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(54) Title: METAL THERMAL STABILIZATION OF POLYDIETHYLSILOXANE AND COPOLYMERS THEREOF

(57) Abstract: A polydiethylsiloxane (PDES) polymer material having enhanced thermal stability and a method of making the same is provided. The PDES polymer material generally comprises a PDES, a mixture of PDES and a second polymer, or a copolymer of PDES; and a thermal additive. The thermal additive being present in an amount ranging from about 0.01 wt. % to about 10 wt. % of the total weight of the PDES polymer material. The PDES polymer material exhibits thermal stability upon exposure to a temperature of 225°C; thermal stability being defined as exhibiting either (i) less than a 20 wt. % loss after exposure for 50 hours of exposure, (ii) no cracking or delamination occurring after exposure for at least 10 hours, or (iii) both (i) and (ii).



METAL THERMAL STABILIZATION OF POLYDIETHYLSILOXANE AND COPOLYMERS THEREOF

[0001] This disclosure relates generally to a method of providing thermal stability to polymers. More specifically, this disclosure relates to the thermal stabilization of polydiethylsiloxane (PDES) and copolymers thereof.

[0002] The statements in this section merely provide background information related to the present disclosure and may not constitute prior art.

[0003] Polydiethylsiloxane (PDES) exhibits a glass transition temperature (T_g) at about 135 K, a rigid crystal to a condic crystal disordering or isotropization temperature (T_i) at about 206 K, and a melting transition temperature (T_m) at 276 K. PDES also exhibits a small endotherm associated with loss of residual order that occurs between about 295-300 K. In addition, cross-linked PDES possesses a number of mechanical properties that are affected by the advent of a mesophase.

[0004] In general, PDES exhibits good waterproof performance, a high resistance to chemical corrosion, a low viscosity-to-temperature coefficient and low vapor pressure. In fact, PDES exhibits better lubricity, compressibility, and frost resistance than polydimethylsiloxane (PDMS). Thus PDES is considered as a candidate to replace PDMS in many application fields, particularly those that require lubricity and low-temperature resistance. However, the use of PDES in high temperature applications is limited due to its poor heat stability. In general, PDES tends to harden, become brittle, crack, and/or delaminate (i.e., lose adhesion) from any underlying substrate upon extended exposure to a high temperature or heat.

BRIEF SUMMARY OF THE INVENTION

[0005] This invention generally comprises a method of making a polydiethylsiloxane (PDES) polymer material having enhanced thermal stability. The PDES polymer material generally comprises a PDES, a mixture of PDES and a second polymer, or a copolymer of PDES; and a thermal additive, such that the PDES polymer material exhibits thermal stability upon exposure to a temperature of 225°C; thermal stability being defined as exhibiting either (i) less than a 20 wt. % loss after exposure for 50 hours of exposure, (ii) no cracking or delamination occurring after exposure for at least 10 hours, alternatively, at least 60 hours, or (iii) both (i) and (ii). The thermal additive is present in an amount ranging from about 0.01 wt. % to about 10 wt. % of the total weight of the PDES polymer material; alternatively, the thermal additive is present in the range of 0.04 wt. % to 5 wt. %. Alternatively, thermal stability is defined as both (I) and (II).

[0006] According to one aspect of the present disclosure, the thermal additive comprises either a metal or metal-containing compound selected as one from the group of vanadium, nickel, copper, iron, cerium, and zirconium or an organic antioxidant. Alternatively, the thermal additive is vanadium metal, a vanadium-containing compound, or an organic oxidant. Alternatively, the vanadium-containing compound is vanadium (V) triisopropoxide oxide. The thermal additive is incorporated into the PDES polymer material by mixing with or by the occurrence of a chemical reaction with the PDES, mixture of the PDES and second polymer, or the copolymer of PDES.

[0007] According to another aspect of the present disclosure, the thermal additive has an average particle diameter in the range of 50 nanometers to 2,500 micrometers. When the thermal additive is a metal or metal-containing compound, it can be deposited, absorbed, or applied to the surface of a hollow, porous, or solid particle core. Examples of such a particle core include, but are not limited to, a silicone, calcium carbonate, or E-powder.

[0008] According to another aspect of the present disclosure, the PDES, mixture of the PDES and second polymer, or the copolymer of PDES is a product of a reaction between an organopolysiloxane and a cross-linker in the presence of a hydrosilylation catalyst, and optionally, a functionalized silicone fluid; wherein the organopolysiloxane has an average of at least 0.1 silicon-bonded unsaturated group per molecule and the cross-linker has an average of at least 2 silicon-bonded hydrogen atoms per molecule.

[0009] According to yet another aspect of the present disclosure, a method of preparing a PDES polymer material that exhibits enhanced thermal stability is provided. This method generally comprises the steps of: providing PDES, a mixture of PDES and a second polymer, or a copolymer of PDES as described above and herein; providing a thermal additive as described above and herein; combining the thermal additive with the PDES, mixture of PDES and a second polymer, or copolymer of PDES to form the PDES polymer material; and optionally, heating the PDES polymer material to a temperature of at least 120°C for 30 to 180 minutes. The thermal additive is present in an amount ranging from about 0.01 wt. % to about 10 wt. % of the total weight of the PDES polymer material. The resulting PDES polymer material exhibits thermal stability upon exposure to a temperature of 225°C; thermal stability being defined as exhibiting either (i) less than a 20 wt. % loss after exposure for 50 hours of exposure, (ii) no cracking or delamination occurring after exposure for at least 10 hours, or (iii) both (i) and (ii).

[0010] According to another aspect of the present disclosure, when the thermal additive is a metal or metal-containing compound, it can be deposited, absorbed, or applied to the surface of a hollow, porous, or solid particle core by direct loading, by chemical reaction, or via the use of a deposition technique. The thermal additive may be combined with the

PDES polymer material by mixing with or by the occurrence of a chemical reaction with the PDES, mixture of the PDES and second polymer, or the copolymer of PDES.

[0011] According to yet another aspect of the present disclosure, a gel, coating, film, composite, or solid-shaped component is provided that comprises a PDES polymer material that exhibits enhanced thermal stability. The PDES polymer material is prepared according to the method described above and herein.

[0012] Further areas of applicability will become apparent from the description provided herein. It should be understood that the description and specific examples are intended for purposes of illustration only and are not intended to limit the scope of the present disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The drawings described herein are for illustration purposes only and are not intended to limit the scope of the present disclosure in any way.

[0014] Figure 1 is an image of gel samples (I-A to I-L) prepared according to the teachings of the present disclosure;

[0015] Figure 2 is an image of the gel samples of Figure 1 aged in air at 225°C for 2 hours;

[0016] Figure 3 is an image of the gel samples of Figure 1 aged in air at 225°C for 5 hours;

[0017] Figure 4 is an image of the gel samples of Figure 1 aged in air at 225°C for 10 hours;

[0018] Figure 5 is an image of the gel samples of Figure 1 aged in air at 225°C for 16 hours; and

[0019] Figure 6 is an image of the gel samples of Figure 1 aged in air at 225°C for 63 hours.

DETAILED DESCRIPTION

[0020] The following description is merely exemplary in nature and is in no way intended to limit the present disclosure or its application or uses. It should be understood that throughout the description, corresponding reference numerals indicate like or corresponding parts and features.

