(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
08 October 2020 (08.10.2020)

WIPO | PCT

(10) International Publication Number
WO 2020/205910 A1

(51) International Patent Classification:
A23L 3/015 (2006.01) *G01L 11/00* (2006.01)
A23L 5/40 (2016.01)

(21) International Application Number:
PCT/US2020/026073

(22) International Filing Date:
01 April 2020 (01.04.2020)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

62/827,715	01 April 2019 (01.04.2019)	US
62/908,986	01 October 2019 (01.10.2019)	US
16/835,983	31 March 2020 (31.03.2020)	US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) Title: THERMOCHROMIC TEMPERATURE SENSOR

(57) Abstract: A temperature sensor, and methods of making and using such a temperature sensor, whereby the temperature sensor includes a reversible thermochromic color-changing system having a dye, a developer, and a solvent. Upon exposure to a preselected temperature threshold, association or disassociation of the dye and the developer results in a visible color change. Further, the color-changing system includes a color-memory property which facilitates retention of the color change to effectively record exposure to the temperature threshold.

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THERMOCHROMIC TEMPERATURE SENSOR

I. BACKGROUND

For temperature-sensitive products, it may be necessary to know whether the product has been exposed to a temperature below or above a threshold, as that temperature threshold may affect the product's quality, safety, etc. As but one illustrative example, if certain vaccines are subjected to temperatures below about 2° Celsius, the efficacy of the vaccine may be compromised. As another illustrative example, some foodstuffs, such as meat, should not be stored at temperatures above about 8° Celsius to ensure food safety.

Thus, a need exists for a temperature sensor which can (i) be reliably associated with a temperature-sensitive product and (ii) function to provide a direct indication of the thermal history thereof.

II. SUMMARY OF THE INVENTION

A broad object of a particular embodiment of the invention can be to provide a temperature sensor, and methods of making and using such a temperature sensor, whereby the temperature sensor includes a thermochromic color-changing system having a dye, a developer, and a solvent. Upon exposure to a preselected temperature threshold, association or disassociation of the dye and the developer results in a visible color change. Further, the color-changing system includes a color-memory property which facilitates retention of the color change to effectively record exposure to the temperature threshold.

Naturally, further objects of the invention are disclosed throughout other areas of the specification, drawings, and claims.

III. A BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1A shows an illustration of a low temperature indicator including a particular embodiment of the instant temperature sensor reliably associated with a temperature-sensitive product, such as a vaccine, prior to exposure to a preselected temperature threshold, whereby the dye and the developer are dissociated and the color-changing system has not undergone a visible color change.

Figure 1B shows an illustration of the particular embodiment of the temperature sensor shown in Figure 1A following exposure to a temperature threshold of about 2° Celsius, whereby

this temperature threshold facilitates association of the dye and the developer and corresponding formation of a visibly colored dye-developer complex to provide a visible color change from colorless to visibly colored.

Figure 1C shows an illustration of the particular embodiment of the temperature sensor shown in Figure 1B following an increase in temperature from the temperature threshold, whereby the color-changing system retains the visible color change.

Figure 2A shows an illustration of a high temperature indicator including a particular embodiment of the instant temperature sensor reliably associated with a temperature-sensitive product, such as a foodstuff, (i) prior to activation, whereby the dye and the developer are dissociated (as shown on the left), and (ii) following exposure to an activation temperature of about -5° Celsius, whereby this activation temperature facilitates association of the dye and the developer and corresponding formation of a visibly colored dye-developer complex (as shown on the right).

Figure 2B shows an illustration of the particular embodiment of the temperature sensor shown in Figure 2A prior to exposure to a preselected temperature threshold, whereby the color-changing system has not undergone a visible color change.

Figure 2C shows an illustration of the particular embodiment of the temperature sensor shown in Figure 2B following exposure to a temperature threshold of about 8° Celsius, whereby this temperature threshold facilitates dissociation of the dye and the developer to provide a visible color change from visibly colored to colorless.

Figure 2D shows an illustration of the particular embodiment of the temperature sensor shown in Figure 2C following a decrease in temperature from the temperature threshold, whereby the color-changing system retains the visible color change.

Figure 3 shows an illustration of hysteresis characteristics of a particular embodiment of the instant color-changing system which has a color-memory property.

Figure 4A shows an illustration of a dual temperature indicator including a particular embodiment of the instant temperature sensor, (i) prior to activation, whereby the dye and the developer of both the first and second color-changing systems are dissociated (as shown on the left), and (ii) following exposure to an activation temperature, whereby the activation temperature facilitates association of the dye and the developer of the second color-changing system and corresponding formation of a visibly colored dye-developer complex (as shown on the right).

Figure 4B shows an illustration of the particular embodiment of the temperature sensor shown in Figure 4A following exposure to a low temperature threshold, whereby this temperature threshold facilitates association of the dye and the developer of the first color-changing system and corresponding formation of a visibly colored dye-developer complex to provide a visible color change from colorless to visibly colored; this color change can be retained upon an increase in temperature.

