

NOVEL HYDRAZIDE COMPOUND AND RESIN COMPOSITION USING SAME

TECHNICAL FIELD

The present invention relates to a novel hydrazide compound. More especially, the present invention relates to a hydrazide compound having a decahydronaphthalene (bicyclo[4.4.0]decane) skeleton, and proposes a resin composition mainly used as an adhesive and a liquid crystal sealant using this compound.

BACKGROUND ART

Hydrazide compounds have been conventionally used as useful materials, such as epoxy resin curing agents, formaldehyde adsorbers, polymer crosslinking agents, polymer-modified adhesives, slime control agents, and as raw materials for hydrazide polymers. Specifically, hydrazide compounds are frequently used in latent curing agents for heat-curable resins, such as epoxy resins and acrylic resins which are widely used in the fields of coating materials, adhesives and the like, in crosslinking agents for ketone group-containing acrylic emulsions, and the like. The reasons for this are considered to be that (1) hydrazide compounds have high reactivity and thus can be cured at low temperatures, (2) hydrazide compounds have excellent storage stability and thus can be stored as a one pack type at an ordinary temperature, (3) their curing temperatures and curing times can be adjusted by their skeletons, and (4) cured products thereof have high

glass transition temperatures, and the like. Furthermore, hydrazide compounds react not only with epoxy resins but also with acrylic resins by the Michael addition reaction, and thus are very fine curing agents also in mixed resin compositions of epoxy resins and acrylic resins.

For the above-mentioned reasons, hydrazide compounds are frequently used in resin compositions for use in adhesives, and hydrazide compounds having various skeletons and adhesives using the compounds have been proposed (Patent Documents 1 to 5).

Patent Document 1: Japanese Unexamined Patent Application, Publication No. S58-96074

Patent Document 2: Japanese Unexamined Patent Application, Publication No. H6-80619

Patent Document 3: Japanese Unexamined Patent Application, Publication No. 11-43473

Patent Document 4: Japanese Unexamined Patent Application, Publication No. 2002-371069

Patent Document 5: Japanese Unexamined Patent Application, Publication No. 2006-316142

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

The present invention proposes a novel hydrazide compound in view of the above-mentioned circumstances. Specifically, the present invention relates to a hydrazide compound having a decahydronaphthalene (bicyclo[4.4.0]decane) skeleton, and also

proposes a resin composition mainly used as an adhesive using this compound.

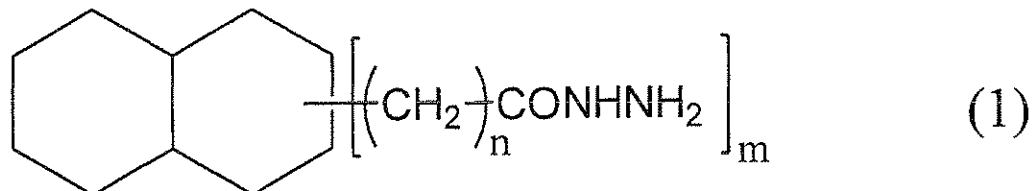
Means for Solving the Problems

The present invention is based on the finding by the present inventors that the hydrazide compounds each having a bicyclo skeleton described in the present application have excellent curability and humidity resistance. Specifically, the present invention relates to the following 1) to 13). In this specification, "(meth)acrylic" means either one or both of "acrylic" and "methacrylic". Likewise, "(meth)acryloyl" means either one or both of "acryloyl" and "methacryloyl".

1)

A hydrazide compound represented by the following formula

(1):



in the formula, n represents an integer of 0 to 6, and m represents an integer of 1 to 4.

2)

The hydrazide compound according to 1), in which m is an integer of 2 to 4 in the formula (1).

3)

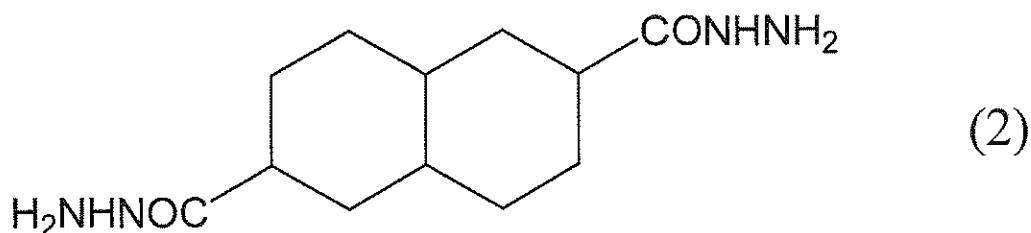
The hydrazide compound according to 1) or 2), in which n is 0 in the formula (1).

4)

The hydrazide compound according to any one of 1) to 3), in which m is 2 in the formula (1).

5)

The hydrazide compound according to any one of 1) to 4), which is represented by the following formula (2):



6)

A resin composition containing (a) the hydrazide compound according to any one of 1) to 5) and (b) a curable resin.

7)

The resin composition according to 6), in which the component (b) is one or two or more selected from epoxy resins, (meth)acrylated epoxy resins and partially (meth)acrylated epoxy resin.