[0021] The present disclosure generally relates to thermally stable polydiethylsiloxane (PDES) and polymer materials or copolymers that partially comprise said PDES, as well as a method for making said thermally stable PDES or polymer materials. More specifically, such thermally stable PDES or polymer materials that partially incorporate said PDES as a copolymer or mixture therewith, generally, also include an organic antioxidant or a metal,

alternatively, a transition metal, or metal compound as a thermal additive. This thermal additive may be solid or hollow particles, coated particles, or powders having an average diameter size ranging from about 10 nanometers to about 5000 micrometers. The incorporation of the thermal additive into the formulated and cross-linked PDES polymer materials (liquid or solids) provides for their enhanced heat resistance upon exposure to or prolonged use at a high temperature, alternatively, at a temperature greater than about 200°C.

[0022] In order to more fully illustrate the concept, the invention is described throughout the following disclosure in terms of a thermally stable, polymeric gel. The thermally stable, polymeric gel is shown to be applied upon and adhered to the surface of a thermally stable substrate as a coating or film. However, one skilled-in-the-art will understand that this concept as demonstrated using a coating or film can be extended to various other composite structures and solid-shaped components without exceeding the scope of the present disclosure.

[0023] According to one aspect of the present disclosure, the PDES polymer materials may include co-polymers of PDES with any aryl-substituted, alkyl-substituted, or halogen-substituted silicone polymers, polycarbonates, or polyimides. A specific example of an aryl, alkyl, and halogen groups present in such substituted silicone polymers includes, phenyl, methyl, and fluorine groups, respectively. Such PDES polymer materials may be prepared as a hydrosilylation reaction product of an organopolysiloxane having an average of at least 0.1 silicon-bonded unsaturated group per molecule and a cross-linker having an average of at least 2 silicon-bonded hydrogen atoms per molecule. Alternatively, the organopolysiloxane has an average of at least 1 silicon-bonded unsaturated group per molecule. The organopolysiloxane and cross-linker can react via hydrosilylation in the presence of a hydrosilylation catalyst. When the formation of a gel is desirable, the PDES polymer materials may also include a functional silicone fluid.

[0024] The unsaturated groups in the organopolysiloxane, include, but are not limited to, vinyl, allyl, butenyl, pentenyl, hexenyl, and heptenyl groups; alternatively, the unsaturated group is a vinyl group. The organopolysiloxane may have a linear molecular structure or a branched linear, or a dendrite molecular structure. The organopolysiloxane may be or include a single polymer, a copolymer, or a combination of two or more polymers. The organopolysiloxane may be further defined as an organoalkylpolysiloxane. Each unsaturated group in the organopolysiloxane is independently selected and may be the same or different. Each unsaturated group may be located as a terminal group or a pendant group relative to the polymer's backbone or chain.

[0025] The organopolysiloxane may further include a resin containing M, D, T, or Q units, which correspond to one or more of $(R_3SiO_{1/2})$, $(R_2SiO_{2/2})$, $(RSiO_{3/2})$, or $(SiO_{4/2})$, respectively, where R is independently selected from a hydrogen atom and a monovalent organic group. Such monovalent organic groups, for example may include, but are not limited to, monovalent hydrocarbon groups and monovalent halogenated hydrocarbon groups. Several specific examples of monovalent hydrocarbon groups include, alkyl groups, such as methyl, ethyl, propyl, pentyl, octyl, undecyl, and octadecyl groups; cycloalkyl groups, such as cyclohexyl groups; alkenyl groups such as vinyl, allyl, butenyl, and hexenyl groups; alkynyl groups, such as ethynyl, propynyl, and butynyl groups; and aryl groups, such as phenyl, tolyl, xylyl, benzyl, and 2-phenylethyl groups. One example of an organopolysiloxane, among many examples, includes $M^{Vi}-D_x-D^{(Et, Et)}_y-M^{Vi}$, wherein the M unit comprises two methyl groups (not shown) and one vinyl (Vi) group, the D units comprise either two methyl groups (not shown) or two ethyl (Et) groups. The subscript x is either zero or an integer and y is an integer. These subscripts define the number of each repeating unit, such that the sum (x+y) may range from about 10 to about 2,000; alternatively, from about 50 to 1000; alternatively, from about 100 to about 500. Other organopolysiloxanes that may be used in the present disclosure are described in co-pending U.S. Application No. 61/544,001, filed on October 6, 2011, the entire contents of which are hereby incorporated by reference.

[0026] The cross-linker may be further defined as, or include, a silane or a siloxane, such as a polyorganosiloxane. When desirable, the cross-linker may include more than 2 silicon-bonded hydrogen atoms per molecule. The cross-linker may have a linear, a branched, or a partially branched linear, cyclic, dendrite, or resinous molecular structure. The silicon-bonded hydrogen atoms may be terminal or pendant. Alternatively, the cross-linker may include both terminal and pendant silicon-bonded hydrogen atoms.

[0027] The cross-linker may also include monovalent hydrocarbon groups which do not contain unsaturated aliphatic bonds, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, decyl, undecyl, or dodecyl groups; cycloalkyl groups, such as cyclopentyl or cyclohexyl groups; aryl groups, such as phenyl, tolyl, or xylyl groups; aralkyl groups, such as benzyl or phenethyl groups; or halogenated alkyl groups, such as 3,3,3- trifluoropropyl or 3-chloropropyl groups. Alternatively, the cross-linker comprises hydrogen groups and either alkyl or aryl groups; alternatively, hydrogen groups and either methyl or phenyl groups.

[0028] The cross-linker may further include a resin containing M, D, T, or Q units, which correspond to one or more of $(R_3SiO_{1/2})$, $(R_2SiO_{2/2})$, $(RSiO_{3/2})$, or $(SiO_{4/2})$, respectively, where R is independently selected from a hydrogen atom and a monovalent hydrocarbon group.

One example of a cross-linker, among many examples, includes $MD_wD^{(H)}_zM$, wherein the M unit comprises three methyl groups (not shown), the D units comprise either two methyl groups (not shown) or one methyl group (not shown) and one hydrogen (H) group. The subscript w is either zero or an integer and subscript z is an integer. These subscripts, w and z, define the number of each repeating unit, such that the sum (x+y) may range from 1 to about 2,000; alternatively, from about 3 to 1000; alternatively, from about 5 to about 500; alternatively, about 8 to about 50.

[0029] The hydrosilylation catalyst may be any known in the art to catalyze a hydrosilylation reaction. The hydrosilylation catalyst may include without limitation, a platinum group metal, such as platinum, rhodium, ruthenium, palladium, osmium or iridium or an organometallic compound comprising said platinum group metal, or combinations thereof. Alternatively, the hydrosilylation catalyst may be further defined as either fine platinum metal powder; platinum black; platinum dichloride; platinum tetrachloride; chloroplatinic acid; alcohol-modified chloroplatinic acid; chloroplatinic acid hexahydrate; and complexes of such compounds, such as platinum complexes of olefins, carbonyls, alkenylsiloxanes, or low molecular weight organopolysiloxanes; and complexes of chloroplatinic acid with β -diketones, olefins, or 1,3-divinyltetramethyldisiloxane. One specific example of a hydrosilylation catalyst, among many examples, includes Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane, which is also known as Karstedt's catalyst.