Figure 4C shows an illustration of the particular embodiment of the temperature sensor shown in Figure 4A following exposure to a high temperature threshold, whereby this temperature threshold facilitates dissociation of the dye and the developer of the second color-changing system to provide a visible color change from visibly colored to colorless; this color change can be retained upon a decrease in temperature.

IV. DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Now referring primarily to Figure 1A through Figure 2D, which illustrate particular embodiments of the inventive temperature sensor (1) operative to provide an indication of exposure to a preselected temperature threshold (2), whereby the temperature sensor (1) includes a color-changing system (3) comprising: a dye (4), a developer (5), and a solvent (6). The developer (5) variably interacts with the dye (4) according to the temperature of the color-changing system (3), whereby upon exposure to the temperature threshold (2), association or disassociation of the dye (4) and the developer (5) results in a visible color change which can be visually observed (for example by a human, i.e. human-readable) or detected (for example by a human, i.e. human-readable, or a machine, i.e. machine-readable).

As to particular embodiments, the color-changing system (3) comprises a thermochromic color-changing system which can be susceptible to a temperature-modulated color change, whereby typically, a lower temperature will result in a colored state and a higher temperature will result in a colorless or substantially colorless state.

Now referring primarily to Figure 1A through Figure 1C, to elaborate on the above, as to particular embodiments, the color-changing system (3) can be formulated such that exposure to the temperature threshold (2) results in association of the dye (4) and the developer (5) to form a visibly colored dye-developer complex (7) which can be visually observed or detected, thereby indicating that the temperature sensor (1) has been exposed to the temperature threshold (2).

Now referring primarily to Figure 2A through Figure 2D, as to other particular embodiments, the color-changing system (3) can be formulated such that exposure to the temperature threshold (2) results in dissociation of the dye (4) and the developer (5) and accordingly, dissociation of the colored dye-developer complex (7), whereby the consequential color change to colorless can be visually observed or detected to indicate that the temperature sensor (1) has been exposed to the temperature threshold (2).

Accordingly, the method of use can include detecting whether or not a color change occurred, for example by visually observing the temperature sensor (1), whereby visual detection of a color change indicates that the temperature sensor (1) has been exposed to the temperature threshold (2). Conversely, visual detection of the absence of a color change, meaning no color change occurred, indicates that the temperature sensor (1) has not been exposed to the temperature threshold (2).

Regarding temperature-sensitive products (8), there is a need for an indicator that can (i) accompany the temperature-sensitive product (8), for example during shipping and storage, and (ii) indicate (preferably, via a direct visual indication) the thermal history of the temperature-sensitive product (8) and particularly, whether the temperature-sensitive product (8) has been exposed to a temperature threshold (2) which may compromise the quality and/or safety of the temperature-sensitive product (8).

Following, the method of use can include reliably associating the temperature sensor (1) with a temperature-sensitive product (8) and subsequently detecting whether or not a color change occurred. Consequently, visual detection of a color change indicates that the temperature-sensitive product (8) has been exposed to the temperature threshold (2), and visual detection of the absence of a color change indicates that the temperature-sensitive product (8) has not been exposed to the temperature threshold (2).

Of note, although the temperature sensor (1) may herein be shown in a highly simplified form for the sake of clarity and generality of presentation thereof, it should be appreciated that the temperature sensor (1) may have a more intricate structure and/or may form a portion of a more extensive marking or indicium, such as a barcode.

Definitions

As used herein, the term “sensor” means a composition or an apparatus which detects or measures a stimulus and reacts to it in a particular way.

As used herein, the term "detect" and forms thereof means to discover or ascertain the presence of.

As used herein, the term "preselected" means predetermined or decided in advance.

As used herein, the term "threshold" means the point which must be reached or exceeded for a certain phenomenon to occur or be manifested.

As used herein, the term "dye" means a chemical compound which can change color, such as a color former capable of reacting with the instant developer (5) to form a dye-developer complex (7) which exhibits optical properties that can be discerned by the human eye.

As used herein, the term "developer" means a chemical compound capable of reacting with the instant dye (4) to form a dye-developer complex (7) which exhibits optical properties that can be discerned by the human eye. The term "developer" can be synonymous with "color developer", both meaning a chemical compound which facilitates a change in color of the dye (4).

As used herein, the term "solvent" can, but need not necessarily, be synonymous with phase-change material, whereby phase-change material is herein defined as a material which changes from one phase to another.

As used herein, the term "temperature-sensitive product" means any product which may benefit from an indication of the thermal history thereof, for example because its quality may be adversely affected if its thermal history includes exposure to a particular temperature or range of temperatures. As but a few illustrative examples, temperature-sensitive products can include foodstuff, pharmaceuticals, chemical materials, biological materials, medical equipment, pigmented compositions (such as paint or stain), adhesives, etc.