8)

The resin composition according to 6) or 7), further containing (c) an inorganic filler.

9)

The resin composition according to any one of 6) to 8), further containing (d) a silane coupling agent.

10)

An adhesive for an electronic part using the resin composition according to any one of 6) to 9).

11)

An adhesive for a liquid crystal display cell using the resin composition according to any one of 6) to 9).

12)

A liquid crystal sealant using the resin composition according to any one of 6) to 9).

13)

A liquid crystal display cell which has been bonded by using the adhesive for a liquid crystal display cell according to 11) or the liquid crystal sealant according to 12).

Effects of the Invention

The novel hydrazide compound of the present invention has very excellent curablility, and also has high hydrophobicity. Therefore, a cured product having excellent reliability of humidity resistance can be attained when the compound is used in an adhesive. Furthermore, in a liquid crystal display element produced by a liquid crystal dropping process, light leakage occurs in the vicinity of a cured product in many cases of sealants using hydrazides each having a straight chain alkyl skeleton (adipic acid dihydrazide (ADH) and sebacic acid dihydrazide (SDH)) and the like, whereas such a phenomenon does not occur in the novel hydrazide compound of the present invention, and the hydrazide compound shows an extremely fine display property.

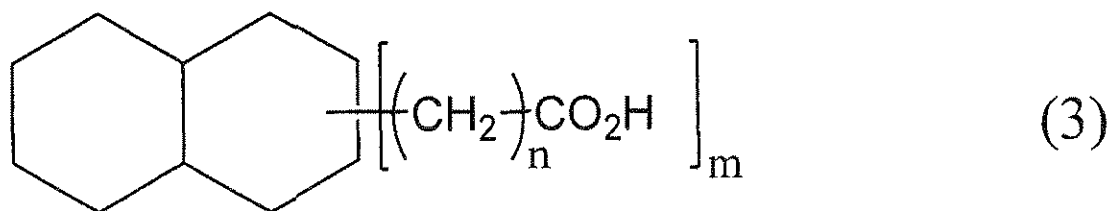
PREFERRED MODE FOR CARRYING OUT THE INVENTION

The present invention will be explained below in detail.

The hydrazide compound represented by the formula (1) according to the present invention can be obtained by reacting a corresponding carboxylic acid compound with an alcohol, converting the product to an alkyl ester, and reacting the alkyl ester with a hydrazine hydrate, or by reacting a corresponding carboxylic acid alkyl ester with hydrazine hydrate.

Specifically, at first, the corresponding carboxylic acid and alcohol are stirred in the presence of an acid catalyst, such as sulfuric acid, at a temperature about 50 to 100°C for 5 to 10 hours to give an alkyl ester of the corresponding carboxylic acid compound.

The corresponding carboxylic acid compound refers to a compound in which a carboxy group is bonded to the bicyclo skeleton of the present invention, and is especially a compound represented by the following formula (3).



In the formula, n represents an integer of 0 to 6, and m represents an integer of 1 to 4.

Although the alcohol used is not especially limited as long as it is a straight chain or branched aliphatic alcohol with a carbon number of 1 to 4, methanol is the most preferable with consideration to easiness of detachment, i.e.,

the reactivity in the subsequent step. The amount used of the alcohol is preferably 10 to 100 mol, more preferably 20 to 50 mol, in the case when the carboxylic acid compound is deemed as 1 mol.

Sulfuric acid is especially preferable as the acid catalyst. The amount used of the acid catalyst is preferably 0.01 to 1 mol, more preferably 0.05 to 0.5 mol, in the case when the carboxylic acid compound is deemed as 1 mol.

It is preferable that the reaction temperature is 50 to 100°C and the reaction time is about 3 to 10 hours. The reaction can be tracked by thin layer chromatography (TLC) or the like. The reaction liquid containing the objective ester may be directly used in subsequent reaction with hydrazine hydrate, or the reaction liquid may be subjected to isolation purification by a separation operation such as extraction, concentration and crystallization, and used in the subsequent reaction.

Subsequent to the above-mentioned step of synthesizing the alkyl ester of the carboxylic acid compound, the alkyl ester of the carboxylic acid compound is mixed with hydrazine hydrate at 0 to 30°C and reacted at 50 to 100°C for 1 to 10 hours.

Although this step does not necessarily require a solvent, it is preferable to conduct this step by using water or a water-soluble organic solvent. Examples of the water-soluble organic solvent may include alcohols, N-methylpyrrolidone and the like, and alcohols are preferable, and isopropanol is

especially preferable.

