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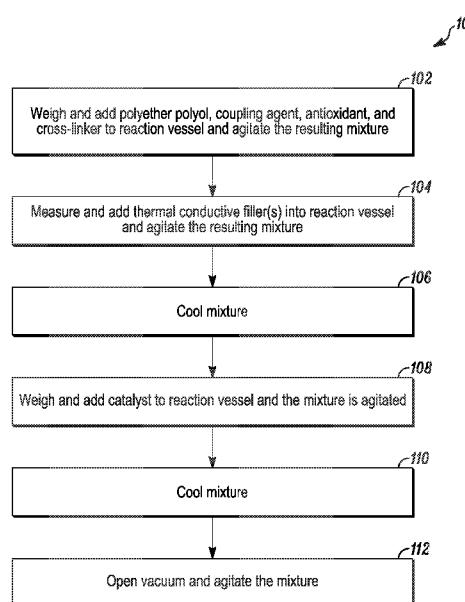
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(54) Title: SILICONE-FREE THERMAL GEL



(57) **Abstract:** The present disclosure provides a silicone free gel that is useful in transferring heat from heat generating electronic devices, such as computer chips, to heat dissipating structures, such as heat spreaders and heat sinks. The thermal interface material includes a polyether polyol, a cross-linker, a coupling agent, an antioxidant, a catalyst, and at least one thermally conductive filler.

FIG. 1



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SILICONE-FREE THERMAL GEL

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Application No. 16/105,456, entitled SILICONE-FREE THERMAL GEL, filed August 20, 2018, and also claims the benefit under Title 35, U.S.C. §119(e) of U.S. Provisional Patent Application Serial No. 62/555,954, entitled SILICONE-FREE THERMAL GEL, filed on September 8, 2017, the disclosures of which are expressly incorporated by reference herein in their entireties.

FIELD OF THE INVENTION

[0002] The present disclosure relates generally to thermal interface materials, and more particularly to a silicone-free thermal gel used in thermal interface materials.

DESCRIPTION OF THE RELATED ART

[0003] Thermal interface materials (TIMs) and thermal gels are widely used to dissipate heat from electronic components, such as central processing units, video graphics arrays, servers, game consoles, smart phones, LED boards, and the like. Thermal interface materials are typically used to transfer excess heat from the electronic component to a heat spreader, such as a heat sink.

[0004] Traditional thermal gels are silicone containing compounds, which can be a good matrix for fillers and provide good flowability for the final composite. However, for some high voltage applications, some of the silicone containing components of the composite could potentially leak from the composite, resulting in a residue which may partially burn, and non-conductive silicon oxide may form on the electrode, which may affect the electrode conductivity and further damage the device functionality.

[0005] Improvements in the foregoing are desired.

SUMMARY OF THE INVENTION

[0006] The present disclosure provides a thermal interface material in the form of a silicone free gel that is useful in transferring heat from heat generating electronic

devices, such as computer chips, to heat dissipating structures, such as heat spreaders and heat sinks. The thermal interface material includes a polyether polyol, a cross-linker, a coupling agent, an antioxidant, a catalyst, and at least one thermally conductive filler.

[0007] In one exemplary embodiment, a thermal gel is provided. The thermal gel includes a matrix including at least one polyether polyol present in an amount between 1 wt.% and 10 wt.% based on the total weight of the thermal gel; a catalyst present in an amount between 0.3 wt.% and 0.6 wt.% based on the total weight of the thermal gel; a crosslinker including a plurality of reactive amine groups, the crosslinker present in an amount between 0.5 wt.% and 2 wt.% based on the total weight of the thermal gel; a coupling agent present in an amount between 0.1 wt.% and 5 wt.% based on the total weight of the thermal gel; and at least one thermally conductive filler present in an amount between 80 wt.% and 98 wt.% based on the total weight of the thermal gel.

[0008] In one more particular embodiment of any of the above embodiments, the thermal gel further includes: an antioxidant present in an amount between 0.2 wt.% and 0.4 wt.% based on the total weight of the thermal gel. In one more particular embodiment of any of the above embodiments, the thermal gel includes silicone based components in an amount less than 1 wt.% based on the total weight of the thermal gel. In one more particular embodiment of any of the above embodiments, the thermal gel has a cure temperature of below 150°C. In one more particular embodiment of any of the above embodiments, the polyol is a polyether polyol, the polyether polyol is a bi-ol polymer with a molecular weight between 200 and 10000 Daltons. In one more particular embodiment of any of the above embodiments, the at least one polyether polyol is present in an amount between 5 wt.% and 10 wt.% based on the total weight of the thermal gel. In one more particular embodiment of any of the above embodiments, the crosslinker is an alkylated melamine formaldehyde resin.

[0009] In one more particular embodiment of any of the above embodiments, the catalyst includes amine neutralized benzene sulfonic acid, amine neutralized dinonylnaphthalene disulfonic acid or amine neutralized dinonylnaphthalenesulfonic acid or other type of thermal acid generator. In one more particular embodiment of any of the above embodiments, the antioxidant includes at least one antioxidant

selected from the group consisting of a phenol-type antioxidant, an amine-type antioxidant, or a sterically hindered, sulfur containing phenolic antioxidant. In one more particular embodiment of any of the above embodiments, the at least one thermally conductive filler includes a first thermally conductive filler and a second thermally conductive filler; the first thermally conductive filler is present in an amount between 35 wt.% and 50 wt.% based on the total weight of the thermal gel; the second thermally conductive filler is present in an amount between 15 wt.% and 25 wt.% based on the total weight of the thermal gel; and the third thermally conductive filler is present in an amount between 15 wt.% and 25 wt.% based on the total weight of the thermal gel.

[0010] In another exemplary embodiment, a method of preparing a thermal gel is provided. The method includes: adding at least one polyether polyol, at least one coupling agent, at least one antioxidant, and at least one crosslinker to a reaction vessel to form a mixture; the at least one polyether polyol present in an amount between 1 wt.% and 10 wt.% based on the total weight of the thermal gel; the at least one crosslinker including a plurality of reactive amine groups, the crosslinker present in an amount between 0.5 wt.% and 2 wt.% based on the total weight of the thermal gel; the at least one coupling agent present in an amount between 0.1 wt.% and 5 wt.% based on the total weight of the thermal gel; adding a catalyst to the reaction vessel, the catalyst present in an amount between 0.3 wt.% and 0.6 wt.% based on the total weight of the thermal gel; agitating the mixture; adding at least one thermally conductive filler to the reaction vessel, wherein the at least one thermally conductive filler present in an amount between 80 wt.% and 98 wt.% based on the total weight of the thermal gel; and cooling the mixture to room temperature.

[0011] In one more particular embodiment of any of the above embodiments, the at least one antioxidant is present in an amount between 0.2 wt.% and 0.4 wt.% based on the total weight of the thermal gel. In one more particular embodiment of any of the above embodiments, the thermal gel includes silicone containing components in an amount less than 1 wt.%. In one more particular embodiment of any of the above embodiments, the polyol is a polyether polyol, the polyether polyol is a bi-ol polymer with a molecular weight between 200 and 10000 Daltons. In one more particular embodiment of any of the above embodiments, the at least one polyether polyol is present in an amount between 5 wt.% and 10 wt.% based on the

total weight of the thermal gel. In one more particular embodiment of any of the above embodiments, the crosslinker is an alkylated melamine formaldehyde resin.

[0012] In one more particular embodiment of any of the above embodiments, the antioxidant includes at least one antioxidant selected from the group consisting of a phenol-type antioxidant, an amine-type antioxidant, or a sterically hindered, sulfur containing phenolic antioxidant. In one more particular embodiment of any of the above embodiments, the catalyst includes amine neutralized benzene sulfonic acid, amine neutralized dinonylnaphthalene disulfonic acid or amine neutralized dinonylnaphthalenesulfonic acid or other type of thermal acid generator. In one more particular embodiment of any of the above embodiments, the at least one thermally conductive filler includes a first thermally conductive filler, a second thermally conductive filler, and a third thermally conductive filler; the first thermally conductive filler is present in an amount between 35 wt.% and 50 wt.% based on the total weight of the thermal gel; the second thermally conductive filler is present in an amount between 15 wt.% and 25 wt.% based on the total weight of the thermal gel; and the third thermally conductive filler is present in an amount between 15 wt.% and 25 wt.% based on the total weight of the thermal gel.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The above-mentioned and other features and advantages of this disclosure, and the manner of attaining them, will become more apparent and the invention itself will be better understood by reference to the following description of embodiments of the invention taken in conjunction with the accompanying drawings, wherein:

[0014] FIG. 1 is a flowchart relating to a method of preparing a silicone-free thermal gel;

[0015] FIG. 2 is related to Example 1 and shows the samples after undergoing a thermal cycling test;

[0016] FIG. 3 is related to Example 2 and shows the sample after undergoing a baking test; and

[0017] FIG. 4 is related to Example 2 and shows the samples after undergoing a thermal cycling test;

[0018] FIG. 5 is related to Examples 5-7 and shows samples after undergoing a thermal cycling test;

[0019] FIG. 6 is related to Examples 5-7 and shows samples after undergoing a baking test;

[0020] FIG. 7 illustrates a dispensing instrument used with Examples 5-7 to measure the dispense rate of the samples; and

[0021] FIG. 8 is a flowchart illustrating a method of preparing the thermal gel in accordance with the present disclosure; and

[0022] FIG. 9 is a perspective view of a dispenser used with the thermal gel of the present disclosure.

[0023] Corresponding reference characters indicate corresponding parts throughout the several views. The exemplifications set out herein illustrate exemplary embodiments of the invention and such exemplifications are not to be construed as limiting the scope of the invention in any manner.

DETAILED DESCRIPTION

A. Thermal Gel

[0024] The present invention relates to a thermal gel that is useful in transferring heat away from electronic components. In one exemplary embodiment, the thermal gel includes a polyether polyol, a cross-linker, a coupling agent, an antioxidant, a catalyst, and at least one thermally conductive filler.

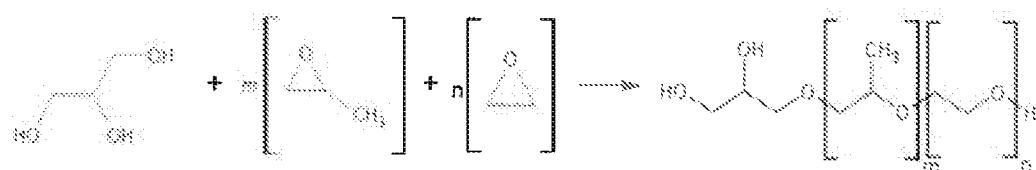
1. Polyether Polyol

[0025] The thermal gel includes one or more polyether polyols. The polyether polyols function to form a polymer matrix. The polyether polyols include at least one hydroxide (-OH) group in the polymer chain. The hydroxide groups provide crosslinking points between the polyols. In one embodiment, the polyether polyols comprise a bi-ol or a tri-ol which include two and three hydroxide groups in the polymer chain, respectively.

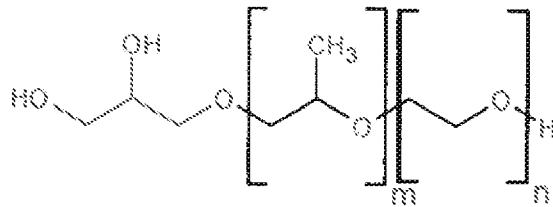
[0026] The hydroxide groups also inversely affect the flowability of the formulations. For example, if the hydroxyl group content of the polyols is too high, the final flowability of the formulation may be limited due to the high extent of resulting crosslinking. In addition, the molecular weight of the polyether polyols also affects the flow properties of the thermal gel. Polyether polyols with substantially high molecular weights reduce the final flowability of formulation while polyether polyols with substantially low molecular weights are unable to provide a stable matrix frame for filler loading.

[0027] Exemplary polyether polyols include 330N available from Sinopec Shanghai Gaogia Petrochemical Co., Ltd. or GEP 828 available from Sinopec Shanghai Gaogia Petrochemical Co., Ltd. Other exemplary polyether polyols include: NJ-360N available from JURONG NINGWU Material Company Limited, GY-7500E available from KUKDO Chemical (KunShan) Co., LTD, SD-75 available from Shanghai Dongda Chemistry, SD-820 available from Shanghai Dongda Chemistry, SD-3000L available from Shanghai Dongda Chemistry, SD-7502 available from Shanghai Dongda Chemistry, and SD-8003 available from Shanghai Dongda Chemistry.