As used herein, the term "foodstuff" means a good, item, or article that can be consumable (including edible or drinkable) or can be useful as an ingredient for making a consumable item or article. As but a few illustrative examples, foodstuffs can include fruits, juices, vegetables, grains, flours, milks, yogurts, sweetened beverages, meats, processed foods, medicaments, and the like.

Two objects, such as a temperature-sensitive product (8) and the temperature sensor (1), can be "reliably associated" if the association between the two objects can be expected not to be disrupted by routine treatment or processes. Non-limiting examples of such reliable association can include adhering one object to another, tying the two objects together, containing both objects in a container, printing one object (for example the temperature sensor (1) configured as a printing

ink) on packaging material or a container used to contain the other object (for example the temperature-sensitive product (8)), affixing one object (for example the temperature sensor (1)) to packaging material or a container used to contain the other object (for example the temperature-sensitive product (8)), and laminating one object (for example the temperature sensor (1)) in a portion of a packaging material used to enclose the other object (for example the temperature-sensitive product (8)).

Temperature Sensor

Simply summarized again, and as shown in Figure 1A through Figure 2D, the instant temperature sensor (1), which may take the form of a composition or an apparatus, includes a color-changing system (3) comprising a dye (4), a developer (5), and a solvent (6). The developer (5) variably interacts with the dye (4) according to the temperature of the color-changing system (3), whereby upon exposure to a preselected temperature threshold (2), association or dissociation of the dye (4) and the developer (5) results in a color change which can be visually observed or detected.

As to particular embodiments, aspects of the instant temperature sensor (1) may be similar to the indicators disclosed in United States Patent No. 10,113,920, United States Patent No. 10,345,278, United States Patent No. 10,585,080, United States Patent No. 10,605,681, and/or United States Patent Application No. 62/971,544, each of which is hereby incorporated by reference in its entirety herein.

Dye and Developer

The color-changing system (3) can be a reversible color-changing system, meaning that the color change can be reversible, as opposed to an irreversible color change or a permanent color change.

Following, as to particular embodiments, the dye (4) of the color-changing system (3) can comprise a leuco dye which can reversibly change between two forms, one of which can typically be colorless or substantially colorless.

As but a few illustrative examples, the leuco dye can be: crystal violet lactone (CAS No.: 1552-42-7); Pigment Blue 63 (CAS No.: 16521-38-3); 2'-(dibenzylamino)-6'-(diethylamino)fluoran (CAS No.: 34372-72-0); Yamamoto Black 15 or 2-(2,4-Dimethylphenylamino)-3-methyl-6-diethylaminofluoran (CAS No.: 36431-22-8); ODB or 7-Anilino-3-diethylamino-6-methyl fluoran (CAS No.: 29512-49-0); ODB-2 or 2-Anilino-6-

dibutylamino-3-methylfluoran (CAS No.: 89331-94-2); 6'-(Diethylamino)-1',3'-dimethylfluoran orange (CAS No.: 21934-68-9); Yamamoto Red 40 or 3,3-bis(1-butyl-2-methyl-1H-indol-3-yl)phthalide (CAS No.: 50292-91-6); Yamamoto Red Blue 63 or 7-[4-(diethylamino)-2-ethoxyphenyl]-7-(1-ethyl-2-methyl-1H-indol-3-yl)furo[3,4-b]pyridin-5(7H)-one; or the like.

As to particular embodiments, the leuco dye can be an electron-donating compound (or proton-accepting compound). Further, the developer (5) can comprise an electron-accepting compound (or proton-donating compound), such as an acid and particularly, a weak acid. Upon interaction (specifically, an electron transfer reaction) between the electron-donating leuco dye and the electron-accepting developer, the leuco dye can reversibly change color, for example from a colorless state to a colored state. In this way, the color-changing system (3) can have two visual appearances which differ from one another depending upon temperature, namely (i) a first visual appearance which may be a colorless appearance, and (ii) a second visual appearance which may be a colored appearance.

As but a few illustrative examples, the developer (5) can be: 3,5-di-*tert*-butylcatechol (CAS No.: 1020-31-1); 4,4'-(1,3-dimethylbutylidene)diphenol (CAS No.: 1020-31-1); 2,2'-biphenol (CAS No.: 1806-29-7); 4-[2-ethyl-1-(4-hydroxyphenyl)hexyl]phenol (PubChem CID 13782487); or the like.

Without being bound by any particular theory of operation, it may be that within the reversible color-changing system (3), upon exposure to a temperature which results in association of the leuco dye and the developer (5), the developer (5) can reversibly interact with the leuco dye via an electron transfer reaction to open up the lactone ring of the leuco dye and stabilize the opened structure, forming a supramolecular colored dye-developer complex (7), to which a color change can be attributable. When open, the lactone ring can be cationic in nature, thereby extending conjugation of its π electrons and allowing absorption in the visible spectrum to provide the colored dye-developer complex (7), whereby the stability of the colored dye-developer complex (7) can be determined, at least in part, by the affinity of the developer (5) for the leuco dye.