[0030] When gelation is required or desired, a functional silicone fluid may optionally be incorporated into the PDES polymer materials. The terminology "functional silicone fluid" describes that the fluid is functionalized such that it can react in a hydrosilylation reaction, i.e., includes unsaturated groups, Si-H groups, or a mixture thereof. However, it is contemplated, without exceeding the scope of the present disclosure, that the functional fluid may include one or more additional functional groups in addition to, or in the absence of, one or more unsaturated or Si-H groups. Functional silicone fluids that may be utilized in the present disclosure are described in one or more of U.S. Pat. Nos. 6,020,409; 4,374,967; and/or 6,001,918, the entire contents of which are expressly incorporated herein by reference. One specific example, among many examples of a functional silicone fluid is phenyldimethylsilane ($PhSiMe_2H$).

[0031] According to one aspect of the present disclosure, the thermal additive that is mixed with or incorporated into the PDES or associated polymeric materials may be in the form of an organic antioxidant, including but not limited to secondary or tertiary amines, or in the form of a metal or a metal compound. Alternatively, the metal or metal compound includes one or more transition metals, such as vanadium, nickel, copper, iron, cerium, or zirconium. Alternatively, the thermal additive is an organic antioxidant, such as tris(3,5-di-t-

butyl-4-hydroxybenzyl)-isocyanurate, or a transition metal or metal compound comprising vanadium or nickel, alternatively, vanadium. A specific example of such a nickel or vanadium compound is nickel (II) acetylacetonate or an oxo-trialkoxo-vanadium complex, including but not limited to $\text{VO}(\text{O-iPr})_3$. When desirable, a mixture of metal compounds and organic antioxidants may be utilized with or without the use of other additives in order to provide for synergistic effects that enhance the heat resistance exhibited by PDES and related polymer materials. The thermal additive may be added to the PDES polymer materials either as a liquid or in powder form. Thermal additive may also be added to the PDES polymer materials as a dispersion or mixture in a solvent, including but not limited to, tetrahydrofuran (THF), toluene, acetone, xylene, or isopropyl alcohol.

[0032] The conversion of a metal compound to a metal, metal oxide, or a mixture thereof is possible by heating the metal compound in the presence of oxygen, air, or an inert atmosphere. The metal compound may be heated for a predetermined amount of time at a temperature of at least about 120°C; alternatively, at least 140°C; alternatively, at least 160°C, ; alternatively, at least 180°C; alternatively, at least 200°C. The predetermined amount of time that the metal compound is heated may range from about 30 to about 180 minutes; alternatively, from about 60 to about 120 minutes; alternatively from about 80 to 100 minutes.

[0033] According to another aspect of the present disclosure, the thermal additive can be mixed with or introduced into the PDES by the occurrence of a chemical reaction between PDES or related polymer materials. A metal or metal compound deposited, absorbed, or applied to the surface of a hollow, porous, or solid particle core can enhance metal dispersion into PDES and its related polymer materials when such metal or metal compounds have limited miscibility with PDES or its related polymer materials. These particle cores may include but not be limited to various inorganic and organic compounds and polymers, such as silicones, calcium carbonate, or E-powder, as well as other functional homo- and co-polymers that fall within the appropriate nanometer or micrometer size range.

[0034] The specific loading method used to apply the metal or metal compounds on these particles include, but are not limited to 1) direct loading (i.e, the mixing of solids or liquids) by dry blending or wet blending mechanisms, 2) various known in-situ chemicals reactions, and 3) deposition mechanisms or techniques, such as electroless deposition, sputtering, physical vapor deposition (PVD) and chemical vapor deposition (CVD). It is contemplated without exceeding the scope of the present disclosure that the thermal additives described herein may also be further treated to provide additional functionality by

physical and/or chemical processes such as surface treatment, heat treatments, calcinations, light treatments, and radiation, to name a few.

[0035] According to another aspect of the present disclosure, the particles upon which the metal or metal compounds are applied may comprise M, D, T, or Q units corresponding to one or more of $(R_3SiO_{1/2})$, $(R_2SiO_{2/2})$, $(RSiO_{3/2})$, or $(SiO_{4/2})$, respectively, where R is independently selected from a hydrogen atom and a monovalent organic group. The particles may also be silicone elastomeric particles, such as an E-powder produced by Dow Corning Toray Silicone Co., Ltd., Japan. Examples of suitable silicones that can be used herein as particles are those described in U.S. Pat. Nos. 4,370,160, 4,742,142, 4,743,670, 5,387,624, 5,492,945, 5,945,471, 5,948,469, 5,969,039 and 7,393,582, the contents of which are hereby incorporated by reference in their entirety.

[0036] The thermal additives can be dispersed or loaded into PDES or one or more of its related polymer materials, blends, or composites, such that the loading of the metal element is within the range of about 0.01 wt. % to about 10 wt. %, alternatively, between about 0.04 wt. % and 5 wt. %; alternatively, about 0.05 wt. % to about 1 wt. % of the total weight of the PDES or polymer material. Alternatively, the loading of the metal in the thermal additive is in the range of about 200 ppm to 1000 ppm, alternatively between about 400 and 700 ppm.

[0037] The particle size of the thermal additives may range from about 10 nanometers to about 5000 micrometers (μm) in average diameter; alternatively, from about 50 nanometers to about 2500 μm , alternatively, about 500 nanometers to about 1000 μm ; alternatively, from about 1 μm to about 500 μm . The surface of the thermal additive may exhibit hydrophobic or hydrophilic properties. The surface of the thermal additive may also be electrically charged (positive or negative) or non-charged/neutral; alternatively, the surface of the thermal additive is positively charged.

[0038] The following specific embodiments are given to illustrate the thermally stable formulations of PDES and its related polymer materials prepared according to the teachings of the present disclosure, as well as method of preparing such formulations, and should not be construed to limit the scope of the disclosure. Those skilled-in-the-art, in light of the present disclosure, will appreciate that many changes can be made in the specific embodiments which are disclosed herein and still obtain alike or similar result without departing from or exceeding the spirit or scope of the disclosure. One skilled in the art will further understand that any properties reported herein represent properties that are routinely measured and can be obtained by multiple different methods. The methods described herein represent one such method and other methods may be utilized without exceeding the scope of the present disclosure.

[0039] Example 1 – Preparation and Testing of Thermally Stable PDES Polymer Materials

[0040] Two different PDES polymer materials, namely, Formulation (I) and Formulation (II) are prepared and tested for thermal stability. In Formulation (I), 100 parts of an organopolysiloxane defined by the general formula $(M^{Vi}-D_{105}-D^{(Et, Et)}_{25}-M^{Vi})$ was mixed with 1.2 parts of a cross-linker defined by the formula $(MD_{3.2}D^H_{5.8}M)$, 1.66 parts of phenyldimethylsilane as a functional silicone fluid, and 0.155 parts of Kasterdt's hydrosilylation catalyst. In formulation (I), the ratio of Si-H to Vinyl groups = 1:1 and the amount of the platinum present is on the order of 8 ppm. This preparation was repeated 12 times yielding PDES polymer materials identified by Mixture No.'s 1-A to 1-L. In Formulation (II), 100 parts of an organopolysiloxane defined by the general formula $M^{Vi}-D_{400}-D^{(Et, Et)}_{50}-M^{Vi}$ was mixed with 0.85 parts of a cross-linker defined by the formula $MD_{3.2}D^H_{5.8}M$, and 0.15 parts of Kasterdt's hydrosilylation catalyst. In formulation (II), the ratio of Si-H to Vinyl groups = 1.1:1 and the amount of the platinum present is on the order of 8 ppm. This preparation was repeated 3 times yielding PDES polymer materials identified by Mixture No.'s 1-M to 1-O.