[0028] In one exemplary embodiment, a polyether polyol is prepared by the polymerization of glycerine with propylene oxide and ethylene oxide in the presence of a base catalyst according to the following equation, followed by fine purification.



[0029] The polyether polyol has the following formula shown below where the values of m and n are dependent on the amount and ratio of propylene epoxide to ethylene oxide as set forth by the reaction conditions. In an embodiment, the values of m and n may each be 1 or greater.



[0030] In some exemplary embodiments, the thermal gel includes one or more polyether polyols in an amount as little as 1 wt.%, 3 wt.%, 5 wt.%, 7 wt.%, as great as 10 wt.%, 14 wt.%, 18 wt.%, 20 wt.% or within any range defined between any two of the foregoing values, such as 1 wt.% to 10 wt.%, 5 wt.% to 10 wt.%, or 1 wt.% to 20 wt.% for example, based on the total weight of the thermal gel.

[0031] In some exemplary embodiments, the thermal gel includes one or more polyether polyols having a weight average molecular weight (as measured by Gel Permeation Chromatography (GPC)) of as little as 200 Daltons, 400 Daltons, 600 Daltons, 800 Daltons, as great as 1000 Daltons, 5000 Daltons, 10000 Daltons, 20000 Daltons, or within any range defined between any two of the foregoing values, such as 200 Daltons to 20000 Daltons, or 400 Daltons to 10000 Daltons, for example.

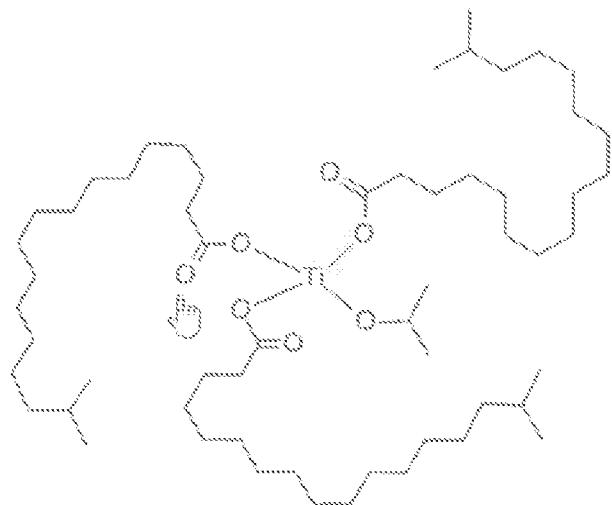
2. Coupling Agent

[0032] In an exemplary embodiment, the thermal gel includes one or more coupling agents that function to interact with both the thermally conductive filler(s) and the polymer matrix to promote a strong bond at the interface, which helps to break filler particle aggregates and disperse the filler particles into the polymer matrix. In addition, the one or more coupling agents create better adhesion of thermally conductive filler(s) to the polyol polymer matrix.

[0033] Exemplary coupling agents include silane coupling agents and organometallic compounds, such as include titanate coupling agents and zirconate coupling agents. Exemplary silane coupling agents include silane coupling agents with an aliphatic group. Exemplary coupling agents include titanium IV 2,2 (bis 2-propenolatomethyl)butanolato, tris(dioctyl)pyrophosphato-O; titanium IV 2-propanolato, tris(dioctyl)-pyrophosphato-O) adduct with 1 mole of dilsooctyl phosphite; titanium IV bis(dioctyl)pyrophosphato-O, oxoethylenediolato, (Adduct),

bis(dioctyl) (hydrogen)phosphite-O; titanium IV bis(dioctyl)pyrophosphato-O, ethylenediolato (adduct), bis(dioctyl)hydrogen phosphite; zirconium IV 2,2-(bis 2-propenolatomethyl)butanolato, tris(diisooctyl)pyrophosphato-O; zirconium IV 2,2-bis(2-propenolatomethyl) butanolato, cyclo di[2,2-(bis 2-propenolatomethyl) butanolato], pyrophosphato-O,O, and hexadecyltrimethoxysilane. In another exemplary embodiment, the coupling agent is KR-TTS available from Kenrich Chemical Company.

[0034] In one exemplary embodiment, the coupling agent is titanium IV 2-propanolato, tris isoctadecanoato, having the following structure shown below (e.g., Kenrich TTS).



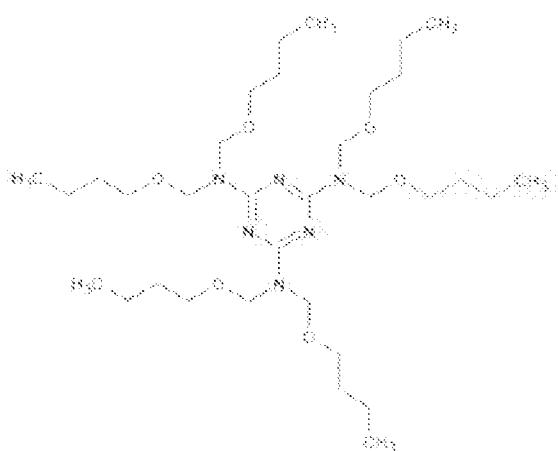
[0035] In some exemplary embodiments, the thermal gel includes one or more coupling agents in an amount as little as 0.01 wt.%, 0.1 wt.%, 1.0 wt.%, as great as 2.0 wt.%, 3.0 wt.%, 4.0 wt.%, 5.0 wt.%, or within any range defined between any two of the foregoing values, such as 0.1 wt.% to 5 wt.% or 0.1 wt.% to 1 wt.%, for example, based on the total weight of the thermal gel.

3. Crosslinker

[0036] In exemplary embodiments, the thermal gel includes a crosslinker to enable crosslinking between polyols — e.g., the crosslinker reacts with the hydroxy groups of the polyol ether molecules. An exemplary crosslinker includes alkylated melamine formaldehyde resin. Other exemplary crosslinkers include Cymel® crosslinkers available from Allnex, for example, Cymel 1158, Cymel 303LF, Cymel

370, Cymel 1156, Cymel 683, and CYMEL MI-97-IX.

[0037] In one exemplary embodiment, the crosslinker is a butylated melamine-formaldehyde with a medium to high degree of alkylation, a low to medium methylol content, and a medium to high amino functionality (e.g., Cymel 1158). In a further exemplary embodiment, the crosslinker has the following structure shown below.



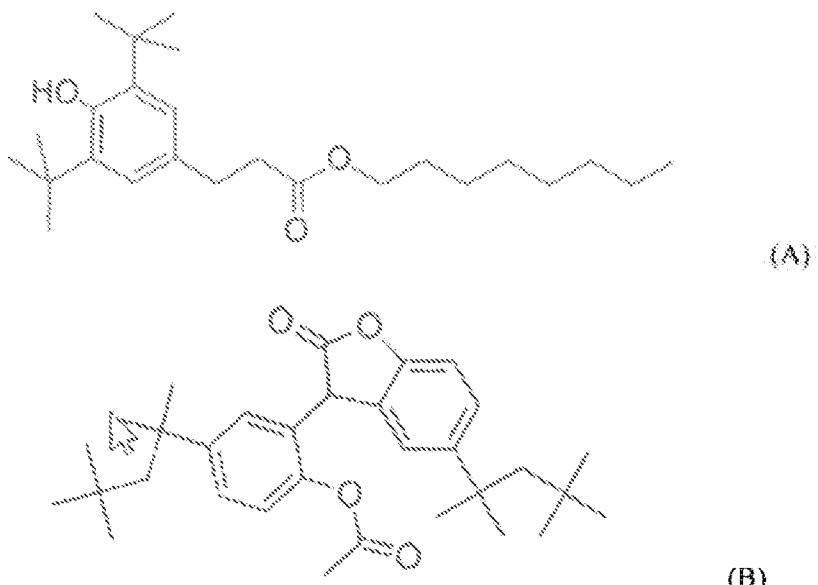
[0038] In some exemplary embodiments, the thermal gel includes the one or more crosslinkers in an amount as little as 0.1%, 0.50 wt.%, 0.75 wt.%, 1 wt.%, as great as 2 wt.%, 3 wt.%, 5 wt.%, 10 wt.%, or within any range defined between any two of the foregoing values, such as 0.5 wt.% to 2 wt.% or 0.75 wt.% to 2 wt.%, for example, based on the total weight of the thermal gel.

4. *Antioxidant*

[0039] In some exemplary embodiments, the thermal gel comprises one or more antioxidants that function to terminate oxidation reactions and reduce the degradation of organic compounds (e.g., polymers reacting with atmospheric oxygen directly to produce free radicals). The antioxidant absorbs free radicals to inhibit free-radical induced degradation. Exemplary antioxidants include phenol type, amine type antioxidants, or any other suitable type of antioxidant, or a combination thereof. The phenol or amine type antioxidant may also be a sterically hindered phenol or amine type antioxidant. Exemplary phenol type antioxidants include octadecyl 3-(3,5-di-(tert)-butyl-4-hydroxyphenyl) propionate. Exemplary amine type antioxidants include 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino)

phenol. Exemplary sterically hindered antioxidants include sterically hindered sulfur containing phenolic antioxidants. Exemplary antioxidants include the Irganox ® antioxidants available from BASF, such as Irganox 1135, Irganox 5057. Another exemplary antioxidant may include IRGASTAB PUR68.

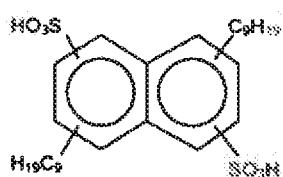
[0040] In one exemplary embodiment, the antioxidant is a mixture of Octyl-3,5-di-tert-butyl-4-hydroxy-hydrocinnamate (Formula A shown below) and 2(3H)-Benzofuranone, 3-[2-(acetoxy)-5-(1,1,3,3-tetramethylbutyl)phenyl]-5-(1,1,3,3-tetramethylbutyl)- (Formula B shown below) (e.g., PUR 68).



[0041] In some exemplary embodiments, the thermal gel includes the one or more antioxidants in an amount as little as 0.1 wt.%, 0.2 wt.%, 0.4 wt.%, as great as 0.6 wt.%, 0.8 wt.%, 1 wt.%, or within any range defined between any two of the foregoing values, such as 0.2 wt.% to 0.4 wt.%, or 0.1 wt.% to 1 wt.%, for example, based on the total weight of the thermal gel.

5. Catalyst

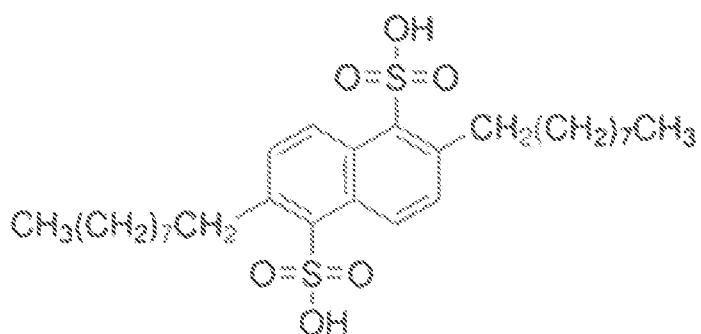
[0042] The thermal gel further includes one or more catalysts to catalyze the crosslinking of the polyol and the crosslinker resin. Exemplary catalysts include thermal acid generators, such as sulfonic acid group containing materials. Exemplary free acids of sulfonic acid groups containing catalysts may have the general formula shown below:



[0043] Exemplary sulfonic acid group containing catalysts include amine blocked compounds, such as: amine neutralized benzene sulfonic acid, amine neutralized dinonylnaphthalene disulfonic acid or amine neutralized dinonylnaphthalenesulfonic acid. Other exemplary catalysts include: NACURE X49-110, NACURE 2107, NACURE 2500, NACURE 2501, NACURE 2522, NACURE 2530, NACURE 2558, NACURE XL-8224, NACURE 4167, NACURE XP-297, from the King Industry.

[0044] Without wishing to be held to any particular theory, it is believed that the catalysts provide favorable package stability and cure response characteristics of the resultant thermal gel. Free acids from the catalysts provide faster cure and a lower curing temperature, and the amine blocked compounds maintain stability of the formulation and provide for a longer shelf-life and, in some cases, a longer pot life.

[0045] In one exemplary embodiment, the catalyst is dinonylnaphthalenedisulfonic acid, and releases acid when heated, for example heated under 80°C and has the following structure shown below (e.g., N-X49-110).



