer, was applied to an upper surface of a base material film (Lumirror U34 made by Toray
20 Industries Inc.) 100μm thick so that the non-crosslinkable adhesive composition become 10μm thick, and thus the adhesive sheet was formed.

[0033]

<Embodiments 2 to 5, Comparative Examples 1 to 4>

For the embodiment 1, the monomer component used to manufacture the
25 acrylic acid ester copolymer was changed as shown in the Table 1. Further, the polymerization condition was changed so that the weight average molecular weight (Mw) and molecular weight distribution (Mw/Mn) of the acrylic acid ester copolymer thus obtained became those shown in the Table 1. The adhesive composition and the adhesive sheet were made in the same way as was done in the
30 embodiment1 including the curing agent except these changes.

[0034]

A result obtained by performing the following evaluations with respect to the adhesive sheets thus obtained in the above-mentioned embodiments and comparative examples is shown in the Table 1.

35 [0035]

(Method for Measuring Acid Value)

The measurements were performed by a neutralization titration method pursuant to JISK0070 as shown below. First, a sample was measured to be taken

into a conical flask. Next, 100ml of acetone and a few drops of a phenolphthalein solution acting as the indicator were added into the flask and then the solution thus made was sufficiently shaken up until the sample was completely dissolved on the solution. Then, the titration was carried out by 0.1mol/l of potassium hydroxide ethanol-solution, and was terminated when a faint showy pink of the indicator visibly continued for 30 seconds. Then, the acid value was calculated by the following formula.

$$A=B*f*5.611/S$$

Formula (1)

where, in the Formula (1), A denotes an acid value (mgKOH/g), B denotes a volume (ml) of 0.1mol/l of the potassium hydroxide ethanol-solution used for the titration, f denotes a factor (concentration compensation coefficient) of 0.1mol/l of the potassium hydroxide ethanol-solution, and S denotes a mass (g) of the sample. [0036]

(Method for Measuring Hydroxyl Value)

The measurement was performed by the neutralization titration method pursuant to JISK0070 as shown below. First, 25g of acetic acid anhydride was taken in a volumetric flask having 100ml capacity, and pyridine was added therein to make the total volume into 100ml, and then the solution was sufficiently shaken up to prepare an acetylating reagent. The acetylating reagent was prevented from contacting with moisture, carbon dioxide, and acid vapor, to be stored in a brown bottle. Next, the sample was measured to be taken in a flat-bottomed flask and 5ml of the acetylating reagent was added thereto using a volumetric pipette. Next, a small infundibulum was put on a mouth of the flask, and an about 1cm bottom portion of the flat-bottomed flask was immersed in a glyceric liquid at 95 to 100 degrees C to be heated. In order to prevent a neck of the flask from increasing in temperature by receiving the heat of the glyceric liquid, a root of the neck of the flask was covered with a cardboard disk in which a round hole was made. Then, an hour later, the flask was taken out of the glyceric liquid and after allowing the flask to cool, 1ml of water was added from the infundibulum, and the flask was shaken up to dissolve the acetic acid anhydride. Further, in order to dissolve perfectly the acetic acid anhydride, the flask was again immersed in the glyceric liquid to be heated for 10 minutes, and then after allowing the flask to cool, walls of the infundibulum and flask were washed by 5ml of ethanol. A few drops of a phenolphthalein solution were added as the indicator into the flask. Then, the titration was carried out by 0.5mol/l of the potassium hydroxide ethanol-solution to be terminated when a faint showy pink of the indicator had continued for 30 seconds. A blank test was practiced without putting the sample as was done in the above. Then, the hydroxyl value was calculated by the following formula.

$$A=((B-C)*f*28.05/S)+D \quad \text{Formula (2)}$$

where, in the Formula (2), A denotes a hydroxyl value (mgKOH/g), B denotes a volume (ml) of 0.5mol/l of the potassium hydroxide ethanol-solution used in the blank test, C denotes a volume (ml) of 0.5mol/l of the potassium hydroxide ethanol-solution used for the titration, f denotes a factor (concentration compensation coefficient) of 0.5mol/l of the potassium hydroxide ethanol-solution, S denotes a mass (g) of the sample, and D denotes the acid value (mgKOH/g).