Solvent

The color-changing system (3) further includes a solvent (6) which effects or controls the reversible interaction between the dye (4) and the developer (5).

As to particular embodiments, a solvent (6) which may be useful with the reversible color-changing system (3) can be (i) a solvent (6) in which both the dye (4) and the developer (5) are soluble, and (ii) a solvent (6) capable of being contained along with the dye (4) and the developer (5), for example within a capsule or microcapsule (9) to provide a corresponding encapsulated or microencapsulated color-changing system (3). When contained within the capsule or microcapsule (9), the solvent (6) can facilitate interaction between the dye (4) and the developer (5).

Without being bound by any particular theory of operation, it may be that within the reversible color-changing system (3), the developer (5) can also interact with the solvent (6) to form a solvent-developer complex, whereby this interaction can be determined, at least in part, by the affinity of the developer (5) for the solvent (6).

Following, it may be hypothesized that the color change can be linked to a competition between the dye (4) and the solvent (6) for complexing with the developer (5), whereby the developer (5) forms a complex with the molecule(s) which it has a greater affinity for.

It should be understood that once a complex forms, the complex can be stable until an amount of energy sufficient to destabilize the complex is input into the system, thereby dissociating the components of the complex.

Relating to the temperature sensor (1), at a higher temperature, the developer (5) can have a greater affinity for the solvent (6) than for the leuco dye and accordingly, the solvent-developer complex can be favored over the colored dye-developer complex (7). Thus, the developer (5) can be precluded from interacting with the leuco dye and correspondingly, the lactone ring can be closed and the leuco dye can be colorless.

Conversely, at a lower temperature, the developer (5) can have a greater affinity for the leuco dye than for the solvent (6); hence, the colored dye-developer complex (7) can form and stabilize.

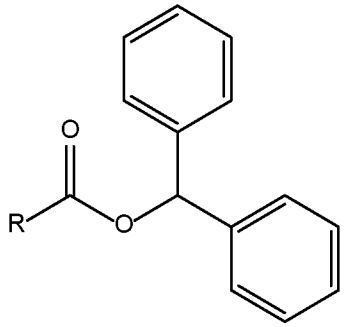
As to particular embodiments, the solvent (6) can be an ester.

As to particular embodiments, the solvent (6) can be an ester as disclosed in United States Patent No. 10,345,278, United States Patent No. 10,585,080, United States Patent No. 10,605,681, and/or United States Patent Application No. 62/971,544, each of which is hereby incorporated by reference in its entirety herein.

As to particular embodiments, the solvent (6) can be a diphenylmethyl ester.

As to particular embodiments, the ester can have Formula I as follows:

I



wherein R can be (i) a straight-chain or branched alkyl group, (ii) a straight-chain or branched alkenyl group, or (iii) a straight-chain or branched alkynyl group, whereby any of the groups can be unsubstituted or substituted.

As to particular embodiments, R can have 5 or more carbon atoms, or can have at least 5 carbon atoms.

As to particular embodiments, R can have 7 or more carbon atoms, or can have at least 7 carbon atoms.

As to particular embodiments, R can have 9 or more carbon atoms, or can have at least 9 carbon atoms.

As to particular embodiments, R can have 11 or more carbon atoms, or can have at least 11 carbon atoms.

As to particular embodiments, R can have 13 or more carbon atoms, or can have at least 13 carbon atoms.

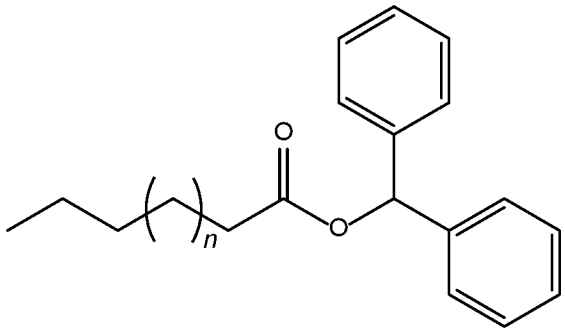
As to particular embodiments, R can have 15 or more carbon atoms, or can have at least 15 carbon atoms.

As to particular embodiments, R can have 17 or more carbon atoms, or can have at least 17 carbon atoms.

As to particular embodiments, R can have 19 or more carbon atoms, or can have at least 19 carbon atoms.