[0046] The thermal gel may include a catalyst in an amount as little as 0.1 wt.%, 0.2 wt.%, 0.3 wt.%, as great as 0.6 wt.%, 0.8 wt.%, 1 wt.%, or within any range defined between any two of the foregoing values, such as between 0.2 wt.% to 0.8 wt.% or between 0.3 wt.% to 0.6 wt.%, based on the total weight of the thermal gel.

In one exemplary embodiment, the thermal gel includes a catalyst in the amount of about 0.373wt.%.

6. *Thermally Conductive Filler*

[0047] The thermal gel includes one or more thermally conductive fillers. Exemplary thermally conductive fillers include metals, alloys, nonmetals, metal oxides and ceramics, and combinations thereof. The metals include, but are not limited to, aluminum, copper, silver, zinc, nickel, tin, indium, and lead. The nonmetals include, but are not limited to, carbon, graphite, carbon nanotubes, carbon fibers, graphenes, boron nitride and silicon nitride. The metal oxides or ceramics include but not limited to alumina (aluminum oxide), aluminum nitride, boron nitride, zinc oxide, and tin oxide.

[0048] In one exemplary embodiment, the one or more thermally conductive fillers include alumina (Al₂O₃) with a 40 micron (mm) average particle size (D₅₀) (e.g., BAK040), alumina (Al₂O₃) with a 5 micron (mm) average particle size (D₅₀) (e.g., BAK005), and alumina (Al₂O₃) with a 5 micron (mm) average particle size (D₅₀) (e.g., AO-502).

[0049] The thermal gel may include the one or more thermally conductive fillers in an amount as little as 15 wt.%, 20 wt.%, 25 wt.%, 50 wt.%, 85 wt.%, 90 wt.%, as great as 92 wt.%, 95 wt.%, 98 wt.%, 99 wt.% or within any range defined between any two of the foregoing values, based on the total weight of the thermal gel, such as 15 wt.% to 50 wt.%, 20 wt.% to 50 wt.%, or 15 wt.% to 99 wt.%, 80 wt.% to 99 wt.%, 80 wt.% to 98 wt.%, 85 wt.% to 95 wt.%, or 90 wt.% to 92 wt.%, for example.

[0050] Exemplary thermally conductive fillers may have an average particle size of as little as 0.1 microns, 1 micron, 10 microns, as great as 25 microns, 40 microns, 50 microns, or within any range defined between any two of the foregoing values, such as 0.1 microns to 50 microns, 1 micron to 40 microns, or 10 microns to 25 microns, for example.

[0051] In one exemplary embodiment, the thermal gel may include a first thermally conductive filler, a second thermally conductive filler, and a third thermally conductive filler, wherein the first thermally conductive filer has a particle size of 40 microns, the second thermally conductive filler has an average particle size of 5

microns, and the third thermally conductive filler has an average particle size of 0.5 microns.

[0052] In one exemplary embodiment, the thermal gel includes a first thermally conductive filler in the amount of as little as 30 wt.%, 35 wt.%, 40 wt.%, as great as 45 wt.%, 50 wt.%, 60 wt.% or within any range defined between any two of the foregoing values such as between 30 wt.% to 60 wt.%, 35 wt.% to 50 wt.%, or 40 wt.% to 50 wt.%, for example, based on the total weight of the thermal gel. The first thermally conductive filler may have an average particle size of as little as 30 microns, 35 microns, 40 microns, as great as 45 microns, 50 microns, 60 microns, or within any range defined between any two of the foregoing values such as between 30 microns to 60 microns, 35 microns to 50 microns, or 40 microns to 45 microns, for example. The exemplary thermal gel further may include a second thermally conductive filler in the amount of as little as 5 wt.%, 10 wt.%, 15 wt.%, as great as 25 wt.%, 27 wt.%, 30 wt.% or within any range defined between any two of the foregoing values such as between 5 wt.% to 30 wt.%, 10 wt.% to 27 wt.%, or 15 wt.% to 25 wt.%, for example, based on the total weight of the thermal gel. The second thermally conductive filler may have an average particle size of as little as 1 micron, 3 microns, 5 microns, as great as 7 microns, 8 microns, 10 microns, or within any range defined between any two of the foregoing values such as between 1 micron to 10 microns, 3 microns to 8 microns, or 5 microns to 7 microns, for example. The exemplary thermal gel further may include a third thermally conductive filler in the amount of as little as 10 wt.%, 15 wt.%, 20 wt.%, as great as 30 wt.%, 35 wt.%, 40 wt.% or within any range defined between any two of the foregoing values such as between 10 wt.% to 40 wt.%, 15 wt.% to 35 wt.%, or 20 wt.% to 30 wt.%, for example, based on the total weight of the thermal gel. The third thermally conductive filler may have an average particle size of as little as 0.1 microns, 0.3 microns, 0.5 microns, as great as 1 micron, 1.5 microns, 2 microns, or within any range defined between any two of the foregoing values such as between 0.1 microns to 2 microns, 0.3 microns to 1.5 microns, or 0.5 microns to 1 micron, for example.

7. Other additives

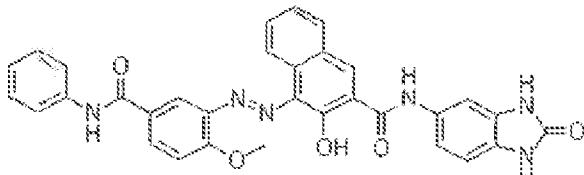
[0053] The thermal gel may also include a coloring agent or other additives. Exemplary organic pigments include: benzimidazolone, such as the blue shade

benzimidazolone pigment Novoperm Carmine HF3C from Clariant International Ltd, Muttenz Switzerland. Exemplary inorganic pigments include carbon black and iron based compounds (e.g., iron green or iron oxide green). Exemplary iron based compounds include iron oxide compounds such as α -Fe₂O₃, α -Fe₂O₃·H₂O, Fe₃O₄, Fe₂O₃·H₂O, and combinations thereof. Exemplary organic dyes include: Benzo[kl]thioxanthene-3,4-dicarboximide,N-octadecyl- (8CI); Benzothioxanthene-3,4-dicarboxylic acid-N-stearyl imide.

[0054] In some exemplary embodiments, the coloring agent is an inorganic pigment selected from the group consisting of $\alpha\text{-Fe}_2\text{O}_3$; $\alpha\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$; and Fe_3O_4 .

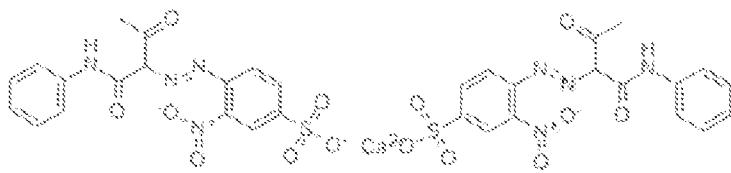
[0055] In some exemplary embodiments, the coloring agent is an organic pigment. In a more particular embodiment, the coloring agent is an organic selected from the group consisting of Formulas (I)- (XVI).

[0056] In a more particular embodiment, the coloring agent is an organic pigment of Formula (I), also known as pigment red 176, and having CAS No. 12225-06-8.



Formula (I)

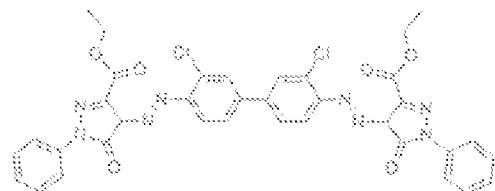
[0057] In a more particular embodiment, the coloring agent is an organic pigment of Formula (II), also known as calcium bis[4-[[1-[(2-methylphenyl)amino]carbonyl]-2-oxopropyl]azo]-3-nitrobenzenesulphonate, and having CAS No. 12286-66-7.



Formula (II)

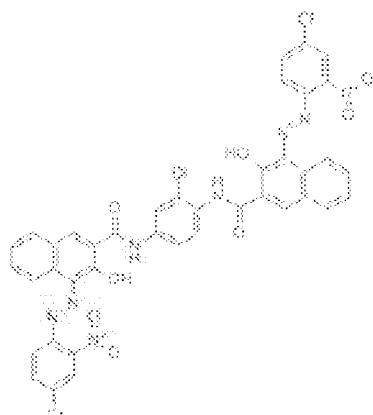
[0058] In a more particular embodiment, the coloring agent is an organic pigment of Formula (III) also known as diethyl 4,4'-(3,3'-dichloro[1,1'-biphenyl]-4,4'-

diyl)bis(azo)]bis[4,5-dihydro-5-oxo-1-phenyl-1h-pyrazole-3-carboxylate], and having CAS No. 6368-87-8.



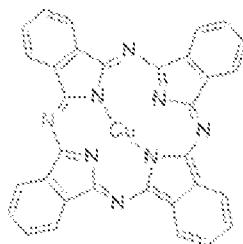
Formula (III)

[0059] In a more particular embodiment, the coloring agent is an organic pigment of Formula (IV) also known as 2,2'-(3,3'-Dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)bis[N-(2,4-dimethylphenyl)-3-oxo-butanamide], and having CAS No. 5102-83-0.



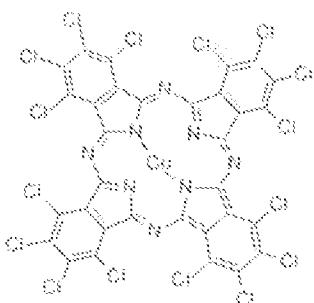
Formula (IV)

[0060] In a more particular embodiment, the coloring agent is an organic pigment of Formula (V) also known as (29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32)copper, and having CAS No. 147-14-8.



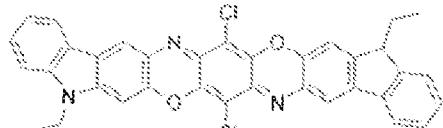
Formula (V)

[0061] In a more particular embodiment, the coloring agent is an organic pigment of Formula (VI) also known as brilliantgreenphthalocyanine, and having CAS No. 1328-53-6.



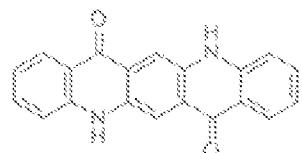
Formula (VI)

[0062] In a more particular embodiment, the coloring agent is an organic pigment of Formula (VII) also known as 9,19-dichloro-5,15-diethyl-5,15-dihydro-diindolo[2,3-c:2',3'-n]triphenodioxazine, and having CAS No. 6358-30-1.



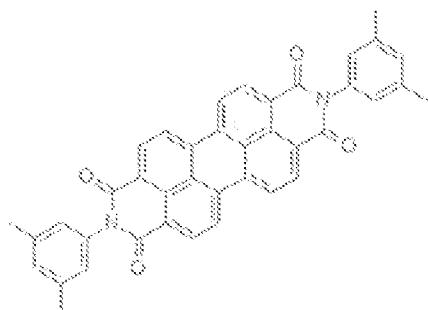
Formula (VII)

[0063] In a more particular embodiment, the coloring agent is an organic pigment of Formula (VIII) also known as 5,12-DIHYDROQUIN[2,3-B]ACRIDINE-7,14-DIONE;5,12-dihydroquino[2,3-b]acridine-7,14-dione, and having CAS No. 1047-16-1.



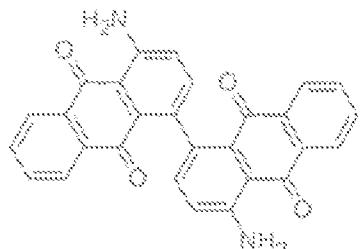
Formula (VIII)

[0064] In a more particular embodiment, the coloring agent is an organic pigment of Formula (IX) also known as 2,9-bis(3,5-dimethylphenyl)anthra[2,1,9-def:6,5,10-d'e'f]diisoquinoline-1,3,8,10(2h,9h)-tetrone, and having CAS No. 4948-15-6.



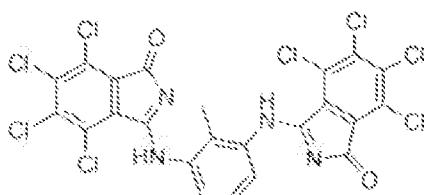
Formula (IX)

[0065] In a more particular embodiment, the coloring agent is an organic pigment of Formula (X) also known as 4,4'-diamino-[1,1'-bianthracene]-9,9',10,10'-tetraone or pigment red 177, and having CAS No. 4051-63-2.



