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(54) Title: THERMALLY CURABLE SEALANT COMPOSITION

(57) Abstract: A thermally curable sealant composition comprises one or more thermally curable resins having a group selected from epoxy group, (meth) acryloyl group, maleimide group, and combination thereof, and a latent curing agent, in which the molar equivalent ratio of epoxy group to (meth) acryloyl group and/or maleimide group in the one or more thermally curable resins is from 0.1 to 5.0. The thermally curable sealant composition possesses an excellent gel time at elevated temperature and an improved resistance to liquid crystal penetration and liquid crystal contamination, a good adhesion and a good reliability.

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THERMALLY CURABLE SEALANT COMPOSITION

Technical field

This invention relates to a thermally curable sealant composition and use thereof. In particular, the invention relates to a thermally curable sealant composition having an excellent gel time at elevated temperature and an improved liquid crystal penetration and liquid crystal contamination resistance, a good adhesion and reliable performance. In particular, the thermally curable sealant composition is suitable for the use in one drop filling (ODF) process of liquid crystal display (LCD) manufacturing.

Background of the invention

Liquid crystal display (LCD) panels having the characteristics of being light-weight and high-definition have been widely used as display panels for a variety of apparatuses including cell phones and TVs. Conventionally, the process for producing a LCD panel is called a one-drop-filling (ODF) process which comprising applying a sealant on a substrate having an electrode pattern and an alignment film under vacuum condition, dropping liquid crystal (LC) on the substrate having the sealant applied thereon, joining opposite facing substrates to each other under vacuum, then releasing the vacuum and performing pure ultraviolet (UV) radiation, pure heating, or the combination of UV radiation and heating to cure the sealant and thereby producing a LCD cell.

Recently, development of LCD has been more towards the direction of “slim border” or “narrow bezel” design. Among several ways to achieve this goal, one is the use of a narrow width of the sealant. However, a thinner line of sealant creates more challenge with typical ODF process due to the fact that the process needs to meet very high reliability to prevent the liquid crystal material from leakage, misalignment and contamination.

In addition, in normal ODF process, radiation curing, such as UV curing, and thermal curing are used to cure the sealant by single use or combination. UV light can be irradiated from color filter side and array side of the cell. In recent years, picture frames of LCD part have been narrowed down for the downsizing of LCD containing

equipment such as mobile phones, mobile game machines. Therefore, patterns of the sealant formed on a substrate is increasingly located at a position overlapping with the black matrix. This may cause a problem as the overlapping portion of sealant on black matrix remains uncured and flowable even after being UV irradiated. The uncured sealant easily elutes from the overlapping portion into liquid crystal which causes LC contamination.

On the other hand, although irradiating UV light from array side is also conceivable, challenges still remain since metal wirings and transistors on the array substrate overlap with the sealant pattern and create shadow area, which may in turn result in "shadow cure" issue as uncured portion of the sealant is apt to elute from sealant and comes into contact with LC which will also cause LC contamination.

Attempts have been made to improve the shadow cure issue and avoid LC contamination for ODF process by using pure heating curing step(s) or the combination of heating and irradiation curing steps.

For example, US 20070096056 A1 discloses to use a thiol compound as a chain transfer agent in a curable sealant composition to improve the shadow curability.

CN 101617267 A discloses to use a thermal radical polymerization initiator and a thiol chain transferring agent both in curable sealant composition for ODF process, which gives an increased curability in light-shielded areas and results in good sealing quality.

JP 3976749 B2 discloses a sealant composition for ODF process comprising an acrylated epoxy, an amine, a thiol, a gelling agent, a thixotropic agent, in which the thixotropic index (TI) of the sealant composition is between 1.2 and 2.

CN 101925852 A discloses a sealant composition for ODF process comprising an epoxy and a latent cure agent, which have a gel time at 100°C of less than 3 minutes, and achieves good stability of sealing shape and long work life.

JP 5597338 B2 discloses a sealant composition for ODF process comprising an alkoxy-silyl-groups modified epoxy resin, a radical polymerizable resin, a latent hardener, whose viscosity tested at 40°C was in the range of 1000 to 100000 Pa.s

after being placed at 80°C for 20 min or 100 mw/cm² illumination and 1000mJ/cm² UV radiation.

However, concerns of LC contamination and/or shadow curability remains for the prior art sealant compositions for ODF process. Thus, there is still a need for a thermally curable sealant composition that can at least partially solve the problem and maintain an excellent performance profile of adhesion.

Summary of the invention

The present invention provides a thermally curable sealant composition especially suitable for ODF process with pure thermal curing. The inventors has found that the thermally curable sealant composition according to the present invention contributes to an improved gel time, and an excellent LC penetration and contamination resistance of the sealant. In particular, the thermally curable sealant composition, comprising:

one or more thermally curable resins having a group selected from epoxy group, (meth)acryloyl group, maleimide group, and combination thereof, and
a latent curing agent,

in which the molar equivalent ratio of epoxy group to (meth)acryloyl group and/or maleimide group in the one or more thermally curable resins is from about 0.1 to about 5.0.

The present invention also provides a process of producing a liquid crystal display having a liquid crystal layer between a first substrate and a second substrate, said process comprising steps of:

- 1) applying the thermally curable sealant composition according to the present invention on a sealing region at a periphery of a surface of the first substrate;
- 2) conducting a first thermal curing of the thermally curable sealant composition at a temperature of about 40°C to about 75°C, and obtaining a partially cured product;
- 3) dropping liquid crystal on a central area encircled by the sealing region of the surface of the first substrate or the corresponding area of the second substrate, and forming the liquid crystal layer;
- 4) overlaying the second substrate on the first substrate; and
- 5) conducting a second thermal curing of the partially cured product.

Detailed description of the invention

In the following passages the present invention is described in more detail. Each aspect so described may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

In the context of the present invention, the terms used are to be construed in accordance with the following definitions, unless a context dictates otherwise.

As used herein, the singular forms “a”, “an” and “the” include both singular and plural referents unless the context clearly dictates otherwise.

The terms “comprising”, “comprises” and “comprised of” as used herein are synonymous with “including”, “includes” or “containing”, “contains”, and are inclusive or open-ended and do not exclude additional, non-recited members, elements or process steps.

The recitation of numerical end points includes all numbers and fractions subsumed within the respective ranges, as well as the recited end points.

All references cited in the present specification are hereby incorporated by reference in their entirety.

Unless otherwise defined, all terms used in the disclosing the invention, including technical and scientific terms, have the meaning as commonly understood by one of the ordinary skill in the art to which this invention belongs to. By means of further guidance, term definitions are included to better appreciate the teaching of the present invention.