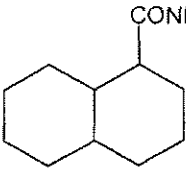
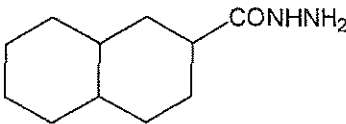
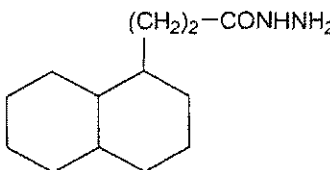
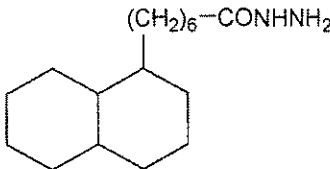
This step is conducted by, for example, dissolving an alkyl ester of the above-mentioned carboxylic acid compound in the above-mentioned organic solvent, and dropping hydrazine hydrate thereon at 0 to 30°C. After the dropping, the solution is heated to 50 to 100°C and reacted for 1 to 10 hours, thereby the objective hydrazide compound can be obtained.

The hydrazine hydrate used in this step is preferably from 1 to 20 mol, further preferably from 5 to 15 mol, with respect to 1 mol of the alkyl ester of the carboxylic acid compound.

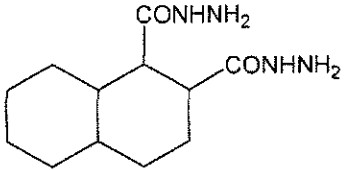
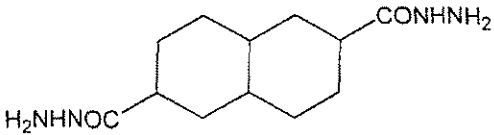
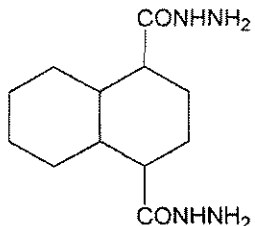
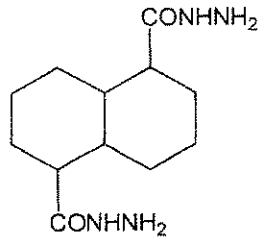
The endpoint of the reaction can be confirmed by thin layer chromatography (TLC) or the like. In the case when isopropanol is used as the organic solvent, the generated hydrazide compound precipitates as a white crystal due to its low solubility. Therefore, the hydrazide compound of the present invention can be easily obtained by separation by filtration and drying.

As the hydrazide compound of the present invention, those listed in Tables 1 to 3 can be exemplified. However, the hydrazide compound is not especially limited to these as long as it satisfies the structure of the formula (1).

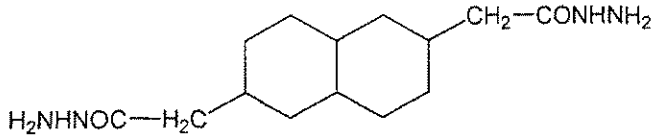
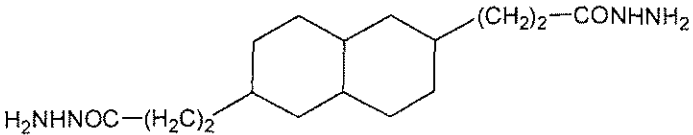
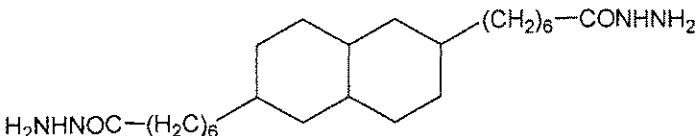
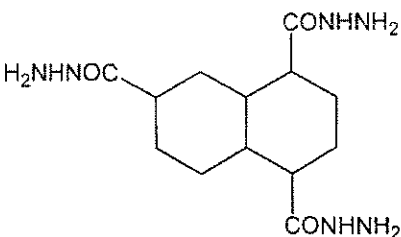
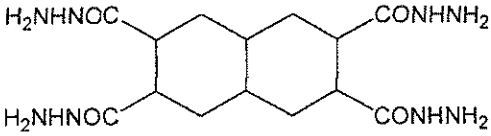
[Table 1]

Compound No.	Structural formula
1	
2	
3	
4	

[Table 2]

Compound No.	Structural formula
5	 <chem>NC(=O)C1CCC2CCCCC2C1C(=O)NN</chem>
6	 <chem>NC(=O)C1CCC2CCCCC2C1C(=O)NN</chem>
7	 <chem>NC(=O)C1CCC2CCCCC2C1C(=O)NN</chem>
8	 <chem>NC(=O)C1CCC2CCCCC2C1C(=O)NN</chem>

[Table 3]

Compound No.	Structural formula
9	
10	
11	
12	
13	

The resin composition using the hydrazide compound of the present invention contains the component (b), which is a curable resin. Examples of this curable resin can include epoxy resins, (meth)acrylated epoxy resins, monomers of (meth)acrylic acid esters, oligomers of (meth)acrylic acid esters, partially (meth)acrylated epoxy resins and the like.

Furthermore, in the case of use in an adhesive, the case of a curable resin formed of one or two or more selected from the epoxy resins, (meth)acrylated epoxy resins and partially (meth)acrylated epoxy resins among the above-mentioned curable resins is especially preferable. Examples may include epoxy resins, mixtures of epoxy resins and (meth)acrylated epoxy resins, (meth)acrylated epoxy resins, partially (meth)acrylated epoxy resins and the like.