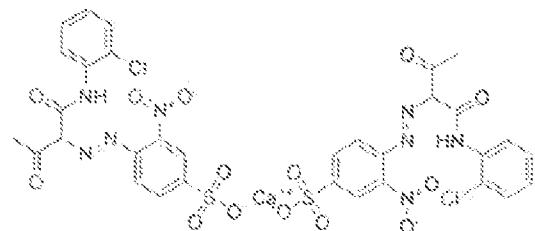
Formula (X)

[0066] In a more particular embodiment, the coloring agent is an organic pigment of Formula (XI) also known as 3,3'-(2-methyl-1,3-phenylene)diimino]bis[4,5,6,7-tetrachloro-1H-isoindol-1-one] , and having CAS No. 5045-40-9.



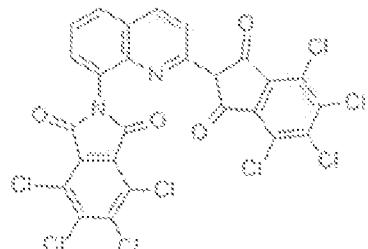
Formula (XI)

[0067] In a more particular embodiment, the coloring agent is an organic pigment of Formula (XII) also known as calcium bis[4-[[1-[[[2-chlorophenyl)amino]carbonyl]-2-oxopropyl]azo]-3-nitrobenzenesulphonate], and having CAS No. 71832-85-4.



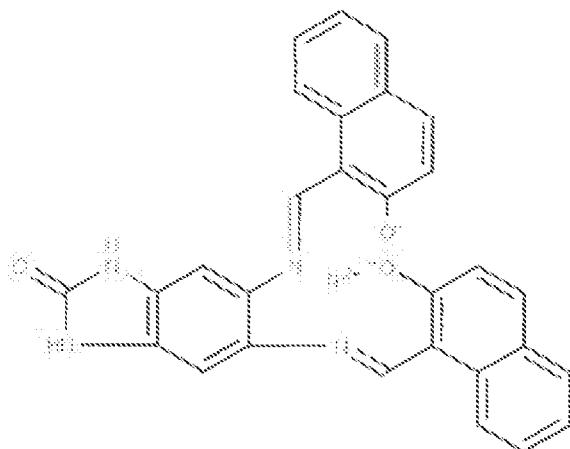
Formula (XII)

[0068] In a more particular embodiment, the coloring agent is an organic pigment of Formula (XIII) also known as 3,4,5,6-Tetrachloro-N-[2-(4,5,6,7-tetrachloro-2,3-dihydro-1,3-dioxo-1H-inden-2-yl)-8-quinolyl]phthalimide, and having CAS No. 30125-47-4.



Formula (XIII)

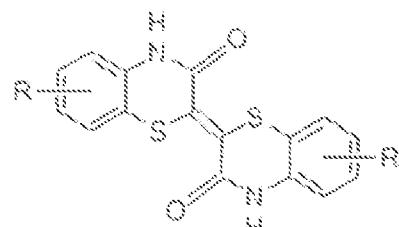
[0069] In a more particular embodiment, the coloring agent is an organic pigment of Formula (XIV) also known as [1,3-dihydro-5,6-bis[(2-hydroxy-1-naphthyl)methylene]amino]-2H-benzimidazol-2-onato(2-)-N5,N6,O5,O6]nickel, and having CAS No. 42844-93-9.



Formula (XIV)

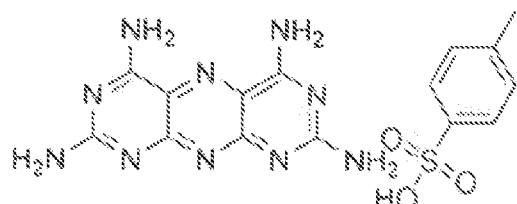
[0070] In a more particular embodiment, the coloring agent is an organic pigment of Formula (XV) also known as Pigment Red 279, and having CAS No.

832743-59-6, wherein each R is independently selected from the group consisting of hydrogen, alkyl, aryl, and halogen. In an even more particular embodiment, each R is independently selected from the group consisting of hydrogen, C₁-C₆ alkyl, phenyl, and halogen. In another more particular embodiment, each R is chlorine, and even more particularly, each R is 7-chloro.



Formula (XV)

[0071] In a more particular embodiment, the coloring agent is an organic pigment of Formula (XVI) also known as Pyrimido[5,4-g]pteridine-2,4,6,8-tetramine, 4-methylbenzenesulfonate, base-hydrolysed, and having CAS No. 346709-25-9.



Formula (XVI)

[0072] In one more particular embodiment, the coloring agent is α -Fe₂O₃, such as such as Iron Red available from BAI YAN. In another more particular embodiment, the coloring agent is α -Fe₂O₃·H₂O, such as such as Iron Yellow available from BAI YAN. In still another more particular embodiment, the coloring agent is Fe₃O₄, such as such as Iron Blue available from BAI YAN. In yet still another more particular embodiment, the coloring agent is the pigment of Formula (I), having the chemical formula C₃₂H₂₄N₆O₅, such as Novoperm Carmine HF3C, available from Clariant International Ltd, Muttenz Switzerland.

[0073] In another embodiment, the additive may be an iron green pigment.

[0074] The present thermal gel may further comprise some other additives, such as pigments or dyes. In one embodiment, the thermal gel includes pigment components in an amount as little as 0.001 wt.%, 0.01 wt.%, 0.05 wt.%, 0.08 wt.%,

as great as 2 wt.%, 5 wt.%, 10 wt.% or within any range defined between any two of the foregoing values such as between 0.001 wt.% to 10 wt.%, 0.05 wt.% to 2 wt.%, or 0.08 wt.% to 5 wt.%, for example, based on the total weight of the thermal gel.

[0075] In one exemplary embodiment, the thermal gel may include a first thermally conductive filler in an amount as little as 30 wt.%, 35 wt.%, or 40 wt.%, as great as 50 wt.%, 55 wt.%, or 60 wt.%, or within any range defined between any two of the foregoing values such as between 30 wt.% to 60 wt.%, 35 wt.% to 55 wt.%, or 40 wt.% to 50 wt.%, for example, based on the total weight of the thermal gel. The first thermally conductive filler may have an average particle size of as little as 30 microns, 35 microns, or 40 microns, or as great as 45 microns, 50 microns, or 60 microns, or within any range defined between any two of the foregoing values such as between 30 microns to 60 microns, 35 microns to 50 microns, 40 microns to 45 microns, or 35 microns to 45 microns, for example. The exemplary thermal gel may further include a second thermally conductive filler in an amount as little as 5 wt.%, 10 wt.%, or 15 wt.%, or as great as 25 wt.%, 27 wt.%, or 30 wt.% or within any range defined between any two of the foregoing values such as between 5 wt.% to 30 wt.%, 10 wt.% to 27 wt.%, or 15 wt.% to 25 wt.%, for example, based on the total weight of the thermal gel. The second thermally conductive filler may have an average particle size of as little as 1 micron, 3 microns, or 5 microns, or as great as 10 microns, 15 microns, or 20 microns, or within any range defined between any two of the foregoing values such as between 1 micron to 20 microns, 3 microns to 15 microns, or 5 microns to 10 microns, for example. The exemplary thermal gel may further include a third thermally conductive filler in an amount as little as 5 wt.%, 10 wt.%, or 15 wt.%, or as great as 25 wt.%, 27 wt.%, or 30 wt.% or within any range defined between any two of the foregoing values such as between 5 wt.% to 30 wt.%, 10 wt.% to 27 wt.%, or 15 wt.% to 25 wt.%, for example, based on the total weight of the thermal gel. The third thermally conductive filler may have an average particle size of as little as 0.1 microns, 0.3 microns, or 0.5 microns, or as great as 1 micron, 1.5 microns, or 2 microns, or within any range defined between any two of the foregoing values such as between 0.1 microns to 2 microns, 0.3 microns to 1.5 microns, or 0.5 microns to 1 microns, for example. The exemplary thermal gel may further include a polyether polyol in an amount as little as 1 wt.%, 3 wt.%, 5 wt.%, 7 wt.%, as great as 10 wt.%, 14 wt.%, 18 wt.%, 20 wt.% or within any range defined

between any two of the foregoing values, such as 1 wt.% to 10 wt.%, 5 wt.% to 10 wt.%, or 1 wt.% to 20 wt.% for example, based on the total weight of the thermal gel. The exemplary thermal gel may further include a crosslinker in an amount as little as 0.1%, 0.50 wt.%, 0.75 wt.%, 1 wt.%, as great as 2 wt.%, 3 wt.%, 5 wt.%, 10 wt.%, or within any range defined between any two of the foregoing values, such as 0.5 wt.% to 2 wt.% or 0.75 wt.% to 2 wt.%, for example, based on the total weight of the thermal gel. The exemplary thermal gel may further include a coupling agent in an amount as little as 0.01 wt.%, 0.1 wt.%, 1.0 wt.%, as great as 2.0 wt.%, 3.0 wt.%, 4.0 wt.%, 5.0 wt.%, or within any range defined between any two of the foregoing values, such as 0.1 wt.% to 5 wt.% or 0.1 wt.% to 1 wt.%, for example, based on the total weight of the thermal gel. The exemplary thermal gel may further include an antioxidant in an amount as little as 0.1 wt.%, 0.2 wt.%, 0.4 wt.%, as great as 0.6 wt.%, 0.8 wt.%, 1 wt.%, or within any range defined between any two of the foregoing values, such as 0.2 wt.% to 0.4 wt.%, or 0.1 wt.% to 1 wt.%, for example, based on the total weight of the thermal gel. The exemplary thermal gel may further include a catalyst in an amount as little as 0.1 wt.%, 0.2 wt.%, 0.3 wt.%, as great as 0.6 wt.%, 0.8 wt.%, 1 wt.%, or within any range defined between any two of the foregoing values, such as between 0.2 wt.% to 0.8 wt.% or between 0.3 wt.% to 0.6 wt.%, based on the total weight of the thermal gel. The exemplary thermal gel may further include an additive (e.g., a pigment) in an amount as little as 0.001 wt.%, 0.01 wt.%, 0.05 wt.%, 0.08 wt.%, as great as 2 wt.%, 5 wt.%, 10 wt.% or within any range defined between any two of the foregoing values such as between 0.001 wt.% to 10 wt.%, 0.05 wt.% to 2 wt.%, or 0.08 wt.% to 5 wt.%, for example, based on the total weight of the thermal gel.

[0076] The present thermal gel may lack any silicone containing components. Silicone containing components include polymerized siloxanes or polysiloxanes, and silicone containing oligomers or polymers that include an inorganic silicon-oxygen backbone chain with functional groups (e.g., organic side groups) attached to the silicon atoms. In one embodiment, the thermal gel includes silicone containing components in an amount of less than 1 wt.%, less than 0.5 wt.%, less than 0.3 wt.%, or less than 0.1 wt.%, for example, based on the total weight of the thermal gel.

[0077] The present thermal gel may also lack any silicon atoms. In one

embodiment, the thermal gel includes silicon atoms in an amount of less than 1 wt.%, less than 0.5 wt.%, less than 0.3 wt.%, or less than 0.1 wt.%, or less than 0.01 wt.%, for example, based on the total weight of the thermal gel.

B. Method of Forming a Thermal Gel

1. Batch Method

[0078] Referring to Fig. 1, a method 100 of preparing a thermal gel is shown. At block 102, a polyether polyol, coupling agent, antioxidant, and cross-linker are weighed and added to a reaction vessel to form a mixture. The mixture is agitated for a period of time. Exemplary agitation rates may be as little as 2000 revolutions per minute (rpm), 2500 rpm, 3000 rpm, as great as 3250 rpm, 3350 rpm, 3500 rpm or within any range defined between any two of the foregoing values such as between 2000 rpm to 3500 rpm, 2500 rpm to 3350 rpm, or 3000 rpm to 3250 rpm, for example. Exemplary time periods for agitation rates are as little as 20 seconds, 25 seconds, 30 seconds, as great as 200 seconds, 250 seconds, 275 seconds, 300 seconds or within any range defined between two of the foregoing values such as between 20 seconds to 300 seconds, 25 seconds to 275 seconds, 30 seconds to 250 seconds, or 30 seconds to 200 seconds, for example. In an exemplary embodiment, the mixture is agitated at a rate of under 3000 rpm for 3 minutes.

[0079] Method 100 then proceeds to block 104 where one or more thermally conductive fillers are added to the reaction vessel. The resulting mixture is then agitated for a period of time. Exemplary agitation rates may be as little as under 2000 revolutions per minute (rpm), 2250 rpm, 2500 rpm, as great as 2600 rpm, 2750 rpm, 3000 rpm or within any range defined between any two of the foregoing values such as between 2000 rpm to 3000 rpm, 2250 rpm to 2750 rpm, or 2500 rpm to 2600 rpm, for example. Exemplary time periods for agitation rates are as little as 1 minute, 2 minutes, 3 minutes, as great as 4 minutes, 4.5 minutes, 5 minutes, or within any range defined between two of the foregoing values such as between 1 minute to 5 minutes, 2 minutes to 4.5 minutes, or 3 minutes to 4 minutes, for example. In an exemplary embodiment, the mixture is agitated at a rate of under 2500 rpm for 3 minutes.