In one aspect, the present invention provides a thermally curable sealant composition, comprising:

- one or more thermally curable resins having a group selected from epoxy group, (meth)acryloyl group, maleimide group, and combination thereof, and
- a latent curing agent,

in which the molar equivalent ratio of epoxy group to (meth)acryloyl group and/or maleimide group in the one or more thermally curable resins is from about 0.1 to about 5.0.

Thermally curable resin

The thermally curable resin(s) comprised in the sealant composition according to the present invention may be selected from epoxy resin, (meth)acrylate resin, maleimide resin, a hybrid resin having at least two groups selected from epoxy group, (meth)acryloyl group, maleimide group, and mixture thereof, provided that the molar equivalent ratio of epoxy group to (meth)acryloyl group and/or maleimide group in the one or more thermally curable resins is from about 0.1 to about 5.0.

In one embodiment, the thermally curable resin comprised in the sealant is two or more, preferably two types of thermally curable resins selected from epoxy resin, (meth)acrylate resin and maleimide resin.

In another embodiment, the thermally curable resin is a hybrid resin having at least two groups selected from epoxy group, (meth)acryloyl group, and maleimide group.

Epoxy resin

In the context of the present invention, the thermally curable resin having an epoxy group, and essentially having or having no (meth)acryloyl group and maleimide group is referred as epoxy resin. The epoxy resin of the present invention may also include any epoxy resin including, but not limited to, bisphenol-type epoxy resins such as bisphenol-A-type epoxy resins, bisphenol-F-type epoxy resins and bisphenol-S-type epoxy resins; novolac-type epoxy resins such as phenol novolac-type epoxy resins and cresol-novolac-type epoxy resins; biphenyl-type epoxy resins; hydrogenated bisphenol-type epoxy resins (those in which the benzene-ring in bisphenol-type epoxy resins such as bisphenol-A-type epoxy resins, bisphenol-F-type epoxy resins and bisphenol-S-type epoxy resins is hydrogenated); dicyclopentadiene-type epoxy resins such as glycidyl ether of dicyclopentadiene phenol novolac; and cyclohexanedimethanol diglycidyl ether.

Suitable commercially available epoxy resin to be used in the present invention are for example JER YL 980, a bisphenol A type epoxy resin, manufactured by Mitsubishi Chemical Corporation.

It is preferred that the epoxy resin has a molecular weight such that the resin becomes liquid. It is preferably liquid and has a viscosity in a range from about 1,000 about to 1,000,000 cps, more preferably a viscosity in a range from about 2,000 to about 700,000 cps at 25°C.

(Meth)acrylate resin

In the context of the present invention, the thermally curable resin having a (meth)acryloyl group, especially (meth)acrylate group (that is to say (meth)acryloyloxy group) and essentially having or having no epoxy group and maleimide group is referred as (meth)acrylate resin. The term (meth)acryloyl denotes both acryloyl and methacryloyl as commonly used. The same applies to (meth)acrylate and the like. The (meth)acrylate resin suitable to be used in the thermal curable resin includes but not limited to a ester compound obtainable by a reaction of a (meth)acrylic acid with a compound having a hydroxyl group, epoxy (meth)acrylate obtainable by a reaction of a (meth)acrylic acid with an epoxy compound, and urethane (meth)acrylate obtainable by a reaction of an isocyanate with a (meth)acrylic acid derivative having a hydroxyl group, and mixture or combination thereof.

The ester compound obtainable by the reaction of a (meth)acrylic acid with a compound having a hydroxyl group is not particularly limited. Examples of the ester compound with a mono-functional group include but not limited to 2-hydroxyethyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, isobutyl (meth)acrylate, phenoxy polyethylene glycol (meth)acrylate, imide (meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, propyl (meth)acrylate, n-butyl (meth)acrylate, cyclohexyl (meth)acrylate, and 2-ethylhexyl (meth)acrylate. Examples of the ester compound with two functional groups include but not limited to 1,6-hexanediol di(meth)acrylate, and 1,9-nonanediol di(meth)acrylate. Examples of the ester compound with three or more functional groups include pentaerythritol tri(meth)acrylate, and trimethylolpropane tri(meth)acrylate.

Also suitable in the present invention is the epoxy (meth)acrylate which is a derivative of epoxide resin which has one or more (meth)acrylate groups and are substantially free of epoxy groups, obtainable by reaction of a (meth)acrylic acid with an epoxy compound. According to the present invention, the epoxy (meth)acrylate refers to a specific type of (meth)acrylate resin, rather than an epoxy resin. Examples include an epoxy (meth)acrylate obtainable by reaction of an epoxy resin with (meth)acrylic acid in the presence of a basic catalyst according to a known method in the art. Preferably, the epoxy (meth)acrylate is a fully (meth)acrylated epoxy in which almost 100% of the epoxy groups can be converted to (meth)acrylic groups.

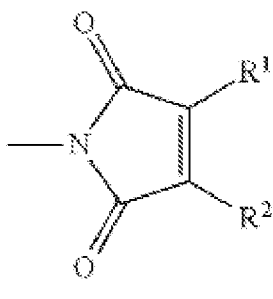
Examples of the epoxy (meth)acrylate commercially available include but not limited to Ebecryl 3708, Ebecryl 3600, Ebecryl 3701, Ebecryl 3703, Ebecryl 3200, Ebecryl 3201, Ebecryl 3600, Ebecryl 3702, Ebecryl 3412, Ebecryl 860, Ebecryl RDX63182, Ebecryl 6040, Ebecryl 3800 (all manufactured by Cytec Industries, Inc.), EA-1020, EA-1010, EA-5520, EA-5323, EA-CHD, EMA-1020 (all manufactured by Shin-Nakamura Chemical Co., Ltd.).

The urethane (meth)acrylate obtainable by reaction of the isocyanate with a (meth)acrylic acid derivative having a hydroxyl group can be obtained by reacting 1 equivalent amount of a compound having two isocyanate groups with 2 equivalent amount of the (meth)acrylic acid derivative having a hydroxyl group in the presence of a catalyst amount of tin compounds.

Examples of the commercially available urethane (meth)acrylate include M-1100, M-1200, M-1210, M-1600 (all manufactured by Toagosei Co., Ltd.), Ebecryl 230, Ebecryl 270, Ebecryl 4858, Ebecryl 8402, Ebecryl 8804, Ebecryl 8803, Ebecryl 8807, Ebecryl 9260, Ebecryl 1290, Ebecryl 5129, Ebecryl 4842, Ebecryl 210, Ebecryl 4827, Ebecryl 6700, Ebecryl 220, Ebecryl 2220 (all manufactured by Daicel UCB Co., Ltd.), Art Resin UN-9000H, Art Resin UN-9000A, Art Resin UN-7100, Art Resin UN-1255, Art Resin UN-330, Art Resin UN-3320HB, Art Resin UN-1200TPK, Art Resin SH-500B (all manufactured by Negami Chemical Industrial Co., Ltd.).