[0037]

(Method for Measuring Adhesive Force)

- 10 (1) Adhesive force (A1) to an adherend with surface roughness $R_z=5\mu\text{m}$

Three test pieces, each 25mm wide and 300mm long, were adopted from each adhesive sheet, and after adhering the three test pieces to an upper surface of a SUS 304 plate (1.5 to 2.0mm thick) ground so that its surface roughness R_z became $5\mu\text{m}$, a rubber roller of 2kg was moved on the surface of each test piece three times from one end to the other and thereby the test pieces were allowed to be subjected to pressurized adhesibility to the surface of the SUS plate. Then, after leaving the test pieces for 1 hour, the adhesive force of each of the test pieces was measured using a tensile testing machine which had such a capacity that the measurement values of the test pieces fell within 15 to 85% of the capacity, and was in accordance with JIS B7721. An unsticking angle and unsticking speed of each test piece were determined as 180 degrees and 300mm/min., respectively. The measurement environment was regulated at 23 degrees C and 50%RH.

[0038]

- 25 (2) Adhesive force (A2) to an adherend with surface roughness $R_z=0.5\mu\text{m}$

Three test pieces, each 25mm wide and 300mm long, were adopted from each adhesive sheet, and after adhering the three test pieces to an upper surface of a SUS 304 plate (1.5 to 2.0mm thick) ground so that its surface roughness R_z became $0.5\mu\text{m}$, a rubber roller of 2kg was moved on the surface of each test piece three times from one end to the other and thereby the test pieces were allowed to be subjected to pressurized adhesibility to the surface of the SUS plate. Then, after leaving the test pieces for 1 hour, the adhesive force of each of the test pieces was measured using a tensile testing machine which was in accordance with JIS B7721 and had such a capacity that the measurement values of the test pieces fell within 15 to 85% of the capacity. The unsticking angle and unsticking speed of each test piece were determined as 180 degrees and 300mm/min., respectively. The measurement environment was regulated at 23 degrees C and at 50%RH

[0039]

(Method for Evaluating Selectivity for Adherend)

When the adhesive forces A1 and A2 measured as described above satisfied the relationship $A1/A2=0.8$ to 1.2 , a mark O was placed, while when not satisfying the relationship, a mark X was placed.

[0040]

5 (Method for Evaluating Adhesive Agent Remaining on Adherend)

When the above adhesive forces of A1 and A2 were measured, the presence or absence of the adhesive agent remaining on the SUS plate after unsticking the tapes was visually evaluated. In the case of the absence of the adhesive agent, a mark O was placed, while in the case of the presence thereof, a mark X was placed.

10 [0041]

[Table 1]

	Embodiment 1	Embodiment 2	Embodiment 3	Embodiment 4	Embodiment 5	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Monomer Component	EA/BA/AN	EA/BA/AN	EA/BA/MEA	EA/BA/MEA	BA/AN	EA/BA/AN	EA/BA/AN	EA/BA/AN	BA/AN/2HEA
Weight Average Molecular Weight (Mw)	700,000	2,000,000	1,000,000	1,200,000	1,500,000	500,000	2,100,000	1,200,000	1,200,000
Molecular Weight Distribution (Mw/Mn)	2.8	5.0	2.5	4.0	4.0	2.6	4.2	6.0	4.0
A1 (Rough Surface)	2.5	2.1	2.2	2.2	2.4	2.6	1.9	2.4	1.1
A2 (Smooth Surface)	2.1	2.6	2	2	2.6	2.2	2.7	1.9	1.9
A1/A2	1.19	0.81	1.10	1.10	0.92	1.18	0.70	1.26	0.58
Selectivity for Adherend	O	O	O	O	O	O	X	X	X
Remaining Adhesive Agent on Adherend	O	O	O	O	O	X	O	X	O

where EA denotes acrylic acid ethyl, BA denotes acrylic acid butyl, AN denotes acrylonitrile, MEA denotes acrylic acid 2-methoxyethyl, 2HEA denotes acrylic acid 2-hydroxyethyl

15 [0042]

The acrylic acid ester copolymers according to the embodiments 1 to 5 and the comparative examples 1 to 3 were 0.1mgKOH/g or less in acid value and were also 0.1mgKOH/g or less in hydroxyl value. The acrylic acid ester copolymer according to the comparative example 4 contains a hydroxyl group as a functional group reacting with the isocyanate-based curing agent or the epoxy-based curing agent, and was 5.0mgKOH/g in hydroxyl value.