[0041] *Formulation (I)* - To each of the PDES polymer materials (Mixture No.'s I-B to I-K), a thermal stabilizer is added to yield a mixture for testing thermal stability. These thermal additives are metal compounds identified as iron(III) acetylacetonate (I-B); ferrocene (I-C); iron (III) 2-ethylhexanoate (I-D) applied in 50% mineral oil; cerium(III) acetylacetonate hydrate (I-E); vanadium (V) triisopropoxide oxide applied as a liquid (I-F), on E-powder (I-G), and on $CaCO_3$ nanoparticles (particle diameter of 15-40 nm) (I-H); copper (II) acetylacetonate (I-I); zirconium acetylacetonate (I-J); and nickel acetylacetonate (I-K). The metal compounds in Mixture No.'s I-B, I-C, I-E, I-I, I-J, and I-K are applied as a dispersion in tetrahydrofuran (THF). Each of the mixtures (see Table 1) contained between about 400 to about 800 ppm metal content, except for mixtures I-A and I-L. In mixture I-A, no metal or organic antioxidant is utilized so that this mixture can be used as a control. In mixture I-L, an organic antioxidant in an amount of 0.15 wt. % is used. This organic antioxidant is identified as a 1,3,5-Tris(3,5-Di-Tert-Butyl-4-Hydroxybenzyl)-1,3,5-Triazine-2,4,6(1H,3H, 5H)-Trione (Ethanox® 314 antioxidant, Albemarle Corporation, Baton Rouge, Louisiana).

[0042] Each of the mixtures is poured into aluminum pan (the "substrate") with a diameter of 6 cm to form a layer having a thickness of (2.0 ± 0.1) mm. Each of the mixtures is then subjected to heat at 120°C for a period of 1 hour prior to exposure to a high temperature for testing thermal stability. Thermal stability being defined as either exhibiting a weight loss after exposure to 225°C in air for greater than 50 hours,

alternatively, greater than 77 hours, that is less than about 20 wt. % or withstanding greater than 10 hours exposure, alternatively, greater than 15 hours exposure, alternatively greater than about 60 hours exposure to a temperature of at least 225°C in air without exhibiting signs of cracking or delamination. Alternatively, thermal stability is defined as both test criteria being met or passed.

[0043] Table 1

Mixture No.	Additive	Metal content (ppm)	Damage time (hr) /225°C, air	Weight loss (wt%) @ 77hr/225°C, air
I-A	none	0	<2	20.6
I-B	Fe(acac) ₃	505	<2	21.9
I-C	Ferrocene	507	<2	21.9
I-D	Fe(EHA) ₃	536	2-5	20.8
I-E	Ce(acac) ₃ •xH ₂ O	528	2-5	20.8
I-F	VO(O-iPr) ₃	813	63-77	16.2
I-G	VO(O-iPr) ₃ in Epowder	558	5-10	17.2
I-H	VO(O-iPr) ₃ in CaCO ₃	591	5-10	16.9
I-I	Cu(acac) ₂	513	5-10	22.8
I-J	Zr(acac) ₄	504	<2	26.6
I-K	Ni(acac) ₂	493	5-10	19.3
I-L	Ethanox 314	0.15wt%*	10-16	18.1

[0044] The results of thermal stability testing are provided in Table 1. The control Mixture No. I-A shows signs of cracking and/or delamination upon exposure to 225°C in less than 2 hours with an overall weight loss exceeding 20% after exposure for 77 hours. Mixture No.'s I-F, I-G, I-H, I-K, and I-L corresponding to vanadium and nickel metals and an organic amine antioxidant are found to pass the test criteria for weight loss being less than 20 wt. % after exposure to 225°C for 77 hours and with respect to no cracking or delamination after exposure to 225°C for greater than 5 hours exposure with vanadium (I-F) and the organic antioxidant (I-L) passing after exposure to greater than 10 hours, and only vanadium (I-F) passing after exposure to greater than 60 hours.

[0045] The results for Mixture No.'s I-A to I-L are further described in Figures 1-6, wherein a solid circle around a sample indicates damage to the same in the form of either cracking or delamination and either no circle or a dotted circle around the sample indicates that no damage has occurred. Referring to Figure 1, Mixture No.'s I-A to I-L are shown prior exposure to a high temperature, wherein each mixture exhibits no cracking or good adherence to the substrate. In Figure 2, each of the mixtures are re-examined after exposure to 225°C for a period of 2 hours with Mixture No.'s I-A, I-B, I-C, and I-J exhibiting cracking and/or delamination from the substrate. In Figure 3, Mixture No.'s I-D, I-E, and I-I are shown to fail the test by exhibiting cracking and/or delamination after exposure to 225°C for a period of 5 hours. In Figure 4, each of the mixtures are re-examined after

exposure to 225°C for a period of 10 hours with Mixture No.'s I-G, I-H, and I-K exhibiting cracking and/or delamination from the substrate. Thus only Mixture No.'s I-F and I-L have not failed after exposure to 225°C for 10 hours. After exposure to 225°C for 16 hours Mixture No. I-L has begun to exhibit cracking and/or delamination. After 16 hours only Mixture No. I-F (highlighted by a star) remains crack-free and exhibits good adhesion to the substrate. Mixture No. I-F continues to show no degradation even after exposure to 225°C for 63 hours.

[0046] *Formulation (II)* - To each of the PDES polymer materials (Mixture No.'s II-N and II-O), a thermal stabilizer is added to yield a mixture for testing thermal stability. These thermal additives are metal compounds identified vanadium (V) triisopropoxide oxide applied as a liquid (II-N) and vanadium (IV) oxide bis(2,4-pentanedionate) applied as a powder (II-O). Each of the mixtures (see Table 2) contains between about 0.20 and 0.25 wt. % metal content based on the total weight of the PDES polymer material, except for Mixture No. II-M. In Mixture No. II-M, no metal or organic antioxidant is utilized so that this mixture can be used as a control.

[0047] Each of the mixtures is poured into aluminum pan (the "substrate") with a diameter of 6 cm to form a layer having a thickness of (2.0 ± 0.1) mm. Each of the mixtures is then subjected to heat at 120°C for a period of 1 hour prior to exposure to a high temperature for testing thermal stability.

[0048] The results of thermal stability testing are provided in Table 2. The control Mixture No. II-M shows signs of cracking and/or delamination upon exposure to 225°C in less than 4 hours with an overall weight loss of 19.3% after exposure for 52 hours. Mixture No. II-N corresponding to a vanadium metal compound passes the test criteria for weight loss being less than 20 wt. % after exposure to 225°C for 52 hours and with respect to no cracking or delamination after exposure to 225°C for 52 hours exposure. Mixture No. II-O exhibits no cracking or delamination after exposure to 225°C for 22 hours.