Maleimide resin

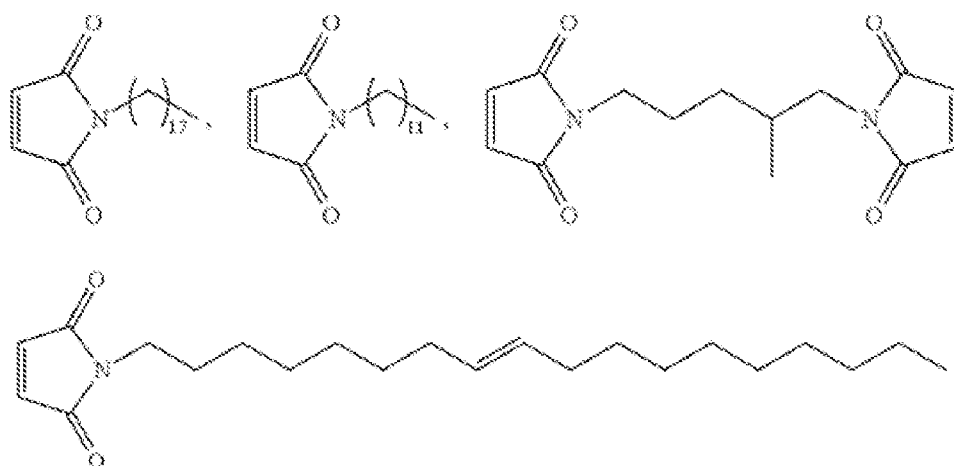
In the context of the present invention, the resin having one or more, preferably one or two substructures represented by moiety (I) and essentially having or having no (meth)acryloyl group and epoxy group is referred as maleimide resin:

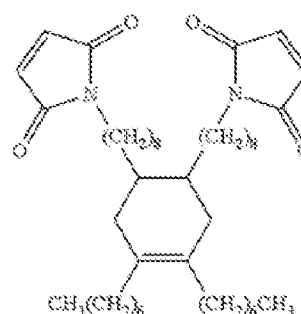
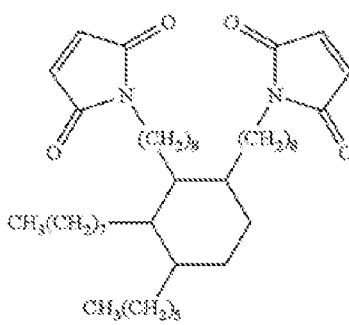
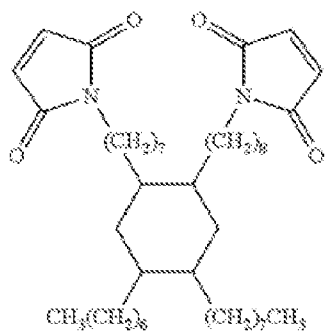
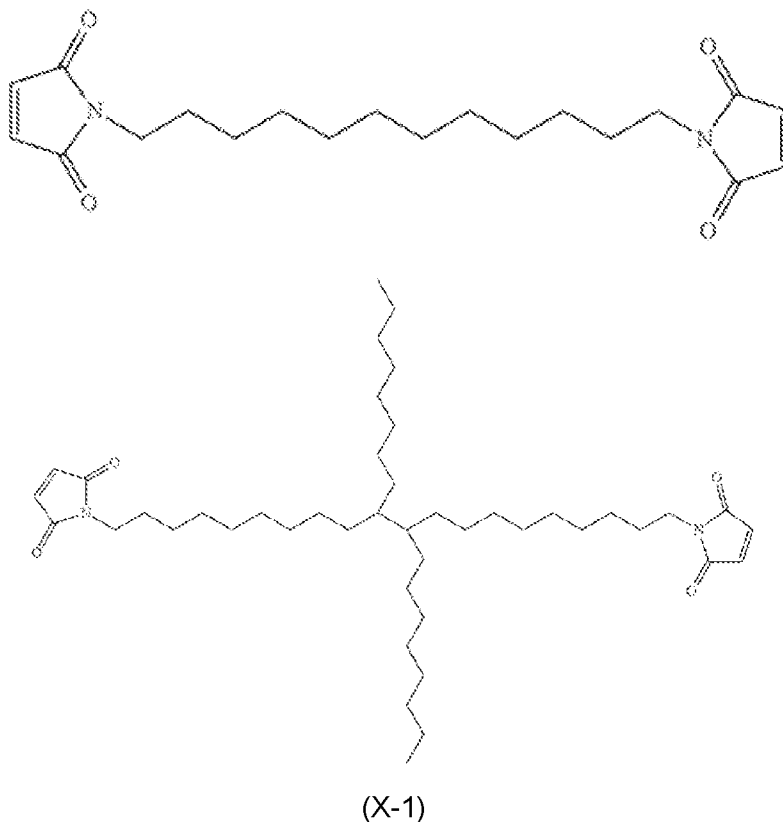


in its molecule. R^1 and R^2 denote H or alkyl group having 1 to 6 carbons, or R^1 and R^2 together denote alkylene group having 2 to 6 carbons. Preferably, both of R^1 and R^2 denote H, or R^1 and R^2 together denote 1,4-butylene group.

The maleimide resin is preferably liquid at room temperature, and therefore the moiety (I) bonds to a group that allows the maleimide resin to be liquid, for example, organic group comprising a branched alkyl, alkylene, alkylene oxide, alkylene carboxyl or alkylene amide structure having sufficient length and branch to render the maleimide resin liquid. The maleimide resin may comprise one, or two or more substructures (I). The compound having two of these groups is bismaleimide compound. In addition, a maleimide compound, even if it is not liquid, may be used if the sealant composition becomes liquid as being mixed with other maleimide compound or mixed with other component.

The maleimide compounds in which the moiety (I) bonds to alkyl group or alkylene group (these groups may comprise double bond and saturated alicyclic) include the following compounds:





Particularly preferred examples includes stearyl maleimide, oleyl maleimide, behenyl maleimide, and X-BMI {X-bismaleimide; formulae (X-1) to (X-4)} available from Henkel Corporation and the combination thereof. X-BMI is synthesized in accordance with the method described in U.S. Pat. No. 5,973,166 (the disclosure of U.S. Pat. No. 5,973,166 is incorporated into the present specification by reference) from 1,20-diamino-10,11-dioctyl eicosane and/or its cyclic isomeric diamine(s). X-BMI contains one, two or more of 1,20-bismaleimide-10,11-dioctyl-eicosane (the resin represented by the formula (X-1)), 1-heptylene maleimide-2-octylene maleimide-4-octyl-5-heptylcyclohexane (the resin represented by the formula (X-2)), 1,2-dioctylene maleimide-3-octyl-4-hexylcyclohexane (the resin represented by the formula (X-3)),

4,5-dioctylene maleimide-1,2-diheptylcyclohexene (the resin represented by the formula (X-4)) and the like. The bismaleimide resins represented by the formulae (X-1) to (X-4) may also be solely used preferably.