As to particular embodiments, the ester can have Formula II as follows:

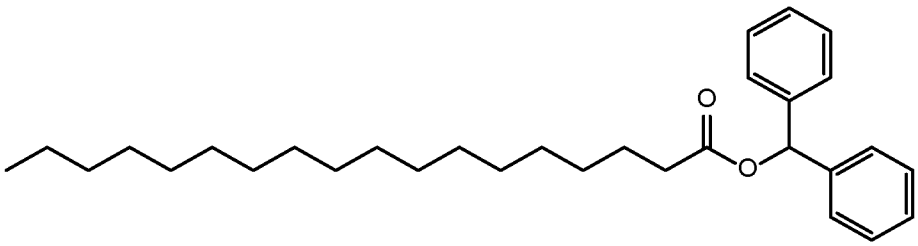
II



wherein *n* can be an integer between 1 and 15.

As to particular embodiments, the ester can have Formula III as follows:

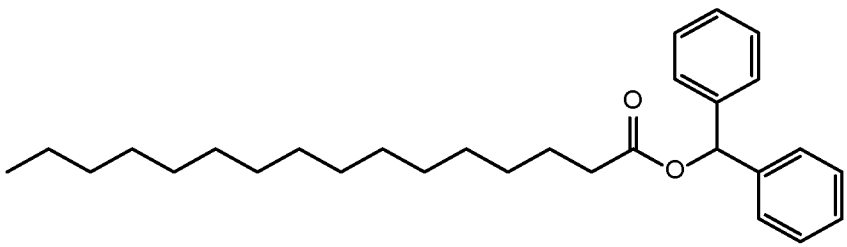
III



whereby this ester may have a molecular formula of $C_{31}H_{46}O_2$, a molecular weight of 450.70 g/mol, and a CAS Registry Number of 103390-75-6.

As to particular embodiments, the ester can have Formula IV as follows:

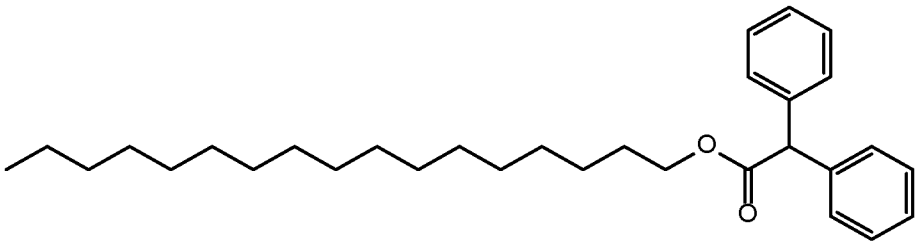
IV



whereby this ester may have a molecular formula of $C_{29}H_{42}O_2$, a molecular weight of 422.64 g/mol, and a CAS Registry Number of 103209-25-2.

As to particular embodiments, the ester can have Formula V as follows:

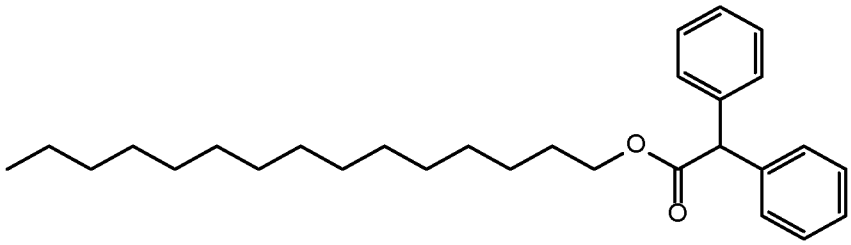
V



whereby this ester may have a molecular formula of $C_{31}H_{46}O_2$, and a molecular weight of 450.70 g/mol.

As to particular embodiments, the ester can have Formula VI as follows:

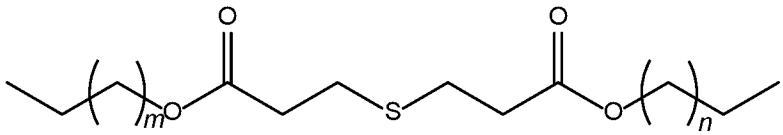
VI



whereby this ester may have a molecular formula of $C_{29}H_{42}O_2$, and a molecular weight of 422.64 g/mol.

As to particular embodiments, the ester can have Formula VII as follows:

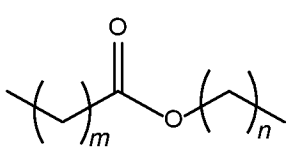
VII



wherein *m* and *n* can each be an integer between 1 and 15.

As to particular embodiments, the ester can have Formula VIII as follows:

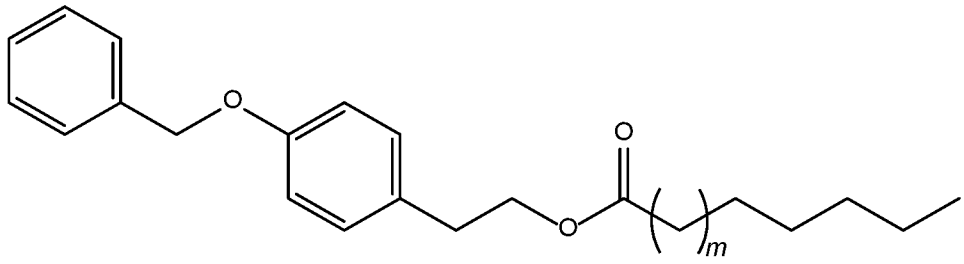
VIII



wherein *m* and *n* can each be an integer between 2 and 15.