[0049] Table 2

Mixture No.	Additive	Metal content (wt%)	Damage time (hr) /225°C, air	Weight loss (wt%) @ 52hr/225°C, air
II-M	none	0	<4	19.3
II-N	VO(O-iPr) ₃	0.24	22	17.4
II-O	VO(acac) ₂	0.2	52	22.4

[0050] The foregoing description of various forms of the invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise forms disclosed. Numerous modifications or variations are possible in light of the above teachings. The forms discussed were chosen and described to provide the best illustration of the principles of the invention and its practical application

to thereby enable one of ordinary skill in the art to utilize the invention in various forms and with various modifications as are suited to the particular use contemplated. All such modifications and variations are within the scope of the invention as determined by the appended claims when interpreted in accordance with the breadth to which they are fairly, legally, and equitably entitled.

CLAIMS

What is claimed is

1. A polydiethylsiloxane (PDES) polymer material having enhanced thermal stability, the PDES polymer material comprising:
a PDES, a mixture of PDES and a second polymer, or a copolymer of PDES;
and
a thermal additive, the thermal additive being present in an amount ranging from about 0.01 wt. % to about 10 wt. % of the total weight of the PDES polymer material;
wherein the PDES polymer material exhibits thermal stability upon exposure to a temperature of 225°C; thermal stability being defined as exhibiting either (i) less than a 20 wt. % loss after exposure for 50 hours of exposure, (ii) no cracking or delamination occurring after exposure for at least 10 hours, or (iii) both (i) and (ii).
2. The PDES polymer material according to Claim 1, wherein the thermal additive comprises either a metal or metal-containing compound selected as one from the group of vanadium, nickel, copper, iron, cerium, and zirconium or an organic antioxidant.
3. The PDES polymer material according to Claim 2, wherein the thermal additive is vanadium metal, a vanadium-containing compound, or an organic oxidant.
4. The PDES polymer material according to Claims 2 or 3, wherein the vanadium-containing compound is vanadium (V) triisopropoxide oxide.
5. The PDES polymer material according to any of Claims 1-4, wherein the thermal additive is present in the range of 0.04 wt. % to 5 wt. %.
6. The PDES polymer material according to any of Claims 1-5, wherein the thermal additive has an average particle diameter in the range of 50 nanometers to 2,500 micrometers.
7. The PDES polymer material according to any of Claims 1-6, wherein the thermal additive is incorporated into the PDES polymer material by mixing with or by the occurrence of a chemical reaction with the PDES, mixture of the PDES and second polymer, or the copolymer of PDES.

8. The PDES polymer material according to any of Claims 1-7, wherein the thermal additive is a metal or metal-containing compound deposited, absorbed, or applied to the surface of a hollow, porous, or solid particle core.

9. The PDES polymer material according to Claim 8, wherein the particle core is selected as one from the group of a silicone, calcium carbonate, or E-powder.

10. The PDES polymer material according to any of Claims 1-9, wherein thermal stability is defined as both (I) and (II).

11. The PDES polymer material according to any of Claims 1-10, wherein no cracking or delamination of the PDES polymer material is observed to occur after exposure for 60 hours.

12. The PDES polymer material according to any of Claims 1-11, wherein the PDES, mixture of the PDES and second polymer, or the copolymer of PDES is a product of a reaction between an organopolysiloxane and a cross-linker in the presence of a hydrosilylation catalyst, and optionally, a functionalized silicone fluid; wherein the organopolysiloxane has an average of at least 0.1 silicon-bonded unsaturated group per molecule and the cross-linker has an average of at least 2 silicon-bonded hydrogen atoms per molecule.

13. A method of preparing a PDES polymer material that exhibits enhanced thermal stability, the method comprising the steps of:

providing PDES, a mixture of PDES and a second polymer, or a copolymer of PDES;

providing a thermal additive;

combining the thermal additive with the PDES, mixture of PDES and a second polymer, or copolymer of PDES to form the PDES polymer material; and

optionally, heating the PDES polymer material to a temperature of at least 120°C for 30 to 180 minutes;

wherein the thermal additive is present in an amount ranging from about 0.01 wt. % to about 10 wt. % of the total weight of the PDES polymer material;

wherein the PDES polymer material exhibits thermal stability upon exposure to a temperature of 225°C; thermal stability being defined as exhibiting either (i) less than a 20 wt. % loss after exposure for 50 hours of exposure, (ii) no cracking or delamination occurring after exposure for at least 10 hours, or (iii) both (i) and (ii).

14. The method according to Claim 13, wherein the thermal additive comprises either a metal or metal-containing compound selected as one from the group of vanadium, nickel, copper, iron, cerium, and zirconium or an organic antioxidant.

15. The method according to Claim 14, wherein the metal or metal-containing compound is deposited, absorbed, or applied to the surface of a hollow, porous, or solid particle core.

16. The method according to any of Claims 13-15, wherein the PDES, mixture of the PDES and second polymer, or the copolymer of PDES is formed as a product of a reaction between an organopolysiloxane and a cross-linker in the presence of a hydrosilylation catalyst, and optionally, a functionalized silicone fluid; wherein the organopolysiloxane has an average of at least 0.1 silicon-bonded unsaturated group per molecule and the cross-linker has an average of at least 2 silicon-bonded hydrogen atoms per molecule.

17. The method according to any of Claims 13-16, wherein the thermal additive is combined with the PDES polymer material by mixing with or by the occurrence of a chemical reaction with the PDES, mixture of the PDES and second polymer, or the copolymer of PDES.

18. The method according to Claim 15, wherein the metal or metal-containing compound is applied to the surface of the particle core by direct loading, by chemical reaction, or via the use of a deposition technique.

19. A gel, coating, film, composite, or solid-shaped component comprising a PDES polymer material exhibiting enhanced thermal stability that is prepared according to the method of any of Claims 13-18.