[0080] Method 100 then proceeds to block 106 where the mixture is cooled to

room temperature. Method 100 then moves to block 108 where a catalyst is weighed and added to the reaction vessel. The resulting mixture is then agitated for a period time. Exemplary agitation rates may be as little as under 2000 revolutions per minute (rpm), 2250 rpm, 2500 rpm, as great as 2600 rpm, 2750 rpm, 3000 rpm or within any range defined between any two of the foregoing values such as between 2000 rpm to 3000 rpm, 2250 rpm to 2750 rpm, or 2500 rpm to 2600 rpm, for example. Exemplary time periods for agitation rates are as little as 1 minute, 2 minutes, 3 minutes, as great as 4 minutes, 4.5 minutes, 5 minutes, or within any range defined between two of the foregoing values such as between 1 minute to 5 minutes, 2 minutes to 4.5 minutes, or 3 minutes to 4 minutes, for example. In an exemplary embodiment, the mixture is agitated at a rate of under 2500 rpm for 3 minutes. A vacuum is then applied to the reaction mixture when the mixture is in a uniform phase. The vacuum is accompanied with low rotating speed that may be as little as 1000 rpm, 1250 rpm, 1500 rpm, as great as 1600 rpm, 1750 rpm, 2000 rpm, or within any range defined between any two of the foregoing values such as between 1000 rpm to 2000 rpm, 1250 rpm to 1750 rpm, or 1500 rpm to 1600 rpm, for example.

[0081] Then, method 100 proceeds to block 110 where the mixture is cooled to room temperature. After cooling, method 100 proceeds to block 112, and the vacuum is opened/removed within the vessel and the mixture is agitated for a period of time. Exemplary agitation rates may be as little as under 2000 revolutions per minute (rpm), 2250 rpm, 2500 rpm, as great as 2600 rpm, 2750 rpm, 3000 rpm or within any range defined between any two of the foregoing values such as between 2000 rpm to 3000 rpm, 2250 rpm to 2750 rpm, or 2500 rpm to 2600 rpm, for example. Exemplary time periods for agitation rates are as little as 1 minute, 2 minutes, 3 minutes, as great as 4 minutes, 4.5 minutes, 5 minutes, or within any range defined between two of the foregoing values such as between 1 minute to 5 minutes, 2 minutes to 4.5 minutes, or 3 minutes to 4 minutes, for example. In an exemplary embodiment, the mixture is agitated at a rate of under 2500 rpm for 3 minutes.

[0082] In some exemplary embodiments, the thermal gel is prepared by combining the individual components in a heated mixer and blending the composition together. The blended composition may then be applied directly to the

substrate without baking.

2. Two component Method

[0083] In another exemplary embodiment, the thermal gel is prepared by preparing a first component and a second component and combining the first and second components in a dispenser. For example, a dual cartridge dispenser apparatus 200 as shown in Fig. 9 can be used in which the first component is stored in container 202 and the second component is stored in container 204. The first and second components are fed through respective tubing 206, 208 to cartridges 214, 216, respectively. From cartridge 214, first component is fed into mixing vessel 210 of dispenser 220. Similarly, from cartridge 216, second component is fed into mixing vessel 210 of dispenser 220. First and second components are then mixed within mixing vessel 210 without additional heating, and the resulting mixed composition is fed through syringe 212 of dispenser 220. In one embodiment, the mixed composition may then be applied directly to the substrate.

[0084] Referring now to Fig. 8, a method 300 for preparing the thermal gel is provided. At step 302, a first component and a second component are prepared in accordance with the components described further herein.

a. First component

[0085] In an exemplary embodiment, the first component of the thermal gel includes a polyether polyol, a catalyst, and at least one thermally conductive filler in accordance with the present description above for the respective components.

b. Second Component

[0086] In an exemplary embodiment, the second component of the thermal gel includes a polyether polyol in accordance with the description above. It is within the scope of the present disclosure that the polyether polyol of the first component and the polyether polyol of the second component are different polyether polyol compounds. It is also within the scope of the present disclosure that the polyether polyol of the first component and the polyether polyol of the second component are the same polyether polyol compounds. The second component of the thermal gel

further includes a crosslinker, at least one thermally conductive filler, and an additive in accordance with the present description above for the respective components.

[0087] Once the components are prepared, method 300 moves to step 304 where the first component and the second component are mixed together in a ratio (first component:second component) of as little 0.1:1, 0.5:1, 1:1, as great as 5:1, 7.5:1, 10:1, or within any range defined between any two of the foregoing values, such as from 0.1:1 to 10:1, for example. Different ratios yield different amounts of cross-linking within the mixture and also different hardness properties. In an exemplary embodiment, the first component and the second component are mixed in a 1:1 ratio by a static mixer.

[0088] After the first component and the second component are mixed, the resulting mixture is then applied onto a surface as indicated by step 306. The mixture can be applied by an automatic dispensing machine or a manual dispensing machine such as a syringe.

C. Properties of the Thermal Gel

[0089] When the thermal gel is applied to a substrate, minimal leakage is experienced due to the cross-linking within the thermal gel. That is, the crosslinker advantageously crosslinks the polyols such that a substantially limited amount of polymer leakage occurs. Limited leakage reduces the contamination of the surrounding ports (e.g., electrical components).

[0090] Generally, cyclic siloxane compounds, such as hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane, are present in electronic products. If some of these cyclic siloxane compounds are deposited on the electrodes within the electronic products, the cyclic siloxane compounds will undergo ring-opening polymerization under certain conditions and form an insulating polysiloxane layer, which will undermine the proper functionality of the electrodes and in turn ruin the functionality of the electronic products. By contrast, the thermal gel of the present disclosure is silicone free which avoids the aforementioned problems if some of the thermal gel may potentially be deposited onto the electrode.

[0091] Furthermore, as will be described in greater detail below, the thermal

gel can be cured at a temperature up to 80°C as measured by thermal cycling under TCB. In TCB, samples are put into an oven and the temperature is controlled (e.g., between -40°C to 80°C). The samples undergo thermal cycling for weeks or months after which, the samples are examined to see whether cracks are present in the samples or whether the samples have slid from their original position prior to thermal cycling. Many electronic components operate at a temperature around 80°C and thus, there is no need for an additional heating step to cure the thermal gel after the gel is applied. Moreover, the gel allows for easy removal if the gel needs to be reapplied or re-worked onto the applied surface. In addition, the thermal conductivity of the thermal gel is as little as 1 W/mK, 2 W/mK, 2.5 W/mK, as great as 4 W/mK, 4 W/mK, 4 W/mK, or within any range defined between any two of the foregoing values such as between 1 W/mK to 5 W/mK, 2 W/mK to 4.5 W/mK, or 2.5 W/mK to 4 W/mK, for example.

[0092] As used herein, the phrase "within any range defined between any two of the foregoing values" literally means that any range may be selected from any two of the values listed prior to such phrase regardless of whether the values are in the lower part of the listing or in the higher part of the listing. For example, a pair of values may be selected from two lower values, two higher values, or a lower value and a higher value.

EXAMPLES

Examples 1-3

[0093] Thermal gels were prepared according to the formulations shown in Table 1 and the description below.

Component	Example 1 (g)	Example 2 (g)	Example 3 (g)
Polyether Polyol (bi-ol)	3.53	7.06	3.53
Polyether polyol (tri-ol)	3.53	-	-
Polyether polyol (hexa-ol)	-	-	3.53
Crosslinker	1.85	1.85	1.85
Coupling Agent	0.59	0.59	0.59
Antioxidant	0.35	0.35	0.35
Catalyst	0.44	0.44	0.44
Thermally Conductive Filler	42.28	42.28	42.28
Thermally Conductive	21.57	21.57	21.57

Filler			
Thermally Conductive Filler	25.86	25.86	25.86

Table 1

[0094] A polyether polyol, a coupling agent, an antioxidant, and a crosslinker are weighed and added to a plastic cup. The mixture is then stirred with a speedmixer at 3000 revolutions per minute (rpm) for 30 seconds.

[0095] The thermally conductive fillers are weighed and added to the plastic cup. The mixture is stirred with a speedmixer under 2500 rpm for 3 minutes and then cooled to room temperature.

[0096] A catalyst is weighed and added to the cup. The mixture is stirred with a speedmixer under 2500 rpm for 3 minutes and then cooled to room temperature. The vacuum is then opened and the mixture is stirred with a speedmixer at 2500 rpm for 3 minutes.

[0097] The resulting paste is filled into a syringe and then dispensed onto a smooth copper plate. A spacer having a thickness of 1.6 mm or 0.3 mm was placed on the edge of the copper plate to create a 1.6 mm or 0.3 mm gap. Glass was then used to compress the paste to a thickness of 1.6 mm or 0.3 mm. The sample was then placed into a TCB (thermal cycling) chamber for three days and subjected to thermal cycling between -55°C and +125°C for 3 days.

[0098] As shown in Fig. 2, in the TCB test, Example 2 exhibited a limited dripping issue while Example 3 exhibited a significant dripping issue. Further, Example 1 exhibited both cracking and dripping issues.

Example 4

[0099] Thermal gels were prepared according to the formulations shown in Table 2 and the description below.

Component	Weight (g)
Polyether polyol (bi-ol, MW: 8000 Daltons)	7
Crosslinker	0.825
Coupling agent	0.5
Antioxidant	0.3

Catalyst	0.375
Thermal conductive filler:	45.75
Thermal conductive filler	22.875
Thermal conductive filler	22.875

Table 2

[00100] A polyether polyol, a coupling agent, an antioxidant, and a crosslinker were weighed and added to a plastic cup. The mixture is then stirred with a speedmixer at 3000 revolutions per minute (rpm) for 30 seconds.

[00101] The thermally conductive fillers were weighed and added to the plastic cup. The mixture is stirred with a speedmixer under 2500 rpm for 3 minutes and then cooled to room temperature.

[00102] A catalyst was weighed and added to the cup. The mixture was stirred with a speedmixer under 2500 rpm for 3 minutes and then cooled to room temperature. The vacuum was then opened and the mixtures were stirred with a speedmixer at 2500 rpm for 3 minutes.

[00103] The formulations of Figs. 3 and 4 were sandwiched between a glass and an exemplary heat sink in a vertically oriented 1.6 mm gap. Sample 3 (Figs. 3 and 4) had the composition shown in Table 2 above with a thickness of 0.3 mm. Sample 3 was subjected to baking in an oven at 125°C for 3 days. As shown in Fig. 3, no cracking was shown in the sample after baking for 3 days at 125°C.

[00104] Samples 1, 2, and 3 as shown in Fig. 4 have the composition listed in Table 2. Sample 1 has a thickness of 3 mm, Sample 2 has a thickness of 1.5 mm, and Sample 3 has a thickness of 0.3 mm. Both samples were subjected to TCB testing where the samples underwent thermal cycling between -40°C and +80°C for 3 months. As shown in Fig. 4, Samples 1 and 2 exhibited no cracking or dripping. However, the samples did exhibit a slight color change as they contained a yellow pigment.

Examples 5-7

[00105] Thermal gels were prepared according to the formulations shown in Table 3 and as described further herein.

Component	Example 5 (g)	Example 6(g)	Example 7 (g)
Polyether polyol (MW: 500-1000 Daltons, bi-ol)	-	5.956	-

Polyester polyol (MW: 500-1000 Daltons, bi-ol)	-	-	5.956
Polyether polyol (MW: ~8000 Daltons, bi-ol)	6.932	-	-
Crosslinker	0.84	1.816	1.816
Coupling agent	0.497	0.497	0.497
Antioxidant	0.298	0.298	0.298
Catalyst	0.373	0.373	0.373
Thermal conductive filler	45.48	45.48	45.48
Thermal conductive filler	22.74	22.74	22.74
Thermal conductive filler	22.74	22.74	22.74

Table 3

[00106] To prepare Examples 5-7, a polyether polyol (or polyester polyol), a coupling agent, an antioxidant, and a crosslinker were weighed and added to a plastic cup to form a mixture. The mixture was then stirred with a speedmixer at 3000 revolutions per minute (rpm) for 30 seconds.