Specifically, in the case when the curable resin is used in an adhesive for a liquid crystal display cell and used on a part that comes directly into contact with a liquid crystal, a curable resin having low contamination property and solubility with respect to a liquid crystal is preferable. Examples of preferable epoxy resins may include, but are not limited to, bisphenol A type epoxy resins, bisphenol F type epoxy resins, bisphenol S type epoxy resins, phenol novolac type epoxy resins, cresol novolac type epoxy resins, bisphenol A novolac type epoxy resins, bisphenol F novolac type epoxy resins, alicyclic epoxy resins, aliphatic chain epoxy resins, glycidyl ester type epoxy resins, glycidyl amine type epoxy resins, hydantoin type epoxy resins, isocyanurate type epoxy resins and phenol novolac type epoxy resins having triphenolmethane skeletons, as well as diglycidyl etherified products of bifunctional phenols, diglycidyl etherified products of bifunctional alcohols, and halogenated products and hydrogen adducts thereof, and the like.

The (meth)acryloylated epoxy resins and partialy

(meth)acryloylated epoxy resins can each be obtained by a well-known reaction between an epoxy resin and (meth)acrylic acid. For example, they can be obtained by adding (meth)acrylic acid, a catalyst (for example, benzyldimethylamine, triethylamine, benzyltrimethylammonium chloride, triphenylphosphine, triphenylstibine or the like), and a polymerization inhibitor (for example, methoquinone, hydroquinone, methylhydroquinone, phenothiazine, dibutylhydroxytoluene or the like) to an epoxy resin at a predetermined equivalent amount ratio, and conducting an esterification reaction, for example, at 80 to 110°C.

Although the epoxy resin as a raw material is not especially limited, a bi- or more functional epoxy resin is preferable, and examples may include bisphenol A type epoxy resins, bisphenol F type epoxy resins, bisphenol S type epoxy resins, phenol novolac type epoxy resins, cresol novolac type epoxy resins, bisphenol A novolac type epoxy resins, bisphenol F novolac type epoxy resins, alicyclic epoxy resins, aliphatic chain epoxy resins, glycidyl ester type epoxy resins, glycidyl amine type epoxy resins, hydantoin type epoxy resins, isocyanurate type epoxy resins and phenol novolac type epoxy resins having triphenolmethane skeletons, as well as diglycidyl etherified products of bifunctional phenols and diglycidyl etherified products of bifunctional alcohols, and halogenated products and hydrogen adducts thereof, and the like. Among these, the bisphenol type epoxy resins and novolac type epoxy resins are more preferable in view of the liquid

crystal contamination property. Furthermore, the ratio of the epoxy group and (meth)acryloyl group is not limited and suitably selected from the viewpoints of suitability for steps and liquid crystal contamination property.

Where necessary, a monomer and/or oligomer of a (meth)acrylic acid ester may also be used in the resin composition of the present invention. Examples of such monomer and oligomer may include, but are not limited to, a reaction product of dipentaerythritol and (meth)acrylic acid, a reaction product of dipentaerythritol-caprolactone and (meth)acrylic acid.

The resin composition of the present invention is preferable for use as an adhesive. In this case, the content of the hydrazide compound as the component (a) is preferably 1 to 20 parts by mass, further preferably 1 to 10 parts by mass, with respect to 100 parts by mass of the curable resin as the component (b). The remainder includes an inorganic filler, a silane coupling agent, a photopolymerization initiator, a heat radical polymerization initiator, a heat curing accelerator and the like.

Examples of the inorganic filler (component (c)) that the resin composition of the present invention may contain may include fused silica, crystalline silica, silicon carbide, silicon nitride, boron nitride, calcium carbonate, magnesium carbonate, barium sulfate, calcium sulfate, mica, talc, clay, alumina, magnesium oxide, zirconium oxide, aluminum hydroxide, magnesium hydroxide, calcium silicate, aluminum silicate,

lithium aluminum silicate, zirconium silicate, barium titanate, glass fibers, carbon fibers, molybdenum disulfide, asbestos and the like, and fused silica, crystalline silica, silicon nitride, boron nitride, calcium carbonate, barium sulfate, calcium sulfate, mica, talc, clay, alumina, aluminum hydroxide, calcium silicate, aluminum silicate are preferable, and fused silica, crystalline silica, alumina and talc are more preferable. These inorganic fillers may also be used by mixing two or more kinds. Specifically in the case of use as an adhesive for the following liquid crystal display cell, if the average particle size of the inorganic filler is too large, defects such as failure in the formation of a gap during attachment of the top and bottom glass substrates in the production of a liquid crystal display cell with a narrow gap are caused. Therefore, the average particle size is suitably 3 μm or less, preferably 2 μm or less. The particle size can be measured by a laser diffraction/scattering type particle size distribution measurement apparatus (dry type) (manufactured by SEISHIN ENTERPRISE Co., Ltd.; LMS-30).