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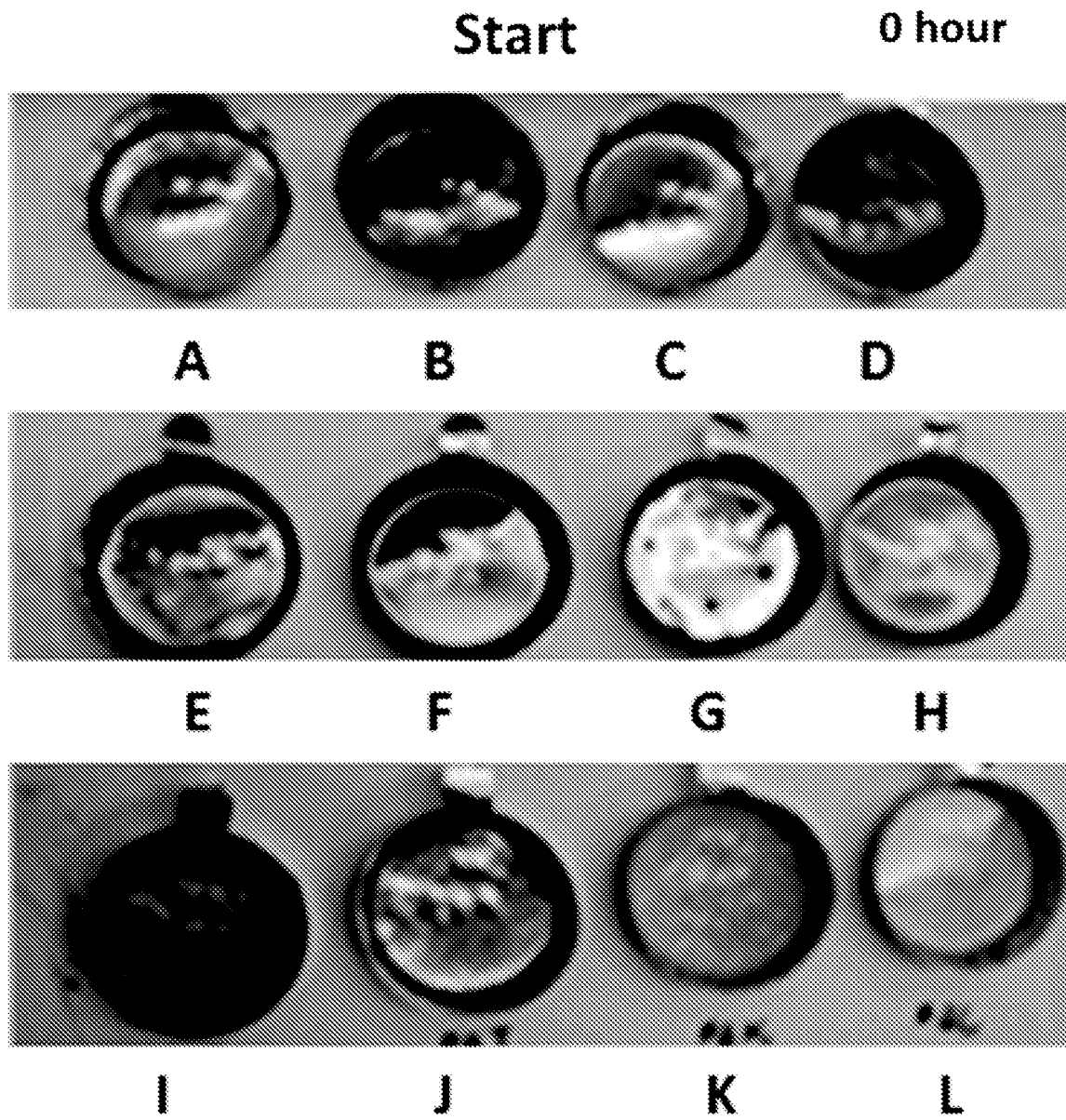


Figure 1

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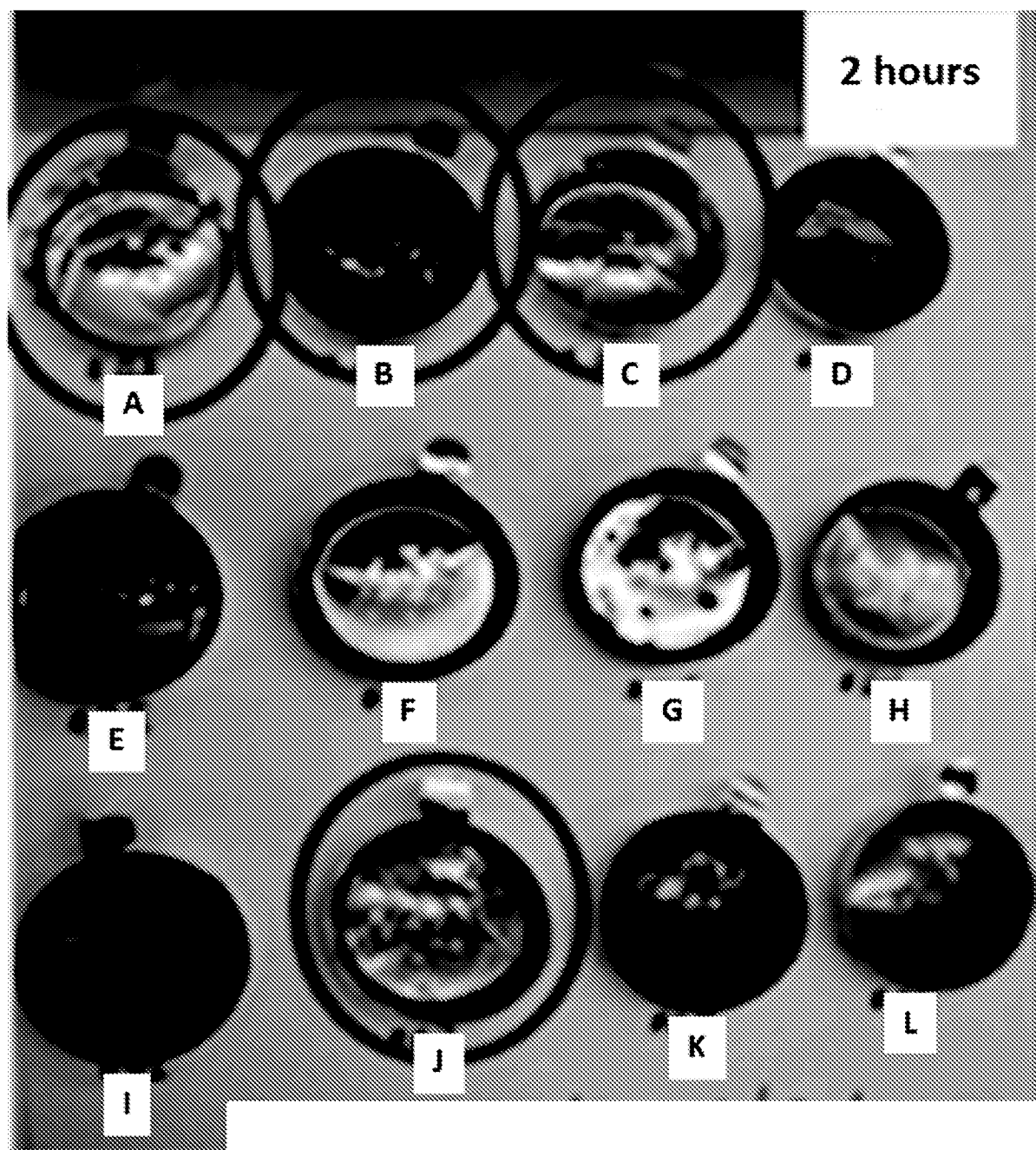