As to particular embodiments, the ester can have Formula IX as follows:

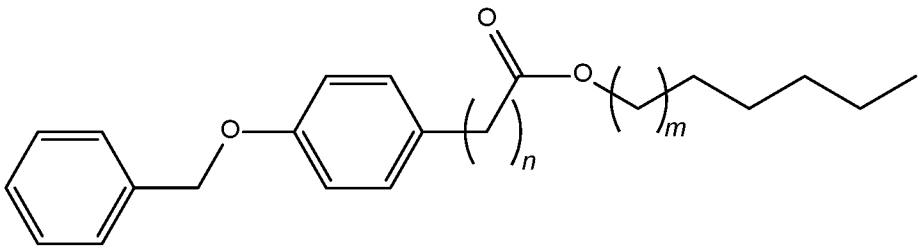
IX



wherein *m* can be an integer between 1 and 10.

As to particular embodiments, the ester can have Formula X as follows:

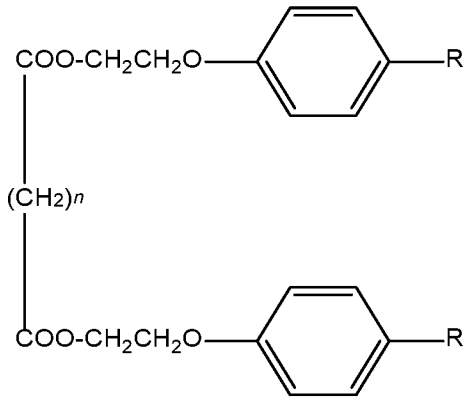
X



wherein *m* can be an integer between 1 and 11, and *n* can be an integer between 1 and 3.

As to particular embodiments, the ester can have Formula XI as follows:

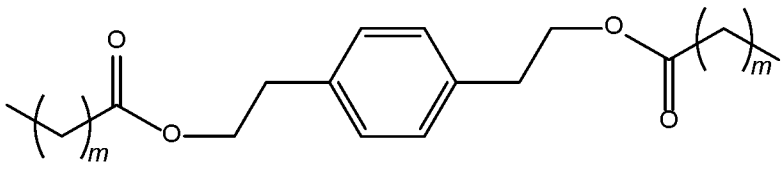
XI



wherein R can be a hydrogen or an alkyl group from C1 to C4, and *n* can be an integer between 1 and 6.

As to particular embodiments, the ester can have Formula XII as follows:

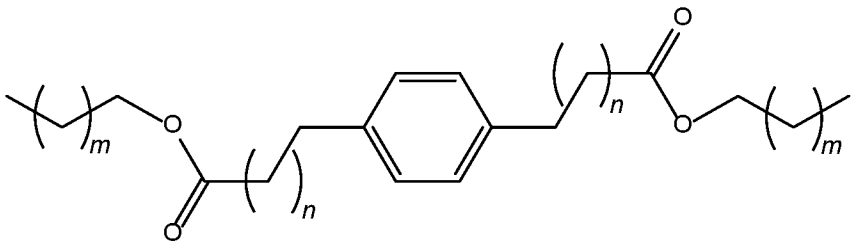
XII



wherein *m* can be an integer between 1 and 10.

As to particular embodiments, the ester can have Formula XIII as follows:

XIII



wherein *m* can be an integer between 1 and 10, and *n* can be an integer between 0 and 2.

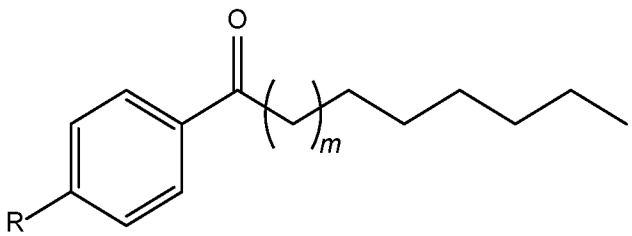
As to particular embodiments, the solvent (6) can be a hydrocarbon.

As to particular embodiments, the solvent (6) can be a ketone.

As to particular embodiments, the solvent (6) can be a ketone as disclosed in United States Patent No. 10,345,278, United States Patent No. 10,585,080, United States Patent No. 10,605,681, and/or United States Patent Application No. 62/971,544, each of which is hereby incorporated by reference in its entirety herein.

As to particular embodiments, the ketone can have Formula XIV as follows:

XIV



wherein R can be a hydrogen or an alkyl group, such as methyl group or an ethyl group; and

wherein *n* can be an integer between 1 and 10.

As to particular embodiments, the solvent (6) can be an alcohol.