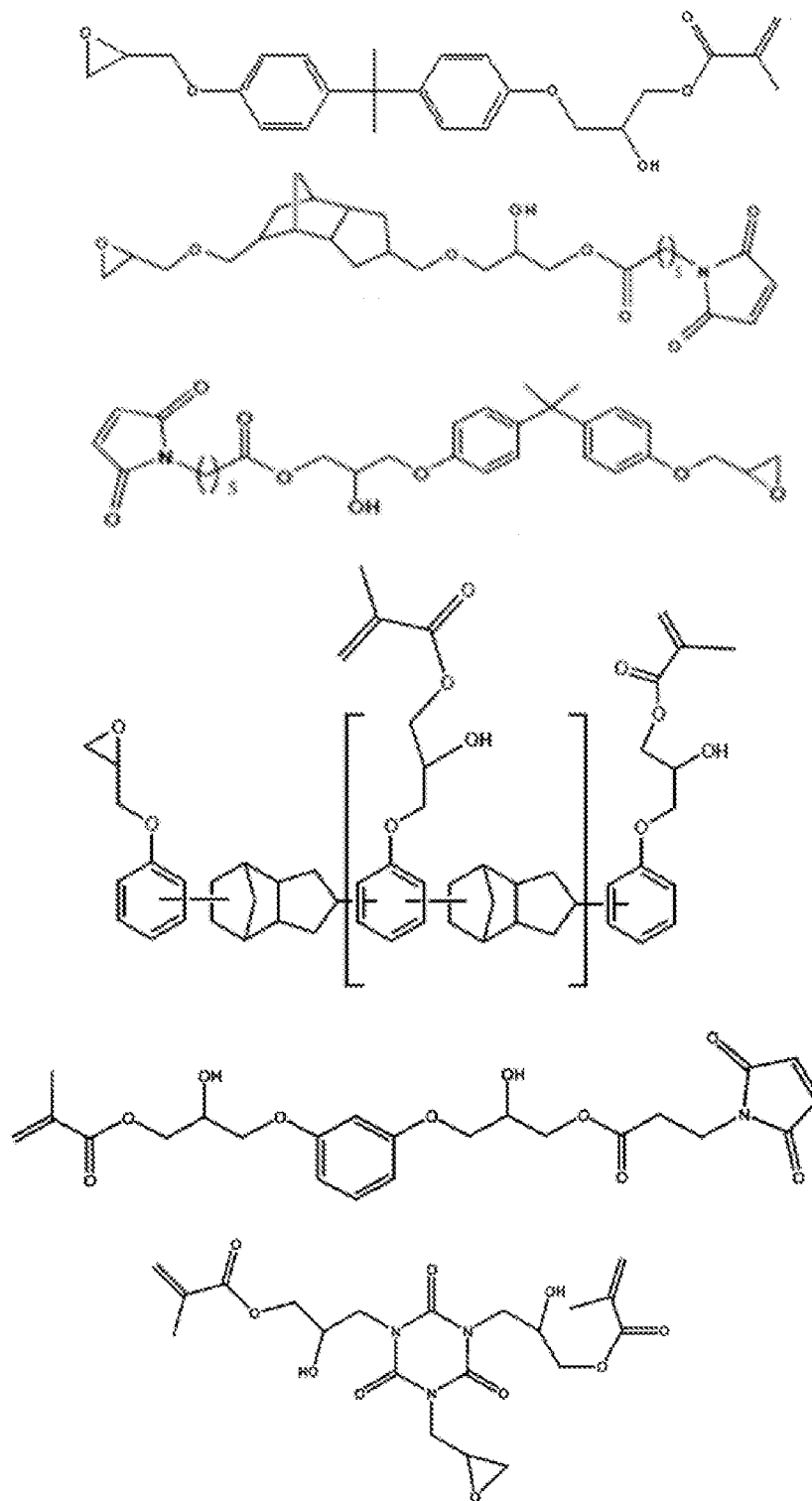
Hybrid resin

In the context of the present invention, the resin having at least two groups selected from epoxy group, (meth)acryloyl group, maleimide group is referred as a hybrid resin. Preferably, the hybrid resin has an epoxy group and a group selected from (meth)acryloyl group and maleimide group in one molecule. More preferably, the hybrid resin has an epoxy group and a group selected from (meth)acryloyl group and maleimide group at the end of the molecule.

The backbone of the hybrid resin have many kinds, such as bisphenol A backbone, dicyclopentadiene based backbone, resorcylic diglycidyl ether based backbone, isocyanurated based backbone, etc., and the end functional group can be epoxy, (meth)acryloyl, or maleimide group, or the combination of them, and the number of the functional group could be higher than 2. Commercially available hybrid resins include but not limited to bisphenol A epoxy and acrylate hybrid resin such as EA1010, EA1010N (manufactured by Shinakamura Co., Ltd), HCT-1, HCT-2 (manufactured by Kagawa chemical Co., Ltd), or those disclosed in patent application PCT/CN2015/083963, which is incorporated by reference herein..

In one embodiment, the hybrid resin has an epoxy group and a (meth)acryloyl group in one molecule, and preferably having a bisphenol A based backbone. In another embodiment, the hybrid resin has an epoxy group and a maleimide group in one molecule, and preferably having a bisphenol A and DCPD (dicyclopentadiene) phenol based backbone.

Exemplary embodiments include, but not limited to:



According to the present invention, the molar equivalent ratio of epoxy group to (meth)acryloyl group and/or maleimide group in the one or more thermally curable resins is from about 0.1 to about 5.0. The inventors surprisingly found that the selection of the molar equivalent ratio of the functional groups of the thermally curable resin(s) is critical to the gel time of the sealant composition, and the LC

penetration and contamination, adhesion, and reliability of the sealant. If the molar equivalent ratio is within the range, the thermally curable sealant will have an excellent balance of LC penetration, contamination, adhesion, and reliability in ODF process. If the range is smaller or higher, the overall performance of the sealant in ODF process will be deteriorated. Preferably, the molar equivalent ratio of epoxy group to (meth)acryloyl group and/or maleimide group is from about 0.2 to about 4.0.

The amount of the thermally curable resin(s) may be appropriately selected depending on the kind of the latent curing agent in the sealing composition. Preferably, the thermally curable resin(s) in the sealing composition is present in an amount of about 30% to about 90% by weight, and more preferably about 50% to about 80% by weight, based on the total weight of the components of the sealant composition.