Figure 2

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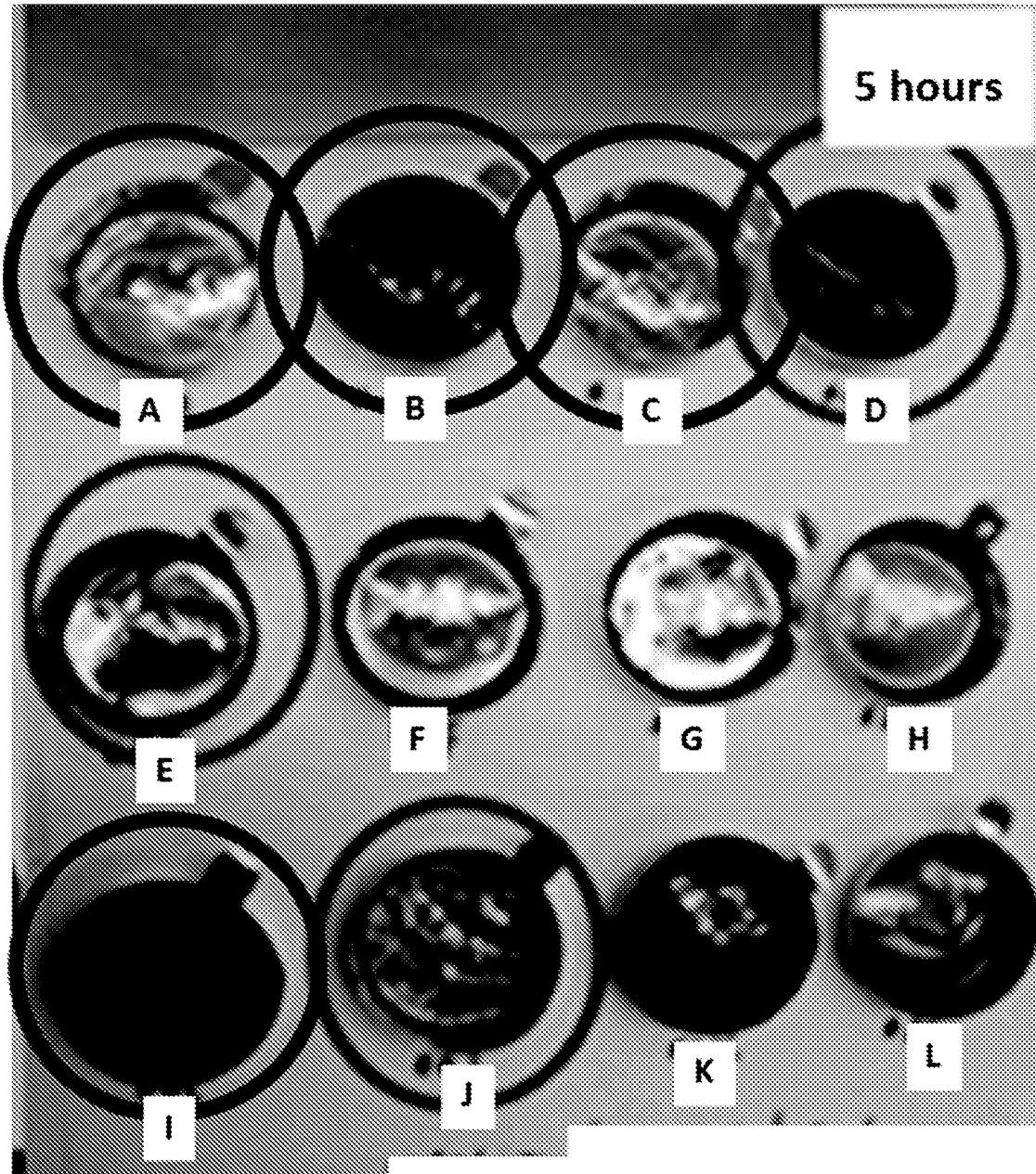


Figure 3

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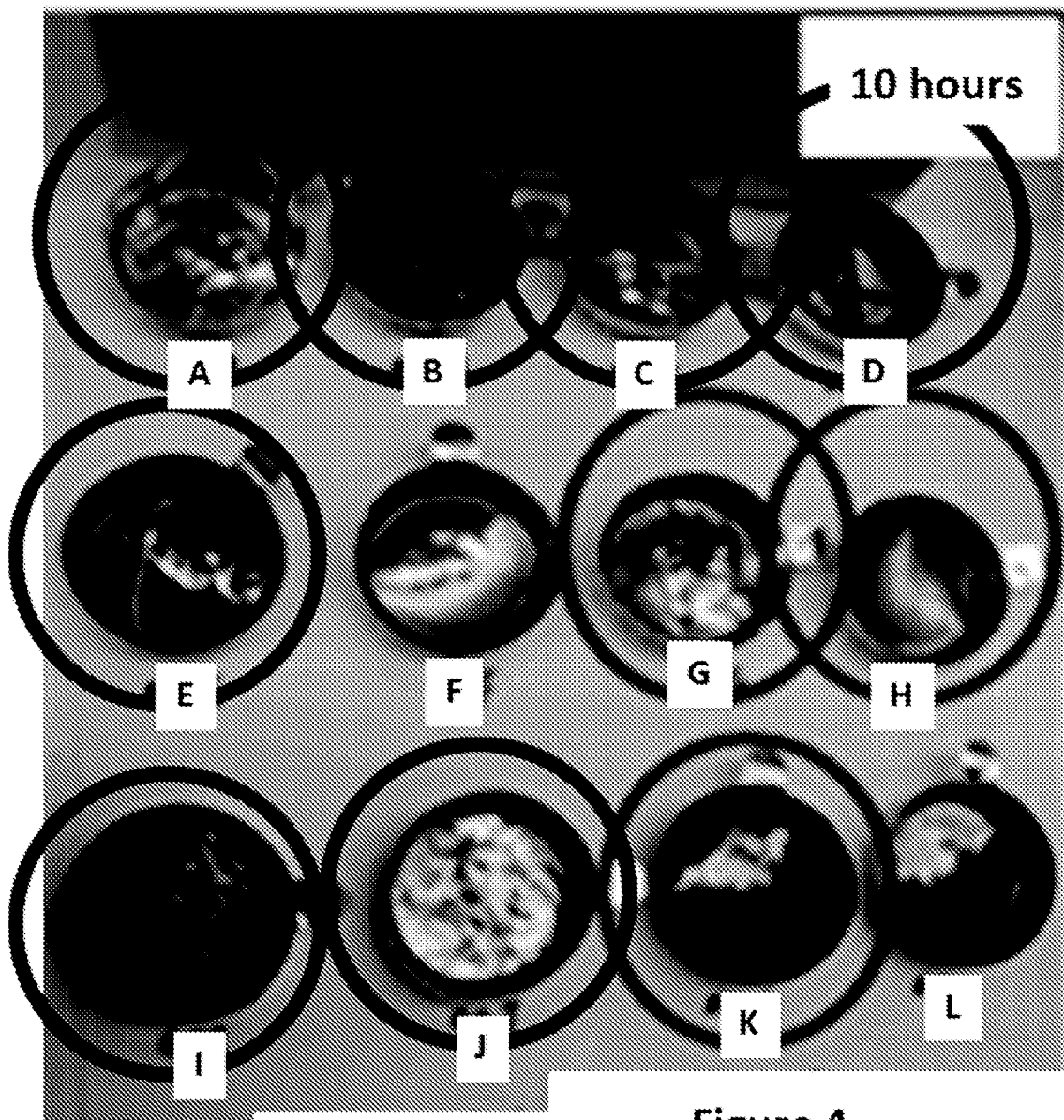