[0043]

Moreover, according to the Table 1, the adhesive sheets (in the embodiments 1 to 5); in which the non-crosslinkable adhesive composition, that is in the range from 700,000 to 2,000,000 in weight average molecular weight and is 5 or less in molecular weight distribution and includes, as a main component, (meth)acrylic acid ester copolymer containing no functional group reacting with the isocyanate-based curing agent or the epoxy-based curing agent, was stacked on one surface of the base material film; properly adhered even to adherends different in surface roughness and left no adhesive agent on the adherends at the time of unsticking.

30

[0044]

On the other hand, in the case (the comparative example 1) where the acrylic acid ester copolymer was 500,000 in weight average molecular weight, though the selectivity for adherend was proper, the adhesive agent was observed to remain on the adherend. This can be understood in such a manner that since the
5 molecular weight was low, the low molecular component remained thereon.

[0045]

Further, in the case (the comparative example 2) where the acrylic acid ester copolymer was 2,100,000 in weight average molecular weight, though no remaining adhesive agent was observed, the selectivity for adherend degraded.
10 This can be understood in such a manner that since the molecular weight was high, the adhesiveness to a rough surface degraded.

[0046]

Moreover, in the case (the comparative example 3) where the acrylic acid ester copolymer was 6 in molecular weight distribution, the selectivity for
15 adherend degraded and a remaining adhesive agent was observed. This can be understood in such a manner that the low molecular component of the non-crosslinkable adhesive composition resulted in adverse effect.

[0047]

Furthermore, in the case (the comparative example 4) where the acrylic
20 acid 2-hydroxyethyl was used as the monomer component of the acrylic acid ester copolymer, and a hydroxyl group was contained as the functional group reacting with the isocyanate-based curing agent or the epoxy-based curing agent, though no remaining adhesive agent was observed, the selectivity for adherend degraded. This can be understood in such a manner that a cross-linking reaction with the
25 curing agent advanced and thereby the adhesiveness to a rough surface remarkably degraded.

[0048]

As described above, the preferred embodiments according to the present invention have been described with reference to the accompanying drawings. The
30 present invention, however, is not limited to these embodiments. It is obvious that those skilled in the art can make various altered embodiments and modifications within the scope of the technical thought disclosed in the present application. Therefore, even these altered embodiments and modifications can be obviously considered to belong to the technical range of the present invention

[Reference Signs List]

[0049]

1adhesive sheet

3····base material film

5····non-crosslinkable adhesive composition layer

Claims:

Claim 1. A non-crosslinkable adhesive composition comprising:
a weight average molecular weight ranging from 700,000 to 2,000,000, and
5 a molecular weight distribution ranging from 2.5 to 4,
wherein a (meth)acrylic acid ester copolymer not containing a carboxylic group or a
hydroxyl group that are a functional group reacting with an isocyanate-based
curing agent, and an isocyanate curing agent are at least included.

10

Claim 2. An adhesive sheet in which the non-crosslinkable adhesive
composition according to claim 1 is stacked on at least one surface of a base
material film, wherein adhesive force (A1) to a SUS 304 steel plate (1.5mm to
2.0mm thick) ground so that its surface roughness Rz becomes $5\mu\text{m}$ and adhesive
15 force (A2) to a SUS 304 steel plate (1.5mm to 2.0mm thick) ground so that its
surface roughness Rz becomes $0.5\mu\text{m}$ satisfy the following relationship:

$$A1/A2=0.8 \text{ to } 1.2.$$

Abstract

An adhesive sheet 1 is used in which a non-crosslinkable adhesive composition layer 5 is provided on a base material film 3 and ranges from 700,000 to 2,000,000 in weight average molecular weight and 5 in molecular weight distribution, and a (meth)acrylic acid ester copolymer containing no functional group reacting with an isocyanate-based curing agent or an epoxy-based curing agent is included as a main component of the composition. The above functional group reacting with an isocyanate-based curing agent or an epoxy-based curing agent may be a carboxyl group or a hydroxyl group.

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