The content of the above-mentioned inorganic filler in the resin composition is generally from 1 to 60 parts by mass, preferably from 5 to 50 parts by mass, when the entirety of the resin composition of the present invention is deemed as 100 parts by mass. In the case when the content of the inorganic filler is too low, the adhesiveness is decreased and the reliability of humidity resistance also becomes poor. Therefore, the decrease in adhesiveness after humidity

absorption may also become significant. On the other hand, in the case when the content of the inorganic filler is too high, in the case of use as an adhesive for a liquid crystal display cell, the gap of the cell cannot be formed.

Examples of the silane coupling agent (component (d)) that the resin composition of the present invention may contain may include 3-glycidoxypropyl trimethoxysilane, 3-glycidoxypropyl methyldimethoxysilane, 3-glycidoxypropyl methyldimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyl trimethoxysilane, N-phenyl- γ -aminopropyl trimethoxysilane, N-(2-aminoethyl)-3-aminopropyl methyldimethoxysilane, N-(2-aminoethyl)-3-aminopropyl methyltrimethoxysilane, 3-aminopropyl triethoxysilane, 3-mercaptopropyl trimethoxysilane, vinyltrimethoxysilane, N-(2-(vinylbenzylamino)ethyl)-3-aminopropyl trimethoxysilane hydrochloride, 3-methacryloxypropyl trimethoxysilane, 3-chloropropyl methyldimethoxysilane, 3-chloropropyl trimethoxysilane and the like. The content of the silane coupling agent in the resin composition is preferably from 0.01 to 3 parts by mass when the entirety of the resin composition of the present invention is deemed as 100 parts by mass.

The photopolymerization initiator that the resin composition of the present invention may contain is not especially limited as long as it is a compound that causes radicals by the irradiation of energy such as ultraviolet light and visible light to initiate a chain polymerization reaction, examples may include benzyldimethyl ketal, 1-

hydroxycyclohexylphenylketone, diethylthioxanthone, benzophenone, 2-ethylanthraquinone, 2-hydroxy-2-methylpropiophenone, 2-methyl-[4-(methylthio)phenyl]-2-morpholino-1-propane, 2,4,6-trimethylbenzoyldiphenylphosphine oxide and the like. Furthermore, in the case of use as an adhesive for the following liquid crystal display and in the case of use in a part that directly comes into contact with a liquid crystal, it is preferable to use a compound having a (meth)acryloyl group in the molecule in view of liquid crystal contamination property. For example, a reaction product of 2-methacryloyloxyethylisocyanate and 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propan-1-one is preferably used. This compound may be obtained by producing using the method described in International Publication No. 2006/027982. The content of this photopolymerization initiator is generally from 0.1 to 20 parts by mass, preferably from 1 to 15 parts by mass, when the entirety of the resin composition of the present invention is deemed as 100 parts by mass.

The heat radical polymerization initiator that the resin composition of the present invention may contain is not especially limited as long as it is a compound that creates radicals by heating to thereby initiate a chain polymerization reaction, examples may include organic peroxides, azo compounds, benzoin compounds, benzoin ether compounds, acetophenone compounds, benzopinacol and the like, and benzopinacol is preferably used. For example, as the organic peroxides, Kayamek A, Kayamek M, Kayamek R, Kayamek L, Kayamek

LH, Kayamek SP-30C, Perdox CH-50L, Perdox BC-FF, Kadox B-40ES, Perdox 14, Trigonox 22-70E, Trigonox 23-C70, Trigonox 121, Trigonox 121-50E, Trigonox 121-LS50E, Trigonox 21-LS50E, Trigonox 42, Trigonox 42LS, Kayaester P-70, Kayaester TMPO-70, Kayaester CND-C70, Kayaester O, Kayaester O-50E, Kayaester AN, Kayabutyl B, Perdox 16, Kayacarbon BIC-75, Kayacarbon AIC-75 (manufactured by Kayaku Akzo Corporation), Permek N, Permek H, Permek S, Permek F, Permek D, Permek G, Perhexa H, Perhexa HC, Perhexa TMH, Perhexa C, Perhexa V, Perhexa 22, Perhexa MC, Percure AH, Percure AL, Percure HB, Perbutyl H, Perbutyl C, Perbutyl ND, Perbutyl L, Percumyl H, Percumyl D, Perloyl IB, Perloyl IPP and Perocta ND (manufactured by NOF Corporation) and the like are available as commercially available products. Furthermore, as the azo compound, VA-044, V-070, VPE-0201, VSP-1001 and the like (manufactured by Wako Pure Chemical Industries, Ltd.) and the like are available as commercially available products. The content of the heat radical polymerization initiator is preferably from 0.0001 to 10 parts by mass, more preferably from 0.0005 to 7 parts by mass, and especially preferably from 0.001 to 3 parts by mass, when the entirety of the resin composition of the present invention is deemed as 100 parts by mass.

Where necessary, the resin composition of the present invention can also contain an organic filler, and additives such as a pigment, a leveling agent, a defoaming agent and a solvent.