As to particular embodiments, the solvent (6) can be an alcohol as disclosed in United States Patent No. 10,345,278, United States Patent No. 10,585,080, United States Patent No. 10,605,681, and/or United States Patent Application No. 62/971,544, each of which is hereby incorporated by reference in its entirety herein.

As to particular embodiments, the solvent (6) can be a single compound.

As to particular embodiments, the solvent (6) can be in an amount of about 50% to about 99% of the color-changing system (3).

As to particular embodiments, the solvent (6) can be in an amount of about 60% to about 75% of the color-changing system (3).

As to other particular embodiments, the solvent (6) can be a mixture of two or more compounds. As to particular embodiments, the solvent (6) can be a mixture of two or more of the solvents (6) described above.

As to particular embodiments, the solvent (6) comprising a mixture of two or more compounds can be in an amount of about 50% to about 99% of the color-changing system (3).

As to particular embodiments, the solvent (6) comprising a mixture of two or more compounds can be in an amount of about 60% to about 75% of the color-changing system (3).

As to particular embodiments, the solvent (6) can be a mixture of the esters shown in Formulas III and IV, whereby the ester shown in Formula III and the ester shown in Formula IV can be in a ratio of 1:1. Of course, as to other particular embodiments, other ratios may be used and are herein contemplated.

Phase Change Material

As to particular embodiments, the solvent (6) can be a phase change material which changes between a liquid phase (or a substantially liquid phase) and a solid phase (or a substantially solid phase) according to the temperature of the color-changing system (3).

As to particular embodiments, the solvent (6) can change from a liquid phase to a solid phase upon exposure to the temperature threshold (2).

As to other particular embodiments, the solvent (6) can change from a solid phase to a liquid phase upon exposure to the temperature threshold (2).

As to particular embodiments, the solid phase of the solvent (6) can facilitate or enable interaction between the leuco dye and the developer (5), whereby the colored dye-developer complex (7) can be a crystalized structure having an extended conjugation of its π electrons.

In contrast, the liquid phase of the solvent (6) can preclude interaction between the leuco dye and the developer (5), rendering the leuco dye colorless.

Color Memory

As described above, the color-changing system (3) can be a thermochromic color-changing system which can be susceptible to a temperature-modulated color change. Additionally, the color-changing system (3) can be a reversible thermochromic color-changing system, whereby the temperature-modulated color change can be reversible, as opposed to an irreversible color change or a permanent color change.

Further, the color-changing system (3) can have a color-memory property whereby after a color change occurs following exposure to the temperature threshold (2), the color change can be retained even upon discontinuation of exposure to the temperature threshold (2); hence, the color change can be retained at temperatures which differ from the temperature threshold (2). Correspondingly, the temperature sensor (1) can effectively record exposure to the temperature threshold (2), thereby functioning as a cumulative exposure indicator, which can be in contrast to a conventional thermometer that only displays the current temperature and does not record temperatures which the thermometer may have been exposed to prior to exposure to the current temperature.

Concerning color-changing characteristics, the color-changing system (3) can include a coloration temperature at which the color-changing system (3) reversibly changes from a colorless state to a colored state. Also, the color-changing system (3) can include a decoloration temperature at which the color-changing system (3) reversibly changes from the colored state to the colorless state.

Significantly, the coloration and decoloration temperatures of the color-changing system (3) can be different, meaning that the coloration temperature can be discrete from the decoloration temperature. For example, the coloration temperature can be less than the decoloration temperature.

Consequently, the color-memory property of the color-changing system (3) can facilitate retention of the color change upon an increase in temperature from the coloration temperature. Accordingly, the color-memory property of the color-changing system (3) can facilitate retention of the colored state upon an increase in temperature from the coloration temperature, as shown in Figure 1B and Figure 1C.

Moreover, the color-memory property of the color-changing system (3) can facilitate retention of the color change upon a decrease in temperature from the decoloration temperature. Accordingly, the color-memory property of the color-changing system (3) can facilitate retention of the colorless state upon a decrease in temperature from the decoloration temperature, as shown in Figure 2C and Figure 2D.

As to particular embodiments, the coloration temperature can be associated with the freezing point of the color-changing system (3) and the decoloration temperature can be associated with the melting point of the color-changing system (3). Accordingly, the color-changing system (3) can include (i) a freezing point at which the color-changing system (3) changes from a colorless state to a colored state, and (ii) a melting point at which the color-changing system (3) changes from a colored state to a colorless state.

Of note, because of the color-memory property of the color-changing system (3), as to particular embodiments, after exposure to a temperature threshold (2) resulting in association of the dye (4) and the developer (5), the colored dye-developer complex (7) can remain stable even when the solvent (6) may be in the liquid phase (for example, upon an increase in temperature).