Figure 4

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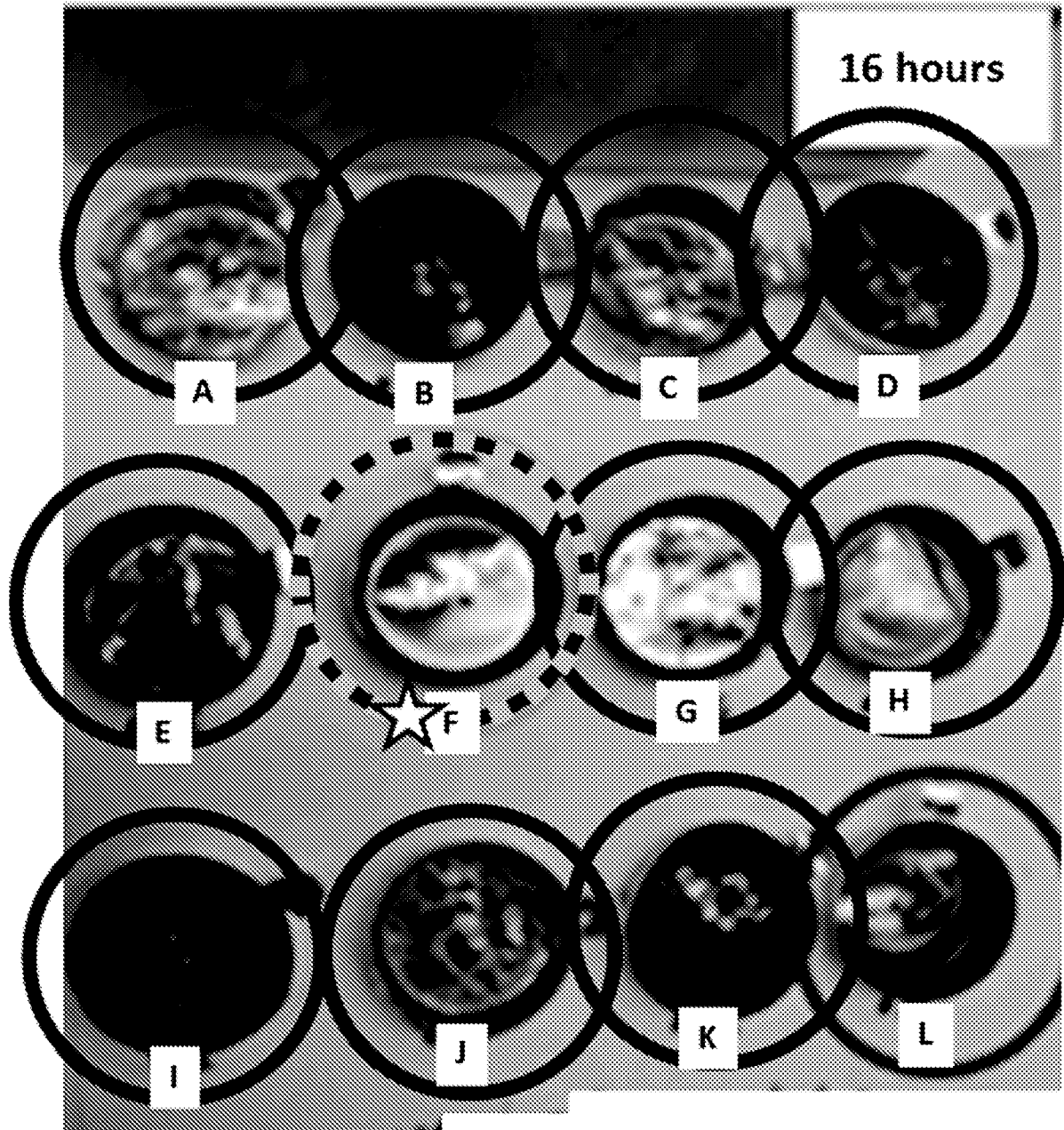


Figure 5

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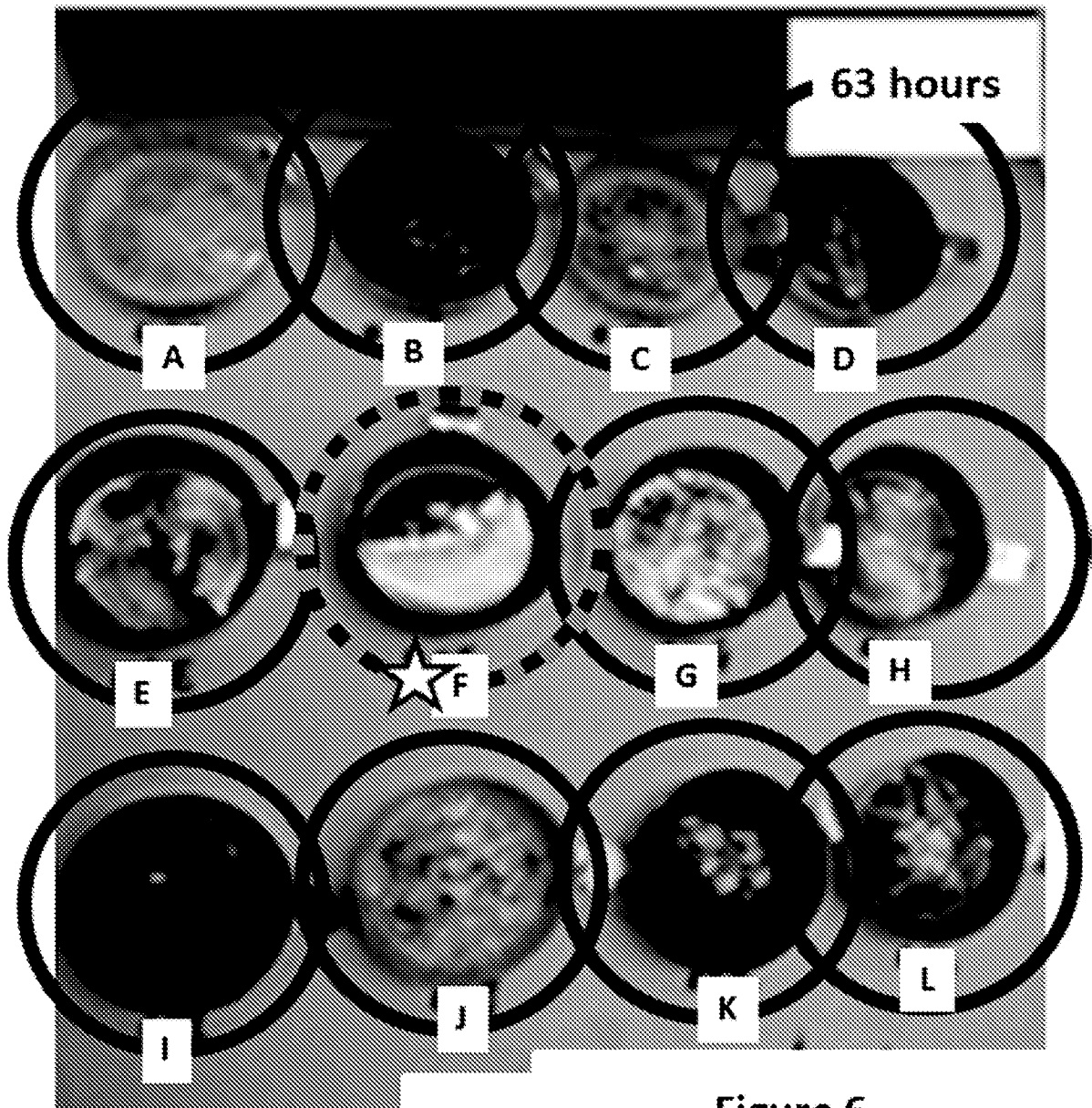


Figure 6

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/025844

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08K3/00 C08K3/22 C08L83/06
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08K C08L

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 230 632 A (CHAPMAN DWAIN R) 28 October 1980 (1980-10-28) column 2, line 50; claim 1 -----	1-19
X	US 2006/142471 A1 (SHINDO TAKUYA [JP]) 29 June 2006 (2006-06-29) paragraph [0024]; claims 1,6 -----	1-19
A	JP H10 95852 A (NIPPON STEEL CORP) 14 April 1998 (1998-04-14) abstract -----	1-19



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

16 July 2014

Date of mailing of the international search report

24/07/2014

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/025844

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4230632	A	28-10-1980	NONE	

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