Latent curing agent

A latent curing agent is based on a latent hardener that will be liberated at a certain temperature. The latent curing agent can be obtained easily from the commercially available latent curing agent and used alone or in a combination of two or more kinds. Specifically, the latent curing agent to be preferably used includes amine-based compounds, fine-powder-type modified amine and modified imidazole based compounds. Examples of the amine-based latent curing agent include dicyandiamide, hydrazides such as adipic acid dihydrazide, oxalic acid dihydrazide, malonic acid dihydrazide, succinic acid dihydrazide, glutaric acid dihydrazide, suberic acid dihydrazide, azelaic acid dihydrazide, sebacic acid dihydrazide, and phthalic acid dihydrazide. The modified amine and modified imidazole based compounds include core-shell type in which the surface of an amine compound (or amine adducts) core is coated with the shell of a modified amine product (surface adduction and the like) and master-batch type hardeners as a blend of the core-shell type curing agent with an epoxy resin.

Examples of commercially available latent curing agents include, but not limited to: Adeka Hardener EH-5011S (imidazole type), Adeka Hardener EH-4357S (modified amine type), Adeka Hardener EH-4357PK (modified amine type), Adeka Hardener EH-4380S (special hybrid type), Adeka Hardener EH-5001P (special modified type), Ancamine 2014FG/2014AS (modified polyamine), Ancamine 2441(modified polyamine), Ancamine 2337s (modified amine type), Fujicure FXR-1081(modified amine

type), Fujicure FXR-1020 (modified amine type), Sunmide LH-210 (modified imidazole type), Sunmide LH-2102 (modified imidazole type), Sunmide LH-2100 (modified imidazole type), Ajicure PN-23 (modified imidazole type), Ajicure PN-23J (modified imidazole type), Ajicure PN-31 (modified imidazole type), Ajicure PN-31J (modified imidazole type), Novacure HX-3722 (master batch type), Novacure HX-3742 (master batch type), Novacure HX-3613 (masterbatch type), and mixture thereof.

In one preferred embodiment, latent curing agents having a melting temperature of about 50 to about 110°C, particularly having a melting temperature of about 60 to about 100°C are suitable to be used in the thermally curable sealant composition.

Preferably, the latent curing agent in the sealing composition is present in an amount of about 1% to about 30% by weight, and more preferably about 5% to about 20% by weight, based on the total weight of the components of the sealant composition.

Other component

The sealant composition may further comprise one or more additives, resin components and the like to improve or modify properties of the sealant composition, such as flowability, dispensing or printing property, storage stability, curing property and physical property after curing.

The components that may be contained in the sealant composition as needed include, but are not limited to, for example, organic or inorganic filler, thixotropic agent, silane coupling agent, diluent, modifier, coloring agent such as pigment and dye, surfactant, preservative-stabilizer, plasticizer, lubricant, defoamer, leveling agent and the like. In particular, the sealant composition preferably comprises an additive selected from the group consisting of inorganic or organic filler, a thixotropic agent, a silane coupling agent, and combination thereof.

Suitable fillers, which can be optionally used in the present invention includes, but are not limited to, inorganic fillers such as silica, diatomaceous earth, alumina, zinc oxide, iron oxide, magnesium oxide, tin oxide, titanium oxide, magnesium hydroxide, aluminium hydroxide, magnesium carbonate, barium sulphate, gypsum, calcium silicate, talc, glass bead, sericite activated white earth, bentonite, aluminum nitride, silicon nitride, and the like; organic fillers, such as polymethyl methacrylate, polyethyl methacrylate, polypropyl methacrylate, polybutyl methacrylate, poly acrylonitrile,

polystyrene, polybutadiene, polypentadiene, polyisoprene, polyisopropylene, and the like. The filler may be used alone or in combination thereof.

Suitable thixotropic agents, which can be optionally used in the present invention includes, but are not limited to, talc, fume silica, superfine surface-treated calcium carbonate, fine particle alumina, plate-like alumina; layered compound such as montmorillonite, spicular compound such as aluminium borate whisker, and the like. Talc, fume silica and fine alumina are preferred thixotropic agents.

The useful silane coupling agents include vinyl methoxysilane, vinyl ethoxysilane, γ -chloropropyl trimethoxysilane, γ -aminopropyl trimethoxysilane, γ -aminopropyl triethoxysilane, N-(β -aminoethyl)- γ -aminopropyl trimethoxysilane, N-(β -aminoethyl)- γ -aminopropyl methyldimethoxysilane, γ -glycidoxypentyl trimethoxysilane, β -(3,4-epoxy cyclohexyl)ethyltrimethoxysilane, γ -methacryloxypropyl trimethoxysilane, γ -methacryloxypropyl methyldimethoxysilane, γ -mercaptopropyl trimethoxysilane and hexamethyl diisilazane. Of these, more preferable are γ -aminopropyl triethoxysilane, N-(β -aminoethyl)- γ -aminopropyl trimethoxysilane, N-(β -aminoethyl)- γ -aminopropyl methyldimethoxysilane, γ -glycidoxypentyl trimethoxysilane and β -glycidoxypentyl methyldimethoxysilane as amino- or epoxy-based silane coupling agents.

The thermally curable sealant composition according to the present invention essentially contains no photoinitiator, preferably contains no photoinitiator. Examples of the photoinitiator may include but not limited to acetophenone-based initiator such as diethoxyacetophenone and benzyl dimethyl ketal, benzoin ether-based initiator such as benzoin and benzoin ethyl ether, benzophenone-based initiator such as benzophenone and methyl o-benzoylbenzoate, α -diketone-based initiator such as butanedione, benzyl and aceto naphthophenone, and thio compound such as methylthioxanthone.

The thermally curable sealant composition according to the present invention may be obtained by mixing the aforementioned each component by means of, for example, a mixer such as a stirrer having stirring blades and a three roll mill. The viscosity of the sealant composition is not limited as long as it can be easily dispensed. Preferably, the sealant composition has a viscosity in the range of about 50 to about 500 Pa.s at 25°C.

In another aspect, the present invention also concerns a process of producing a liquid crystal display having a liquid crystal layer between a first substrate and a second substrate, said process comprising steps of:

- 1) applying the thermally curable sealant composition according to the present invention on a sealing region at a periphery of a surface of the first substrate;
- 2) conducting a first thermal curing of the thermally curable sealant composition at a temperature of about 40°C to about 75°C, and obtaining a partially cured product;
- 3) dropping liquid crystal on a central area encircled by the sealing region of the surface of the first substrate or the corresponding area of the second substrate, and forming the liquid crystal layer;
- 4) overlaying the second substrate on the first substrate; and
- 5) conducting a second thermal curing of the partially cured product.