[00107] The thermally conductive fillers were then weighed and added to the plastic cup. The mixture was stirred with a speedmixer at 2500 rpm for 3 minutes after which, the mixture was cooled to room temperature.

[00108] A catalyst was then weighed and added to the cup. The mixture was stirred with a speedmixer at 2500 rpm for 3 minutes and then cooled to room temperature. The vacuum was then opened, and the mixtures were stirred with a speedmixer at 2500 rpm for 3 minutes.

[00109] For thermal reliability testing, the three formulations were sandwiched between a glass and a copper plate in a vertically oriented 0.3 mm gap between the glass and the copper plate. The three samples were baked in an oven at 125°C for 24 hours. As shown in Fig. 5, no cracking or dripping was exhibited by the samples during the test.

[00110] For TCB testing, the three formulations were sandwiched between a glass and an copper plate in a vertically oriented 0.3 mm gap. The samples were then subjected to TCB testing where the samples underwent thermal cycling between -40°C and +80°C for 24 hours. As shown in Fig. 6, Example 5 and Example 6 (polymer is polyether polyol) exhibited no cracking issues, if any; however, Example 7 (polymer is polyester polyol) exhibited serious cracking issues.

[00111] The dispense rate of Examples 5-7 were measured in the instrument as shown in Fig. 7. As shown in Table 4 below, formulations derived from polyether polyol (i.e., Example 5 and Example 6) exhibited a higher dispense rate than formulations derived from polyester polyol (i.e., Example 6).

	Dispense rate (g/min)
Example 5	42
Example 6	111
Example 7	6

Table 4

[00112] While this invention has been described as having exemplary designs, the present invention can be further modified within the spirit and scope of this disclosure. This application is therefore intended to cover any variations, uses, or adaptations of the invention using its general principles. Further, this application is intended to cover such departures from the present disclosure as come within known or customary practice in the art to which this invention pertains and which fall within the limits of the appended claims.

CLAIMS

1. A thermal gel, comprising:

a matrix including at least one polyether polyol present in an amount between 1 wt.% and 10 wt.% based on the total weight of the thermal gel;

a catalyst present in an amount between 0.3 wt.% and 0.6 wt.% based on the total weight of the thermal gel;

a crosslinker including a plurality of reactive amine groups, the crosslinker present in an amount between 0.01 wt.% and 10 wt.% based on the total weight of the thermal gel;

a coupling agent present in an amount between 0.1 wt.% and 5 wt.% based on the total weight of the thermal gel; and

at least one thermally conductive filler present in an amount between 80 wt.% and 98 wt.% based on the total weight of the thermal gel.

2. The thermal gel of claim 1, further including:

an antioxidant present in an amount between 0.2 wt.% and 0.4 wt.% based on the total weight of the thermal gel.

3. The thermal gel of claim 1, wherein the thermal gel includes silicone based components in an amount less than 1 wt.% based on the total weight of the thermal gel.

4. The thermal gel of claim 1, wherein the thermal gel has a cure temperature of below 150°C.

5. The thermal gel of claim 1, wherein the polyol is a polyether polyol, the polyether polyol is a bi-ol polymer with a molecular weight between 200 and 10000 Daltons.

6. The thermal gel of claim 5, wherein the at least one polyether polyol is present in an amount between 5 wt.% and 10 wt.% based on the total weight of the thermal gel.

7. The thermal gel of claim 1, wherein the crosslinker is an alkylated melamine formaldehyde resin.

8. The thermal gel of claim 2, wherein the catalyst includes amine neutralized

benzene sulfonic acid, amine neutralized dinonylnaphthalene disulfonic acid or amine neutralized dinonylnaphthalenesulfonic acid or other type of thermal acid generator.

9. The thermal gel of claim 2, wherein the antioxidant includes at least one antioxidant selected from the group consisting of a phenol-type antioxidant, an amine-type antioxidant, or a sterically hindered, sulfur containing phenolic antioxidant.

10. The thermal gel of claim 1, wherein:

the at least one thermally conductive filler includes a first thermally conductive filler and a second thermally conductive filler;

the first thermally conductive filler is present in an amount between 35 wt.% and 50 wt.% based on the total weight of the thermal gel;

the second thermally conductive filler is present in an amount between 15 wt.% and 25 wt.% based on the total weight of the thermal gel; and

the third thermally conductive filler is present in an amount between 15 wt.% and 25 wt.% based on the total weight of the thermal gel.

11. A method of preparing a thermal gel comprising:

adding at least one polyether polyol, at least one coupling agent, at least one antioxidant, and at least one crosslinker to a reaction vessel to form a mixture;

the at least one polyether polyol present in an amount between 1 wt.% and 10 wt.% based on the total weight of the thermal gel;

the at least one crosslinker including a plurality of reactive amine groups, the crosslinker present in an amount between 0.5 wt.% and 2 wt.% based on the total weight of the thermal gel;

the at least one coupling agent present in an amount between 0.1 wt.% and 5 wt.% based on the total weight of the thermal gel;

adding a catalyst to the reaction vessel, the catalyst present in an amount between 0.3 wt.% and 0.6 wt.% based on the total weight of the thermal gel;

agitating the mixture;

adding at least one thermally conductive filler to the reaction vessel, wherein the at least one thermally conductive filler present in an amount between 80 wt.% and 98 wt.% based on the total weight of the thermal gel; and

cooling the mixture to room temperature.

12. The method of claim 11, wherein the at least one antioxidant is present in an amount between 0.2 wt.% and 0.4 wt.% based on the total weight of the thermal gel.

13. The method of claim 11, wherein the thermal gel includes silicone containing components in an amount less than 1 wt.%.

14. The method of claim 11, wherein the polyol is a polyether polyol, the polyether polyol is a bi-ol polymer with a molecular weight between 200 and 10000 Daltons.

15. The method of claim 14, wherein the at least one polyether polyol is present in an amount between 5 wt.% and 10 wt.% based on the total weight of the thermal gel.

16. The method of claim 11, wherein the crosslinker is an alkylated melamine formaldehyde resin.

17. The method of claim 14, wherein the antioxidant includes at least one antioxidant selected from the group consisting of a phenol-type antioxidant, an amine-type antioxidant, or a sterically hindered, sulfur containing phenolic antioxidant.

18. The method of claim 11, wherein the catalyst includes amine neutralized benzene sulfonic acid, amine neutralized dinonylnaphthalene disulfonic acid or amine neutralized dinonylnaphthalenesulfonic acid or other type of thermal acid generator.

19. The method of claim 11, wherein:

the at least one thermally conductive filler includes a first thermally conductive filler, a second thermally conductive filler, and a third thermally conductive filler;

the first thermally conductive filler is present in an amount between 35 wt.% and 50 wt.% based on the total weight of the thermal gel;

the second thermally conductive filler is present in an amount between 15 wt.% and 25 wt.% based on the total weight of the thermal gel; and

the third thermally conductive filler is present in an amount between 15 wt.% and 25 wt.% based on the total weight of the thermal gel.

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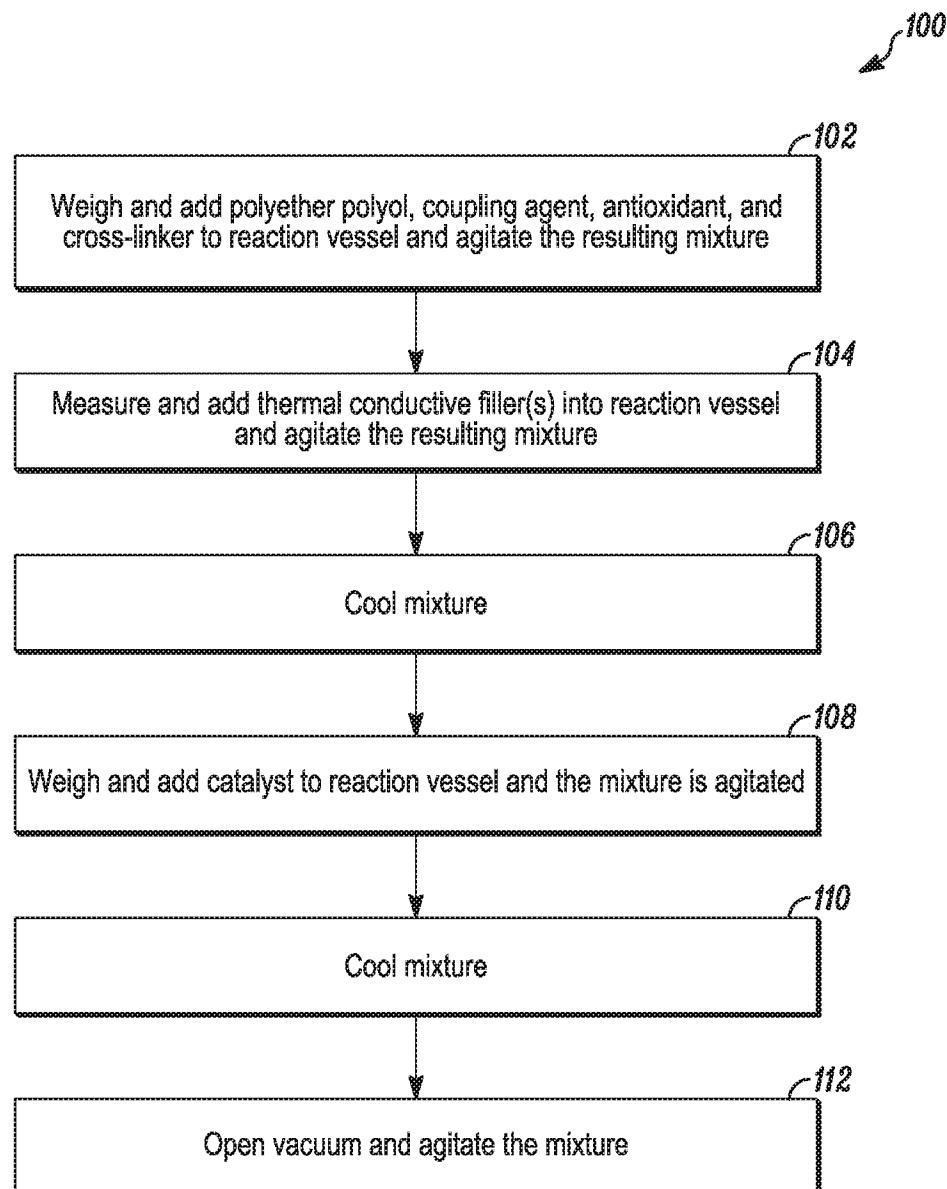