A method is described below as one example of a method

for obtaining the resin composition of the present invention. First, a photopolymerization initiator is dissolved in a curable resin (component (b)) while being heated, the solution is cooled to room temperature, the solution is mixed with the hydrazide compound of the present invention (component (a)), an inorganic filler (component(c)), a silane coupling agent (component(d)), a heat radical polymerization initiator and the like and uniformly mixed with a known mixing apparatus, for example, a three-roller milling machine, a sand mill, a ball mill or the like, and filtered with a metal mesh, whereby the resin composition of the present invention can be produced.

The resin composition of the present invention is very useful as an adhesive for an electronic part. Examples of the adhesive for an electronic part may include, but are not limited to, adhesives for flexible printed circuit boards, adhesives for TABs, adhesives for semiconductors, adhesives for various displays and the like.

Furthermore, the resin composition of the present invention is very useful as an adhesive for a liquid crystal display cell, especially as a liquid crystal sealant. An example of a liquid crystal display cell in the case when the resin composition of the present invention is used as a liquid crystal sealant will be shown below.

The liquid crystal display cell produced by using the adhesive for a liquid crystal display cell of the present invention is obtained by arranging one pair of substrates on which prescribed electrodes are formed facing each other at a

prescribed interval, sealing the circumference with the liquid crystal sealant of the present invention, and enclosing a liquid crystal in the space. The kind of the enclosed liquid crystal is not particularly limited. Herein, the substrates are formed of a combination of substrates such as glass, quartz, plastic, and silicon, in which at least one of the substrates is light-transmitting. As the manufacturing method thereof, the liquid crystal sealant of the present invention is combined with a spacer such as a glass fiber (space control material), and then the liquid crystal sealant is applied onto one of the pair of substrates using a dispenser, or a screen print apparatus or the like, and then temporary curing is performed at 80 to 120°C as necessary. Then, liquid crystal is dropped into the inside of the pool of the liquid crystal sealant, and the other glass substrate is superposed in a vacuum to perform gap formation. After the gap formation, the portion of the liquid crystal sealant is irradiated with ultraviolet light using an ultraviolet light irradiation machine to perform the photocuring. The amount of ultraviolet light irradiated is preferably 500 to 6,000 mJ/cm², and more preferably 1,000 to 4,000 mJ/cm². Then, as necessary, curing is performed at 90 to 130°C for 1 to 2 hours, thereby the liquid crystal display cell of the present invention can be obtained. The liquid crystal display cell of the present invention thus obtained does not have display defects due to contamination of the liquid crystal, and is excellent in terms of adhesiveness and reliability of humidity resistance.

Examples of the spacer may include glass fibers, silica beads, polymer beads and the like. The diameter thereof varies depending on the purpose, but typically from 2 to 8 μm , and preferably from 4 to 7 μm . The amount used is typically from 0.1 to 4 parts by mass, preferably from 0.5 to 2 parts by mass, and further preferably from 0.9 to 1.5 parts by mass with respect to 100 parts by mass of the liquid crystal sealant of the present invention.

The novel hydrazide compound of the present invention is very suitable for use in an adhesive. Specifically, the compound has good storage stability despite its good reactivity and also has high hydrophobicity, and thus has a significant effect on the humidity resistance reliability of the cured product. Furthermore, the resin composition using the hydrazide compound of the present invention is very useful as an adhesive for an electronic part and an adhesive for a liquid crystal display cell.

EXAMPLES

Hereinafter the present invention will furthermore be explained in detail with Examples, but the present invention is not limited to the Examples. Meanwhile, "part" and "%" in the text are on a mass basis unless otherwise stated.

Example 1

Synthesis of 2,6-decahydronaphthalenedicarboxylic acid dihydrazide (3,8-bicyclo[4.4.0]decanedicarboxylic acid

dihydrazide) (Compound No. 6 in Table 2)

(Step 1)

30.0 g of 2,6-decahydronaphthalenedicarboxylic acid (3,8-bicyclo[4.4.0]decanedicarboxylic acid: synthesized by the method described in Example 1 of Japanese Unexamined Patent Application, Publication No 2004-331645) was dissolved in 127 g of methanol, and 1.3 g of sulfuric acid was added thereto. The solution was stirred under reflux for 8 hours, and the methanol was removed with an evaporator. Toluene was added to the obtained liquid, a 7% aqueous solution of sodium hydrogen carbonate was also added thereto, and the solution was stirred and subjected to liquid separation. Subsequently, a 7% aqueous solution of sodium hydrogen carbonate was added to the organic layer, and the solution was stirred and subjected to liquid separation. These operations were repeated until the aqueous layer became neutral, which was checked using pH test paper. Subsequently, ion-exchanged water was added to the organic layer, and the solution was stirred and subjected to liquid separation. These operations were repeated twice. The toluene was removed with an evaporator to give 32 g of 2,6-decahydronaphthalenedicarboxylic acid dimethyl ester (3,8-bicyclo[4.4.0]decanedicarboxylic acid dimethyl ester). This compound is also commercially available as H-NDCM (manufactured by Mitsubishi Gas Chemical Company Inc.).