The first substrate and the second substrate in the context of the present invention are transparent substrates made of glass or plastics. Generally, transparent electrodes, active matrix elements (such as TFT), alignment film(s), a color filter and the like are formed on at least one of the opposed faces of the two substrates. These constitutions may be modified according to the type of the LCD. The manufacturing method according to the present invention may be thought to be applied for any type of the LCD. The plastic substrate includes substrates made from plastics such as from polyester, from polyarylate, from polycarbonate and from poly(ether sulfones).

In the step (a), the sealant composition is applied on the periphery portion of the surface (the faces opposing to another substrate) of the first substrate of one of the substrates so as to lap around the substrate circumference in the shape of a frame. As described herein, the portion where the sealant composition is applied in the shape of a frame is referred as a seal region. At this moment, the sealant composition is flowable so that it can be applied and may be applied by a known method such as screen printing and dispensing.

In the step (b), the thermal curable sealant composition was treated with a first thermal pre-curing step under a temperature of about 40 to about 75°C for about 1 to about 10 min so as to thicken and temporally cure the sealant composition at such a level that displacement does not occur by handling, whereby the two substrates are temporally fixed. The temporary curing can prevent LC penetration after assembling

the opposite substrate preferably in vacuum condition. Also, it can prevent that the component of the sealant composition goes into the liquid crystal during the post curing.

In the step (c), the liquid crystal is then dropped onto the center region surrounded by the seal region in the shape of the frame on the surface of the first substrate. This step is preferably conducted under reduced pressure, preferably under vacuum condition. In the step (d), said second substrate is then placed over said first substrate, and a second/post thermal curing is conducted to the partially cure sealant so as to completely cure the sealant composition. The post curing normally is conducted under a temperature of about 80°C to about 150°C for about 30 to about 90 min. By the aforementioned process, the major part of the LCD panel is completed.

The sealant composition to be used in the present invention may be also used for other applications than the ODF process, especially the pure thermal curing ODF process as mentioned above, for LCD manufacturing, where precise assembling without displacement is necessary.

The thermal curable sealant composition possesses a gel time at 90°C of less than about 3 min. The gelling of the thermal curable sealant composition can be determined by inserting or contacting a wood stick in the sealant composition and pulling the wood stick out of the sealant composition during the thermal curing, and visually checking whether a thread of the sealant composition forms. At the beginning of curing, the sealant composition is flowable, and no sealant thread forms between the end of the stick and the sealant. With the continuing of thermal curing and gelling, the flowability of the sealant composition decreases and its viscosity increases so that thread forms when inserting the wood stick into the sealant composition and pulling the wood stick out of the sealant composition. The gel time is defined as the time when no thread adheres to the wood stick from the beginning of thermal curing. If the gel time is more than 3 min, even after the viscosity of the sealant composition increases after the first thermal curing, there is high risk of liquid crystal penetration during the post curing.

Examples

The following examples are intended to assist one skilled in the art to better understand and practice the present invention. The scope of the invention is not limited by the examples but is defined in the appended claims. All parts and percentages are based on weight unless otherwise stated.

Materials

Thermally curable resin 1:

Ebecryl 3708, modified bisphenol A type epoxy diacrylate, manufactured by Cytec Industries Inc.

Thermally curable resin 2:

YL980, bisphenol A type epoxy, manufactured by Mitsubishi Chemical Inc.

Thermally curable resin 3:

24-414A, bismaleimide resin, manufactured by Henkel Corporation.

Thermally curable resin 4:

378538, maleimide and epoxy hybrid resin (molar equivalent ratio of epoxy group to maleimide group is about 1), manufactured by Henkel Corporation.

Thermally curable resin 5:

EA1010N epoxy and acrylate hybrid resin (molar equivalent ratio of epoxy group to acrylate group is about 1), manufactured by Shin-nakamura Chemical Co., Ltd.

Silane coupling agent:

Silquest A-187, epoxy functional silanes, manufactured by Momentive Performance Materials Inc.

Filler:

SO-E2, silica fillers, manufactured by Admatechs Co., Ltd.

Latent curing agent:

EH-4357S, polyamine type latent cure agent, manufactured by Adeka Corporation.

Photoinitiator:

OXE02, oxime ester radical photoinitiators, manufactured by BASF.

Preparation

The thermally curable sealant compositions having the formulations shown in Table 1 according to the present invention were prepared as Examples (EXs) 1 to 7. All components were sufficiently mixed by a stirrer and then a three roll miller to obtain a homogenous sealant composition. After being filtered through a 5 μ m mesh, the composition was degassed to remove the bubble in the composition. Comparative examples (CEs) 1 to 5 were also prepared in the same way except the presence of certain component and weight ratio and the formulations are also listed in Table 1.

Table 1. Formulations and properties of thermally curable sealant compositions (parts by weight)

Component	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex. 6	Ex.7	CE.1	CE.2	CE.3	CE.4	CE.5
Thermally curable resin 1	5	10	-	-	5	15	17	20	-	-	10	18.5
Thermally curable resin 2	15	10	-	-	10	5	3	-	20	-	10	1.5
Thermally curable resin 3	-	-	-	-	5	-	-	-	-	20	-	-
Thermally curable resin 4	-	-	20	-	-	-	-	-	-	-	-	-
Thermally curable resin 5	-	-	-	20	-	-	-	-	-	-	-	-
Silane coupling agent	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Filler	2	2	2	2	2	2	2	2	2	2	2	2
Latent curing agent	10	10	5	5	10	10	10	6	10	8	10	10
Photoinitiator	-	-	-	-	-	-	-	-	-	-	0.1	-
Molar equivalent ratio*	0.23	0.70	0.71	1.00	0.61	2.10	3.98	-	-	-	0.61	8.66
Gel time@90°C (min)	1.2	1.5	1.8	1.2	1.5	2.0	2.5	5.5	1.0	3.5	1.5	3.0

* "Molar equivalent ratio" refers to the molar equivalent ratio of epoxy group to (meth)acryloyl group and/or maleimide group in the thermally curable resin(s).

Test methods and results

Gel time

A glass plate was preheated to 90°C and equilibrated for 10 min. Then 1 gram of the inventive examples and comparative examples were each weighed out on the hot plate, and the gel time of each example was recorded. The gel time was determined by inserting or contacting a wood stick in the sealant composition and pulling the wood stick out of the sealant composition, and visually checking whether a thread of the sealant composition formed. The testing results of gel time is shown in Table 1.

Viscosity

The viscosity at 25°C of each example was measured by a rheometer (TA, AR2000 ex) at a shear rate of 1.5 s^{-1} , and the thixotropic index (TI) was counted by the viscosity at $1.5 \text{ s}^{-1} / 15 \text{ s}^{-1}$.