FIG. 1

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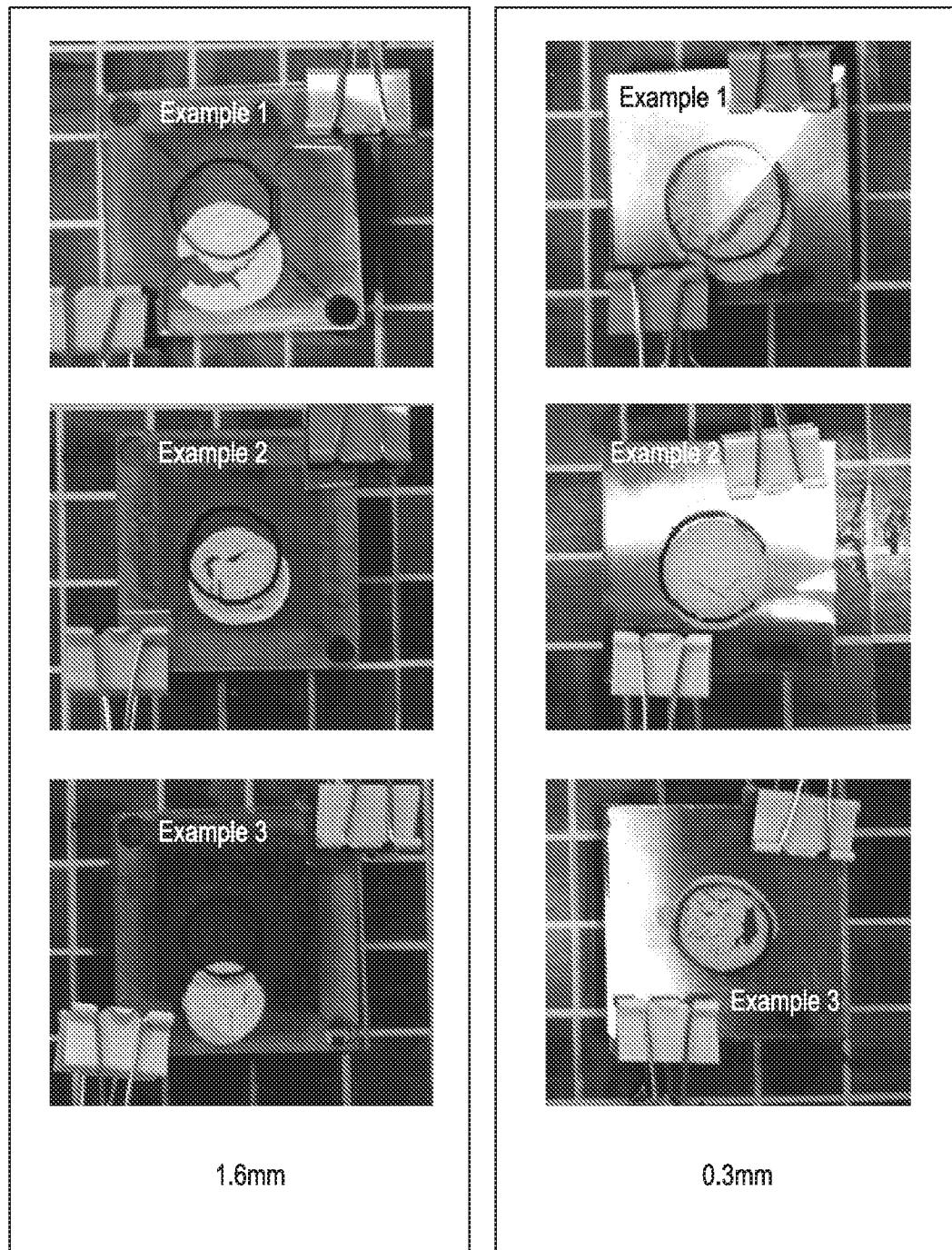
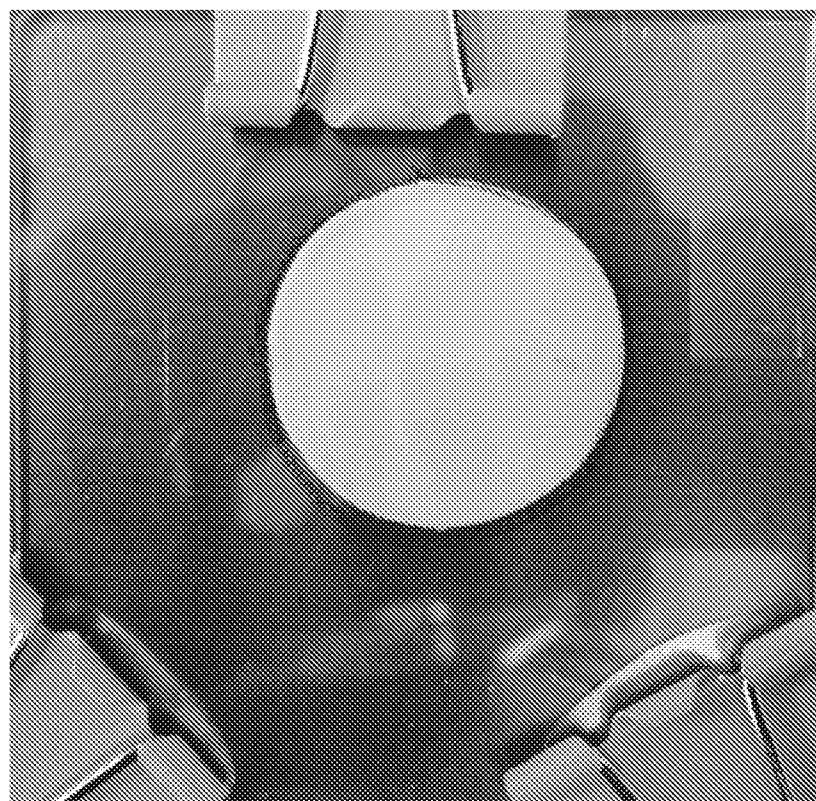


FIG. 2

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Sample 3

FIG. 3

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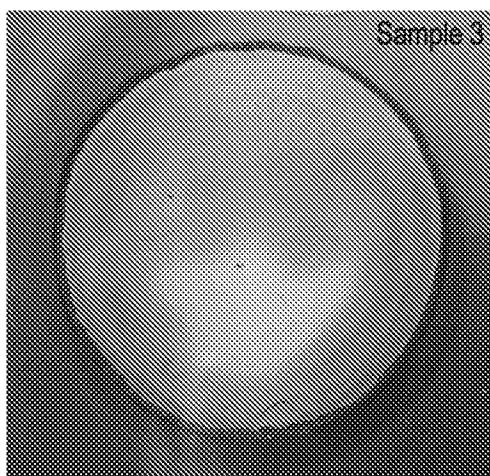
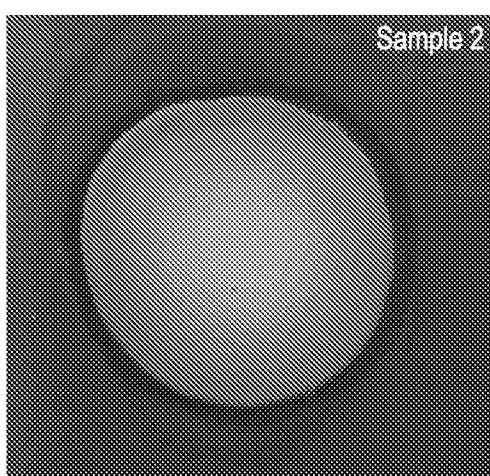
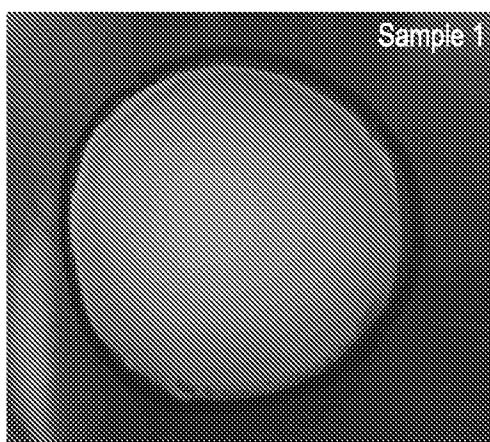
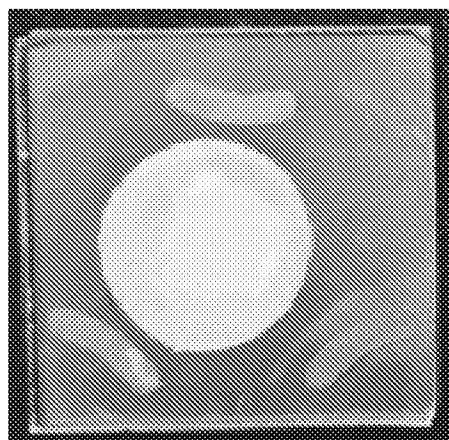


FIG. 4

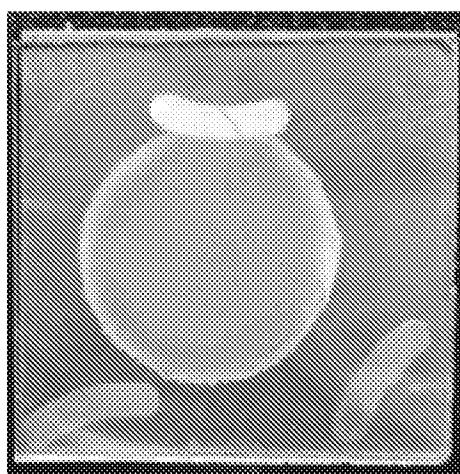
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125°C/24hrs



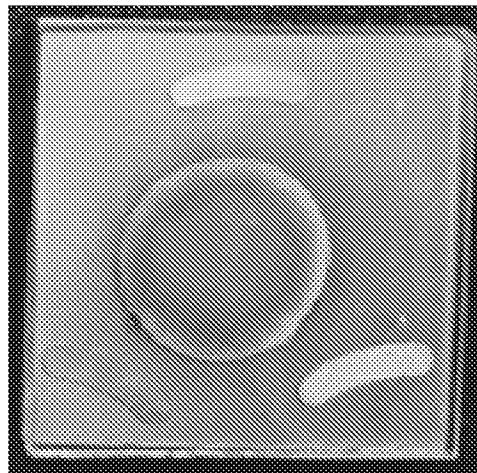
Example 5

125°C/24hrs



Example 6

125°C/24hrs

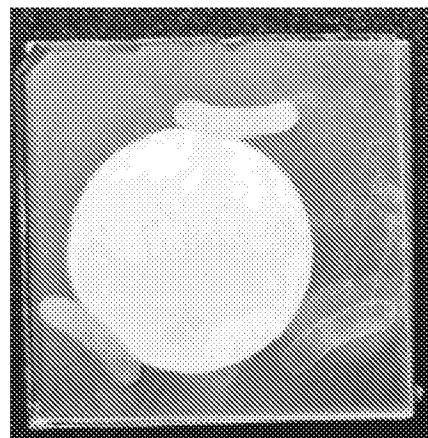


Example 7

FIG. 5

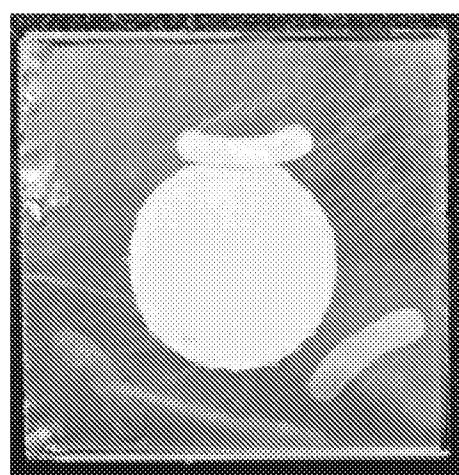
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TCB/24hrs



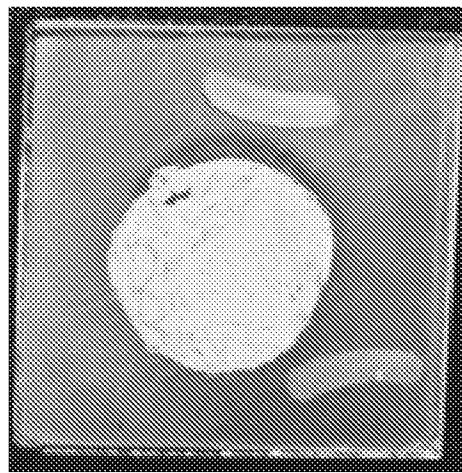
Example 5

TCB/24hrs



Example 6

TCB/24hrs



Example 7

FIG. 6

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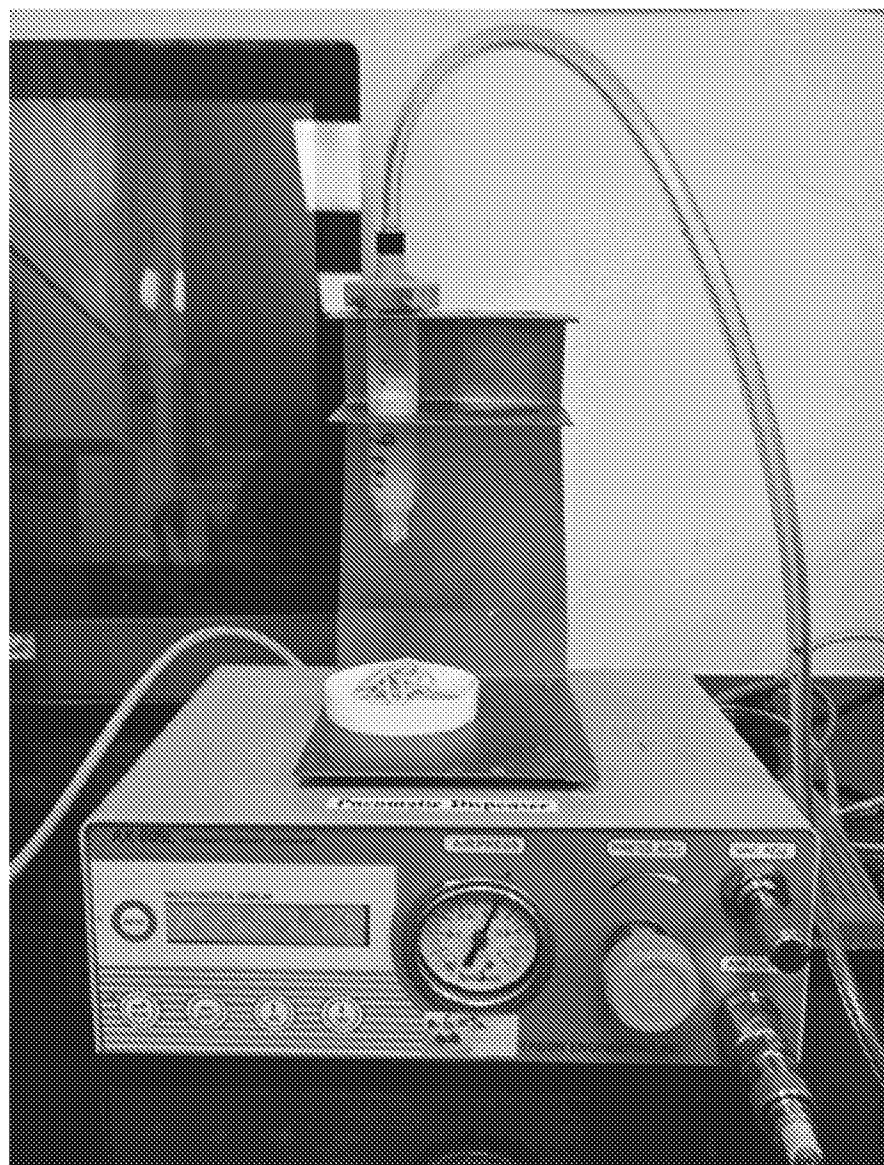