(Step 2)

20.0 g of the 2,6-decahydronaphthalenedicarboxylic acid dimethyl ester (3,8-bicyclo[4.4.0]decanedicarboxylic acid

dimethyl ester) synthesized in Step 1 was dissolved in 74 mL of isopropanol, and 44.4 g of hydrazine monohydrate was added dropwise by a dropping funnel over 30 minutes. Thereafter the temperature was raised to 80°C, and stirring was conducted over 3 hours. The precipitated crystal was collected by filtration and dried to give 8.8 g of the objective 2,6-decahydronaphthalenedicarboxylic acid dihydrazide (3,8-bicyclo[4.4.0]decanedicarboxylic acid dihydrazide).

¹H-NMR data: 8.9 (2H), 4.1 (4H), 2.0-2.1 (2H), 1.6-1.7 (4H), 1.4-1.5 (8H), 1.2 (2H).

Reference Synthesis Example 1

Synthesis of epoxy acrylate of bisphenol A type epoxy resin

282.5 g of a bisphenol A type epoxy resin (product name: YD-8125, manufactured by Nippon Steel & Sumikin Chemical Co., Ltd.) was dissolved in 266.8 g of toluene, 0.8 g of dibutylhydroxytoluene as a polymerization inhibitor was added thereto, and the temperature was raised to 60°C. Thereafter 117.5 g of acrylic acid, which was the 100% equivalent amount of the epoxy group, was added, the temperature was further raised to 80°C, 0.6 g of trimethylammonium chloride as a reaction catalyst was added thereto, and stirring was conducted at 98°C for about 30 hours to give a reaction liquid. The obtained reaction liquid was washed with water, and the toluene was distilled off to give 395 g of the objective bisphenol A type epoxy acrylate (KAYARAD[®] R-93100).

(Preparation of liquid crystal sealant)

Example 2

Curable resin components (component (b)) were mixed in the ratio shown in the Table 4 to be described below, and stirred. A photopolymerization initiator was added thereto and dissolved by heating at 90°C. The solution was cooled to room temperature, an inorganic filler (component (c)), a silane coupling agent (component (d)), the curing agent synthesized in Example 1 (component (a)) were added thereto, and the mixture was stirred, dispersed with a three roll mill and filtered with a metal mesh (635 mesh) to thereby prepare the liquid crystal sealant.

Comparative Example 1

The liquid crystal sealant was prepared in a similar manner to Example 2, except that 0.65 g of adipic acid dihydrazide (manufactured by Otsuka Chemical Co., Ltd.) was used as a curing agent instead of the compound synthesized in Example 1.

Comparative Example 2

The liquid crystal sealant was prepared in a similar manner to Example 2, except that 0.96 g of tris(2-hydrozinocarbonyl) isocyanurate (manufactured by Japan Finechem Company Inc.) was used as a curing agent instead of the compound synthesized in Example 1.

The evaluation tests were conducted by the following methods.

(Measurement of adhesiveness)

1 g of 5 μm glass fibers was added as a spacer to 100 g of each of the liquid crystal sealants as prepared, and the liquid crystal sealant was mixed by stirring. This liquid crystal sealant was applied onto a glass substrate of 50 mm $\times$ 50 mm, 1.5 mm $\times$ 1.5 mm glass fragments were applied onto the liquid crystal sealant, and irradiated with 3,000 mJ/cm² of ultraviolet light using an UV irradiation machine, and then placed in an oven and cured by heating at 120°C for 1 hour. The shear adhesive strength of the glass fragments was measured with a bond tester (SS-30WD: manufactured by Seishin Trading Co., Ltd.). The result is shown in Table 4.

(Measurement of moisture-resistant adhesiveness)

The same measurement sample as that in the above-mentioned adhesiveness test was prepared. The measurement sample was put into a pressure cooker tester (TPC-411: manufactured by Tabai Espec Corporation) under the conditions of 121°C, 2 atm and a humidity of 100% for 12 hours, and the sample was measured by the above-mentioned bond tester. The result is shown in Table 4.

(Test for panel display property)

Each of the liquid crystal sealants as prepared was filled into a syringe and degassed, and then was applied onto a glass substrate (a glass substrate obtained by applying an oriented film: SE-6414: manufactured by Nissan Chemical

Industries, Ltd. thereto, and rubbing) with a dispenser (SHOT MASTER 300 manufactured by Musashi Engineering, Inc.), and a suitable amount of a liquid crystal was dropped into the frame of the seal. The substrate was put on a vacuum adhesion apparatus, another substrate was superposed thereon in vacuum, and the substrates were subjected to curing at 120°C for 1 hour. The obtained simulation panel was electrically charged and observed on a polarizing film. Furthermore, plural instances of vibrations or pressures were applied in the vicinity of the site where the liquid crystal and liquid crystal sealant were in contact with each other, and the site was observed under a microscope. The observed result was judged as follows.

OK: Alignment defect was not confirmed, and light leakage in the vicinity of the sealing was not found.

NG: Alignment defect was confirmed, and light leakage in the vicinity of the sealing was found.

The result is shown in Table 4.