Adhesion strength

The sealant composition of each example was dispensed on the ITO glass (50 mm × 60 mm) having an “L” shape, with the line width is 0.5 mm. Each examples were placed into an oven for a first curing in terms of the first heat step condition. The opposite ITO glass plate was superposed and the two glass plates were clamped. The examples were then placed into an oven at 120°C for 1 hour to completely cure the sealant composition. One glass plate was pulled by an Instron strength tester in a speed of 1.27 mm/s. The average adhesion strength of 5 specimens for each example was recorded respectively.

For Comparative Example 4, after dispensing the sealant composition on the substrate, the opposite glass substrate was directly overlaid, and the two glass substrates were clamped. One of the substrates was covered by a mask with 30% UV light transmission. The specimen was placed into a UV oven for 3000 mJ/cm² (100 mW/cm² × 30s) radiation with the mask, and then post cured under 120°C for 1 hour.

To test the adhesion strength after aging, another 5 specimens for each example were prepared and placed into a Presssure Cooking Test oven (at 120°C, 100% humidity, 2 atm, manufactured by ESPEC Corporation, Model of EHS-221M) for 24

hours, and then the adhesion strength was tested in an Instron strength tester by recording the average data.

Voltage Holding Ratio (VHR)

0.03 g of each sealant composition and 0.27 g of liquid crystal was weighed out, mixed and put into a 120°C oven for 1 hour. The mixture was removed and held at room temperature, and filled into a specific test cell. VHR was tested by Toyo 6254 analyzer (manufactured by Toyo Corporation) at 60°C, 5V and 60Hz.

NI point change (from nematic to isotropic phase of liquid crystal)

0.03 g of each sealant composition and 0.27 g of liquid crystal was weighed out, mixed and put into a 120°C oven for 1 hour. The mixture was removed and put into a DSC (differential scanning calorimetry) pan, and the temperature was ramped up at 5°C /min to 120°C. The temperature change between pure liquid crystal and liquid crystal mixture with the sealant composition was recorded.

Water vapor transmitting ratio (WVTR)

0.5 g of each sealant composition was filled into a specific module, and was cured at 120°C for 1 hour, and a round specimen more than 10cm² with thickness of 0.3mm was obtained. Then the specimen was put into a Mocon PERMATRAN-W® Model 3/61 instrument (manufactured by Mocon Inc.) to test the water vapor transmitting ratio at 50°C and 100% RH.

LCD panel sealing performance

1 part by weight of 3.5 µm spacer was added to 100 parts by weight of the sealant composition. After degassing, the sealant composition was dispensed by a Musashi screw dispensing machine in a rectangular shape at periphery of the surface of a glass substrate (200 mm x 200 mm). A larger rectangular shape of sealant composition surrounding the rectangular shape was dispensed as the close dummy seal, the diameter of dispensing nozzle is 0.15 mm, the dispensing speed is 70 mm/s, the final line width of the resin composition is 500 µm.

The substrate dispensed with the sealant was put into an oven for a first curing in terms of the curing condition as shown in Table 2. The substrate was taken out and later some grams liquid crystal (105% LC quantity calculated in term of the sealing volume) was dripped on the central area encircled by the sealing region and degassed in vacuum, followed by overlaying a second glass substrate on the first

substrate at 3 Kpa. After the attachment of two glass substrates, the vacuum was released to obtain the LCD cell, and then the assembly was put into a 120°C oven to apply the second curing.

For Comparative Example 4, the liquid crystal was directly dripped onto the substrate after dispensing, and then the second substrate was attached, with covering a mask which only 30% UV light can transmit. A UV radiation of 3000 mJ/cm² (100 mW/cm² × 30s) was applied to the substrates attaching by the sealant. The LCD cell was put into a 120°C oven for post curing.

The LCD cell was then checked under microscope. If the penetration width from liquid crystal to the frame cured sealant composition is less than 50 μm, it was recorded as “good” for the penetration resistance. If the penetration width from liquid crystal to the frame cured resin composition is in the range of 50 to 200 μm, it was recorded as “generic” for the penetration resistance. And if the penetration width from liquid crystal to the frame cured resin composition is more than 200 μm, it was recorded as “bad” for the penetration resistance.

In the LCD performance test, “Mura” effect would occur if the colour inconsistency appeared when applying a voltage of 5V direct current on the LCD cell. The Mura issue normally occurred near the frame of the LCD cell. If there was no obvious colour inconsistency near the frame, the Mura effect performance was recorded as “good”. If there was slight colour inconsistency near the frame, the Mura effect performance was recorded as “generic”. And if there was serious colour inconsistency near the frame, the Mura effect performance was recorded as “bad”.

The LCD cells as prepared were each placed in an oven under 60°C and 90% RH for 3 days aging. Then the Mura effect of each LCD cell after aging was tested by applying a voltage of 5V direct current on the LCD cell. If there was no obvious colour inconsistency near the frame, the Mura effect resistance was recorded as “good”. If there was slight colour inconsistency near the frame, the Mura effect resistance was recorded as “generic”. And if there was serious colour inconsistency near the frame, the Mura effect resistance was recorded as “bad”.

The testing results of viscosity, adhesion strength, VHR, NI change point, WVTR and LCD panel sealing performance are shown in Table 2.

Table 2. Testing conditions and results

	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	CE.1	CE.2	CE.3	CE.4
Viscosity@25°C(Pa.s)	310	496	485	498	389	320	230	170	495
TI	1.23	1.41	1.23	1.21	1.3	1.08	1.45	1.15	1.41
Adhesion strength before PCT (N)	3.9	4.73	3.9	4.2	4.6	3.33	3.39	4.24	4.1
Adhesion strength after PCT(N)	3.6	4.47	3.8	3.9	4.5	1.76	1.66	4.13	3.9
VHR (%)	98.9	98.8	98.8	99.1	98.8	98.7	99.0	98.6	98.8
NI point change (°C)	1.6	1.5	1.6	1.4	1.4	2.0	2.2	1.8	1.6
WWTR (g/m ² /day)	13.8	14.2	19.4	18.8	12.1	65	9.6	16.8	14.2
Temperature for first curing (°C)	65	60	65	60	60	75	65	70	-
Heating duration for first curing (min)	3	5	3	5	5	5	3.5	5	-
Temperature for second curing (°C)	120	120	120	120	120	120	120	120	-
Heating duration for second curing (h)	1	1	1	1	1	1	1	1	-
Penetration resistance	Good	Good	Good	Good	Good	Bad	Good	Generic	Generic
Mura effect resistance	Good	Good	Good	Good	Good	Generic	Bad	Generic	Generic
Mura effect resistance after aging	Good	Good	Good	Good	Good	Bad	Bad	Generic	Generic

As shown in Tables 1 and 2, the inventive examples of sealant composition possess satisfactory properties such as a gel time 90°C of less than 3 min, good adhesion, dispensing property and exhibited excellent resistance to LC penetration, LC contamination and Mura effect.