FIG. 7

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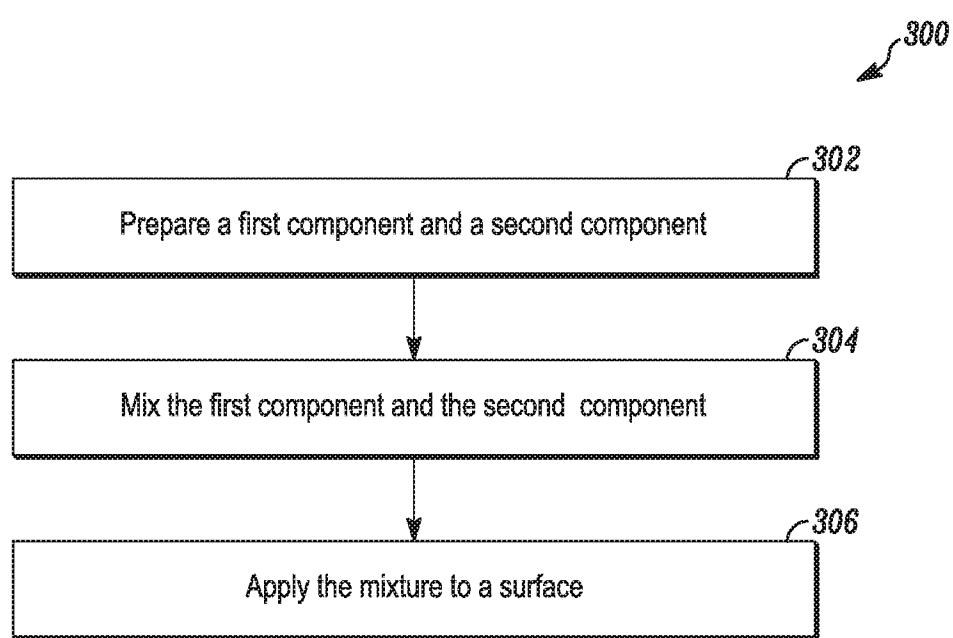


FIG. 8

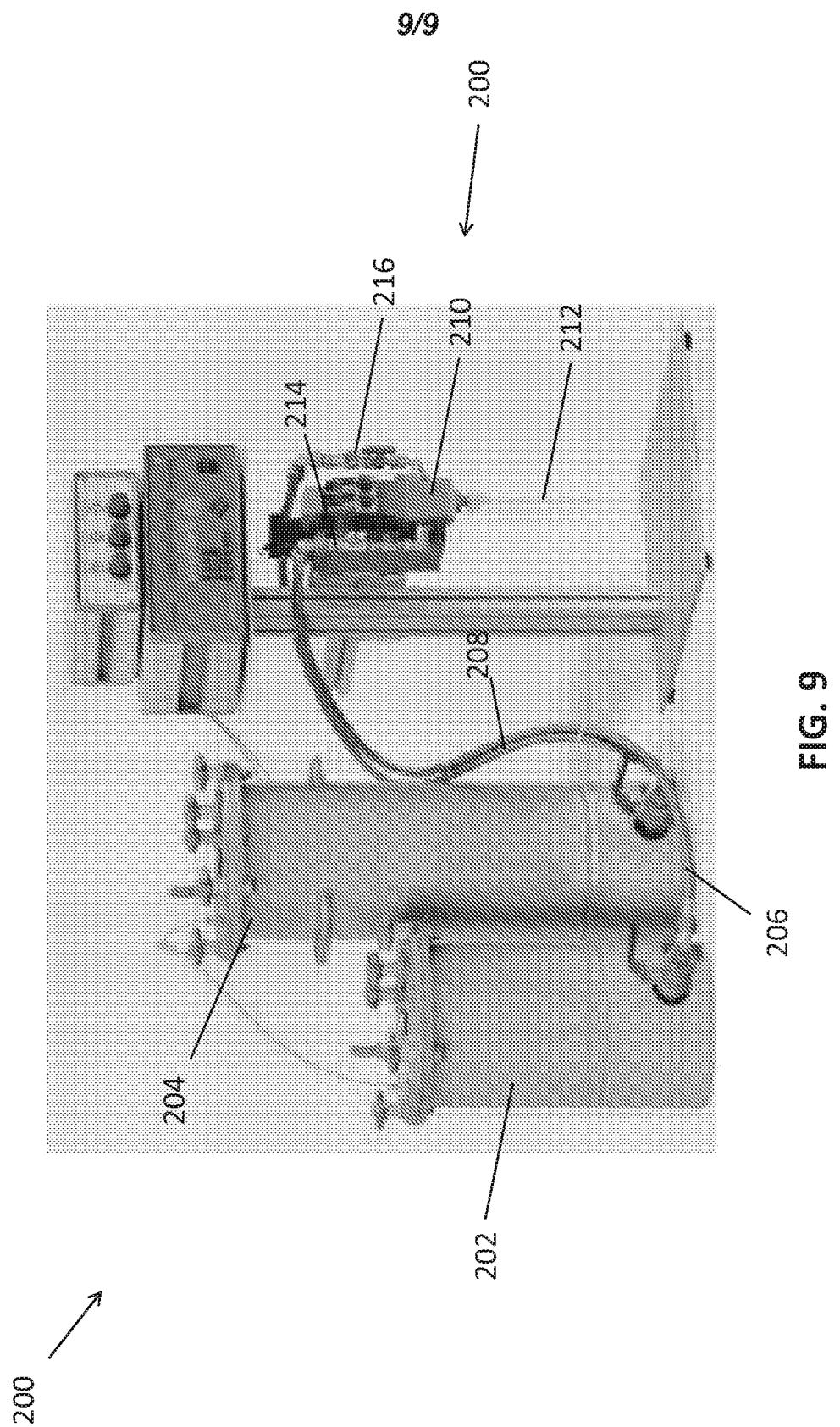


FIG. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/049218

A. CLASSIFICATION OF SUBJECT MATTER

C08J 3/075(2006.01)i, C08L 71/02(2006.01)i, C08L 61/28(2006.01)i, C08G 65/48(2006.01)i, C08K 5/00(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)

C08J 3/075; B32B 3/00; C08K 3/04; C08K 3/38; C08L 1/00; F28D 17/00; H01G 9/022; H01G 9/15; H05K 7/20; C08L 61/28; C08G 65/48; C08K 5/00

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: thermal gel, polyether polyol, catalyst, crosslinker, coupling agent, thermally conductive filler, antioxidant

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2004-0097635 A1 (FAN, SHOUSHAN et al.) 20 May 2004 See paragraphs [0025], [0026], [0035], [0037], [0039], [0043]; example; and claims 1, 5, 10-12.	1-19
Y	US 2002-0132896 A1 (NGUYEN, MY) 19 September 2002 See paragraphs [0008], [0022], [0023], [0032], [0041]; and claims 1, 25.	1-19
A	US 2007-0097651 A1 (CANALE, PHILIP L. et al.) 03 May 2007 See the entire document.	1-19
A	US 2011-0192564 A1 (MOMMER, CEDRIC et al.) 11 August 2011 See the entire document.	1-19
A	US 2008-0116416 A1 (CHACKO, ANTHONY P.) 22 May 2008 See the entire document.	1-19

 Further documents are listed in the continuation of Box C. See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 28 December 2018 (28.12.2018)	Date of mailing of the international search report 28 December 2018 (28.12.2018)
Name and mailing address of the ISA/KR International Application Division Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea Facsimile No. +82-42-481-8578	Authorized officer KWON, Yong Kyong Telephone No. +82-42-481-3371

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2018/049218

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2004-0097635 A1	20/05/2004	CN 1296994 C CN 1501483 A JP 2004-161996 A JP 4897188 B2 US 6924335 B2	24/01/2007 02/06/2004 10/06/2004 14/03/2012 02/08/2005
US 2002-0132896 A1	19/09/2002	AU 2003-222193 A1 AU 2003-243715 A1 CA 2433637 A1 CN 100351075 C CN 101126016 A CN 101126016 B CN 1307048 C CN 1512933 A CN 1512933 C CN 1638952 A CN 1688437 A CN 1868736 A EP 1401641 A1 EP 1401641 A4 EP 1483110 A1 EP 1483110 A4 EP 1542862 A1 EP 1542862 A4 JP 2005-508767 A JP 2005-538210 A JP 2006-502248 A JP 4237505 B2 KR 10-0685013 B1 KR 10-0747363 B1 KR 10-0773656 B1 KR 10-0854178 B1 KR 10-2004-0002866 A KR 10-2004-0081453 A KR 10-2005-0057278 A KR 10-2007-0020156 A KR 10-2007-0086591 A KR 10-2008-0006639 A SG 160196 A1 TW 200404868 A TW I286514 B TW I308171 B US 2003-0068487 A1 US 2004-0137216 A1 US 2006-0057364 A1 US 2007-0098971 A1 US 2007-0241307 A1 US 6451422 B1 US 6673434 B2	02/09/2003 29/03/2004 05/12/2002 28/11/2007 20/02/2008 24/10/2012 28/03/2007 14/07/2004 02/08/2006 13/07/2005 26/10/2005 29/11/2006 31/03/2004 12/12/2007 08/12/2004 27/06/2005 22/06/2005 27/06/2007 07/04/2005 15/12/2005 19/01/2006 11/03/2009 20/02/2007 07/08/2007 05/11/2007 26/08/2008 07/01/2004 21/09/2004 16/06/2005 16/02/2007 27/08/2007 16/01/2008 29/04/2010 01/04/2004 11/09/2007 01/04/2009 10/04/2003 15/07/2004 16/03/2006 03/05/2007 18/10/2007 17/09/2002 06/01/2004

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2018/049218

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		US 6797382 B2 US 6908669 B2 US 7244491 B2 US 7608324 B2 US 7867609 B2 WO 02-096636 A1 WO 03-064148 A1 WO 2004-022330 A1	28/09/2004 21/06/2005 17/07/2007 27/10/2009 11/01/2011 05/12/2002 07/08/2003 18/03/2004
US 2007-0097651 A1	03/05/2007	CN 101288353 A EP 1839469 A2 WO 2007-053571 A2 WO 2007-053571 A3	15/10/2008 03/10/2007 10/05/2007 19/06/2008
US 2011-0192564 A1	11/08/2011	CN 102687304 A CN 102687304 B EP 2517285 A2 EP 2517285 A4 JP 2013-514631 A JP 2014-223809 A JP 5638089 B2 KR 10-1524506 B1 KR 10-2012-0104592 A TW 201144074 A TW I408053 B WO 2011-084804 A2 WO 2011-084804 A3	19/09/2012 30/09/2015 31/10/2012 13/05/2015 25/04/2013 04/12/2014 10/12/2014 01/06/2015 21/09/2012 16/12/2011 11/09/2013 14/07/2011 06/10/2011
US 2008-0116416 A1	22/05/2008	CN 101622324 A CN 101622324 B US 7554793 B2 WO 2008-067198 A2 WO 2008-067198 A3	06/01/2010 24/04/2013 30/06/2009 05/06/2008 02/04/2009