[Table 4]

			Example 1	Comparative Example 1	Comparative Example 2
Component (a)	#1	2,6-Decahydronaphthalenedicarboxylic acid dihydrazide	0.95	0	0
	#2	Adipic acid dihydrazide	0	0.65	0
	#3	Tris(2-hydrozinocarbonyl) isocyanurate	0	0	0.96
	#4	1,3,5-tris(2-carboxyethyl)isocyanurate	0	0	0.23
Component (b)	#5	Bisphenol A type epoxy acrylate	16	16	16
	#6	Bisphenyl A type epoxy resin	1.5	1.5	1.5
Component (c)	#7	Talc	1.5	1.5	1.5
	#8	Silica	1	1	1
Component (d)	#9	3-glycidoxypyrroltrimethoxysilane	0.1	0.1	0.1
	#10	Reaction product of 2-methacryloyloxyethylisocyanate and 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propan-1-one	1	1	1
Adhesive strength			67	62	65
Moisture-resistance adhesiveness (retention rate)			58 (87%)	45 (65%)	37 (57%)
Panel display property			OK	NG	OK

#1 : Synthesized by Example 1

#2 : ADH (Manufactured by Otsuka Chemical Co., Ltd.)

#3 : HCIC (Manufactured by Japan Finechem Company, Inc.)

#4 : CIC acid (manufactured by Shikoku Chemicals Corporation)

#5 : R-93100 (Synthesized by Reference Synthesis Example 1)

#6 : YD-8125 (Manufactured by Nippon Steel & Sumikin Chemical Co., Ltd.)

#7 : D-600F (Manufactured by Nippon Talc Co., Ltd.)

#8 : Admafine SEZ (manufactured by Admatechs)

#9 : Sila-Ace S-510 (manufactured by Chisso Corporation)

#10 : Synthesized by the method described in WO 2006/027982

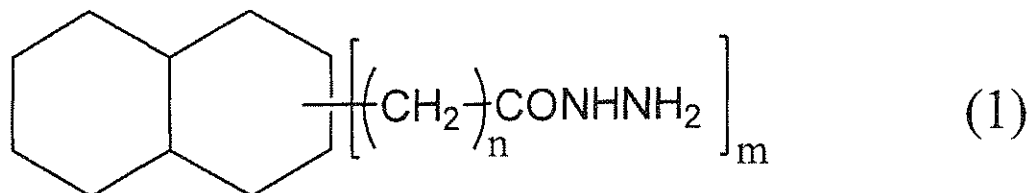
It was confirmed from the results in Table 4 that the hydrazide compound of the present invention has good curability and is excellent in terms of humidity resistance, and also shows good panel display properties when used as a curing agent for a liquid crystal sealant.

INDUSTRIAL APPLICABILITY

The novel hydrazide compound and the resin composition using the compound of the present invention are very useful as adhesives for electronic parts, especially as liquid crystal sealants.

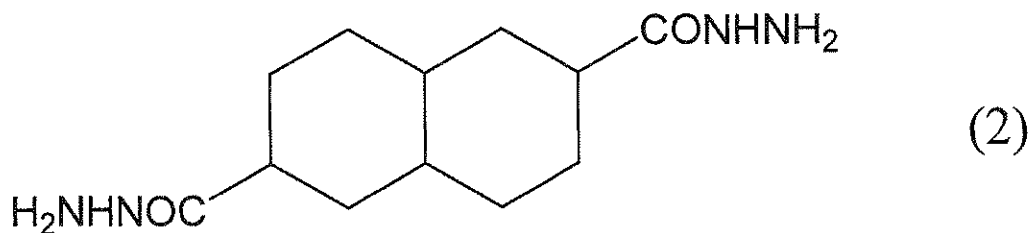
CLAIMS

1. A hydrazide compound represented by the following formula (1):



wherein, n represents an integer of 0 to 6, and m represents an integer of 1 to 4.

2. The hydrazide compound according to claim 1, wherein m is an integer of 2 to 4 in the formula (1).
3. The hydrazide compound according to claim 1 or 2, wherein n is 0 in the formula (1).
4. The hydrazide compound according to any one of claims 1 to 3, wherein m is 2 in the formula (1).
5. The hydrazide compound according to any one of claims 1 to 4, which is represented by the following formula (2):



6. A resin composition comprising (a) the hydrazide compound according to any one of claims 1 to 5, and (b) a curable resin.

7. The resin composition according to claim 6, wherein the component (b) is one or two or more selected from epoxy resins, (meth)acrylated epoxy resins and partially (meth)acrylated epoxy resin.

8. The resin composition according to claim 6 or 7, further comprising (c) an inorganic filler.

9. The resin composition according to any one of claims 6 to 8, further comprising (d) a silane coupling agent.

10. An adhesive for an electronic part, using the resin composition according to any one of claim 6 to 9.

11. An adhesive for a liquid crystal display cell, using the resin composition according to any one of claims 6 to 9.

12. A liquid crystal sealant, using the resin composition according to any one of claims 6 to 9.

13. A liquid crystal display cell which has been attached by using the adhesive for the liquid crystal display cell according to claim 11 or the liquid crystal sealant according to claim 12.