As for CEs. 1 and 3, the curing of the sealant composition was cured by the Michael addition reaction between acrylate/maleimide and latent amine. The curing speed is very slow as shown in the gel time at 90°C. In the test, even a higher temperature and more duration was used to pre-cure the sealant composition close to the critical margin, it still had bad penetration resistance during 120°C post curing, and the slower curing speed consequentially induced an interaction between the sealant composition and LC, and resulted in LC contamination, which rendered the Mura effect resistance as generic. Due to a poor barrier performance, the Mura effect resistance became worse in the reliability test.

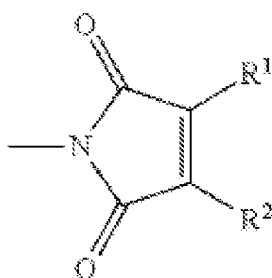
As for CE. 2, the sealant composition was cured by the reaction of epoxy and latent amine. Although the reaction speed was fast as shown in gel time test, the Mura performance is bad as the epoxy could easily go into the liquid crystal, and contaminate the LC, which is shown by a NI point change of 2.2°C, the largest of all these examples.

As for CE. 4, The LCD cell was fixed by applying 3000 mJ/cm² UV light, and then cured under 120°C for 1 hour. A mask was used so as to keep 70% of the UV light blocked by the mask, and the majority area of the substrate were in shadow area. As shown in the test, the sealant composition under the shadow area had serious curing issues, and resulted in a unsatisfactory LC penetration and contamination resistance and was also generic in Mura effect resistance.

From above results, it was clearly demonstrated that the sealant compositions according to the present invention is suitable to be used in a two-step thermal curing ODF process as such sealant compositions well balanced the barrier property, adhesion strength, resistance to LC penetration and Mura effect.

What is claimed is:

1. A thermally curable sealant composition, comprising:
 one or more thermally curable resins having a group selected from epoxy group, (meth)acryloyl group, maleimide group, and combination thereof, and a latent curing agent,
 in which the molar equivalent ratio of epoxy group to (meth)acryloyl group and/or maleimide group in the one or more thermally curable resins is from 0.1 to 5.
2. The thermally curable sealant composition according to claim 1, wherein the one or more thermally curable resins are selected from epoxy resin, (meth)acrylate resin, maleimide resin, a hybrid resin having at least two groups selected from epoxy group, (meth)acryloyl group, maleimide group, and mixture thereof.
3. The thermally curable sealant composition according to claim 2, wherein the epoxy resin is selected from bisphenol-A-type epoxy resin, bisphenol-F-type epoxy resin and bisphenol-S-type epoxy resin.
4. The thermally curable sealant composition according to claim 2, wherein the (meth)acrylate is epoxy (meth)acrylate, preferably fully (meth)acrylated epoxy.
5. The thermally curable sealant composition according to claim 2, wherein the maleimide resin having one or more, preferably one or two substructures represented by moiety (I)



(1)

wherein R^1 and R^2 are H or alkyl group having 1 to 6 carbons, or R^1 and R^2 together is alkylene group having 2 to 6 carbons.

6. The thermally curable sealant composition according to claim 1, wherein the one or more thermally curable resins are two or more, preferably two thermally

curable resins selected from epoxy resin, (meth)acrylate resin and maleimide resin.

7. The thermally curable sealant composition according to claim 1, wherein the one or more thermally curable resins is a hybrid resin having at least two groups selected from epoxy group, (meth)acryloyl group, and maleimide group.
8. The thermally curable sealant composition according to any of claims 1 to 4, wherein the molar equivalent ratio of epoxy group to (meth)acryloyl group and/or maleimide group in the one or more thermally curable resins is from 0.2 to 4.0.
9. The thermally curable sealant composition according to any of claims 1 to 8, wherein the one or more thermally curable resin in the sealing composition is present in an amount of 30% to 90% by weight, and more preferably 50% to 80% by weight, based on the total weight of the components of the sealant composition.
10. The thermally curable sealant composition according to any of claims 1 to 4, wherein the latent curing agent has a melting temperature of 50 to 110°C, particularly having a melting temperature of 60 to 100°C.
11. The thermally curable sealant composition according to any of claims 1 to 5, wherein the latent curing agent is present in an amount of 1% to 30% by weight, and more preferably 5% to 20% by weight, based on the total weight of the components of the sealant composition.
12. The thermally curable sealant composition according to any of claims 1 to 6, wherein the thermally curable sealant composition essentially contains no photoinitiator, preferably contains no photoinitiator.
13. The thermally curable sealant composition according to any of claims 1 to 6, wherein the thermally curable sealant composition has a gel time at 90°C of less than 3 min.

14. A process of producing a liquid crystal display having a liquid crystal layer between a first substrate and a second substrate, said process comprising steps of:
 - 1) applying the thermally curable sealant composition according to any of claims 1 to 13 on a sealing region at a periphery of a surface of the first substrate;
 - 2) conducting a first thermal curing of the thermally curable sealant composition at a temperature of 40°C to 75°C, and obtaining a partially cured product;
 - 3) dropping liquid crystal on a central area encircled by the sealing region of the surface of the first substrate or the corresponding area of the second substrate, and forming the liquid crystal layer;
 - 4) overlaying the second substrate on the first substrate; and
 - 5) conducting a second thermal curing of the partially cured product.

15. The use of the thermally curable sealant composition according to any of claims 1 to 13 or the process of producing a liquid crystal display according to claim 14 in one-drop-filling process of manufacturing liquid crystal devices.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2017/070936

A. CLASSIFICATION OF SUBJECT MATTER

C09K 3/10(2006.01)i; C08G 59/17(2006.01)i; C08G 59/44(2006.01)i; C08F 290/14(2006.01)i; G02F 1/1339(2006.01)i

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)

C09K; C08G; C08F; G02F

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)

CNPAT, CNKI, WPI, EPODOC, ISI, CA, STN: henkel, thermal, curable, sealant, epoxy, (meth) acryloyl, maleimide, latent curing agent, molar equivalent ratio, LCD, liquid crystal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	CN 101676315 A (HENKEL CORP.) 24 March 2010 (2010-03-24) description page 3 paragraph 2-page 4 paragraph 2, page 5 paragraph 6-page 6 paragraph 2	1-2, 5-6, 8-15
X	CN 102812396 A (MITSUI CHEMICALS, INC.) 05 December 2012 (2012-12-05) description paragraphs [0020]-[0029]	1-4, 6-11, 13-15
X	CN 102640040 A (SEKISUI CHEM. CO. LTD.) 15 August 2012 (2012-08-15) description paragraphs [0010], [0015]-[0018], [0044]	1-4, 6-15
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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

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Date of mailing of the international search report

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Name and mailing address of the ISA/CN

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2017/070936

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				US	2013128435	A1	23 May 2013
				KR	20130031370	A	28 March 2013
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