Likewise and again because of the color-memory property of the color-changing system (3), as to particular embodiments, after exposure to a temperature threshold resulting in dissociation of the dye (4) and the developer (5), the dye (4) and the developer (5) can remain dissociated even when the solvent (6) may be in the solid phase (for example, upon a decrease in temperature).

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by at least one selected from the group including or consisting of: at least about 20 Celsius degrees, at least about 25 Celsius degrees, at least about 30 Celsius degrees, at least about 35 Celsius degrees, at least about 40 Celsius degrees, at least about 45 Celsius degrees, at least about 50 Celsius degrees, at least about 55 Celsius degrees, at least about 60 Celsius degrees, at least about 65 Celsius degrees, at least about 70 Celsius degrees, at least about 75 Celsius degrees, at least about 80 Celsius degrees, at least about 85 Celsius degrees, at least about 90 Celsius

degrees, at least about 95 Celsius degrees, at least about 100 Celsius degrees, and greater than about 100 Celsius degrees.

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by at least about 20 Celsius degrees, meaning that the decoloration temperature can be at least about 20 Celsius degrees greater than the coloration temperature.

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by at least about 25 Celsius degrees, meaning that the decoloration temperature can be at least about 25 Celsius degrees greater than the coloration temperature.

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by at least about 30 Celsius degrees, meaning that the decoloration temperature can be at least about 30 Celsius degrees greater than the coloration temperature.

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by at least about 35 Celsius degrees, meaning that the decoloration temperature can be at least about 35 Celsius degrees greater than the coloration temperature.

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by at least about 40 Celsius degrees, meaning that the decoloration temperature can be at least about 40 Celsius degrees greater than the coloration temperature, whereby as to particular embodiments, at least about 40 Celsius degrees may be the preferable minimal difference.

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by at least about 45 Celsius degrees, meaning that the decoloration temperature can be at least about 45 Celsius degrees greater than the coloration temperature, whereby as to particular embodiments, at least about 45 Celsius degrees may be the preferable minimal difference.

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by at least about 50 Celsius degrees, meaning that the decoloration temperature can be at least about 50 Celsius degrees greater than the coloration temperature, whereby as to particular embodiments, at least about 50 Celsius degrees may be the preferable minimal difference.

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by at least about 55 Celsius degrees, meaning that the decoloration temperature can be at least about 55 Celsius degrees greater than the coloration temperature, whereby as to particular embodiments, at least about 55 Celsius degrees may be the preferable minimal difference.

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by at least about 60 Celsius degrees, meaning that the decoloration temperature can be at least about 60 Celsius degrees greater than the coloration temperature.

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by at least about 65 Celsius degrees, meaning that the decoloration temperature can be at least about 65 Celsius degrees greater than the coloration temperature.

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by at least about 70 Celsius degrees, meaning that the decoloration temperature can be at least about 70 Celsius degrees greater than the coloration temperature.

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by at least about 75 Celsius degrees, meaning that the decoloration temperature can be at least about 75 Celsius degrees greater than the coloration temperature.

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by at least about 80 Celsius degrees, meaning that the decoloration temperature can be at least about 80 Celsius degrees greater than the coloration temperature.

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by at least about 85 Celsius degrees, meaning that the decoloration temperature can be at least about 85 Celsius degrees greater than the coloration temperature.

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by at least about 90 Celsius degrees, meaning that the decoloration temperature can be at least about 90 Celsius degrees greater than the coloration temperature.

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by at least about 95 Celsius degrees, meaning that the decoloration temperature can be at least about 95 Celsius degrees greater than the coloration temperature.

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by at least about 100 Celsius degrees, meaning that the decoloration temperature can be at least about 100 Celsius degrees greater than the coloration temperature.

As to particular embodiments, the coloration temperature can differ from the decoloration temperature by greater than about 100 Celsius degrees.

Now referring primarily to Figure 3, hysteresis characteristics of a particular embodiment of the reversible color-changing system (3) having a color-memory property can be described by illustrating the dependence of color density on temperature.

Now more specifically, the *y* axis shows the color density and the *x* axis shows the temperature. The color density of the color-changing system (3) changes with temperature along the curve in the direction shown by the arrow marks. Point A indicates the color density at the highest temperature T_1 for achieving the completely colored state (whereby T_1 can be the complete coloration temperature). Point B indicates the color density at the highest temperature T_2 for retention of the completely colored state (whereby T_2 can be the decoloration initiation temperature). Point C indicates the color density at the lowest temperature T_3 for achieving a completely colorless state (whereby T_3 can be the complete decoloration temperature). Point D indicates the color density at the lowest temperature T_4 for retention of the completely colorless state (whereby T_4 can be the coloration initiation temperature).

While both the completely colored state and the completely colorless state can exist between T_4 and T_2, the state retained can be dependent upon the state previously achieved. For example, if the completely colored state was previously achieved upon exposure to T_1, the completely colored state will be retained until exposure to a temperature equal to or greater than T_2. Alternatively, if the completely colorless state was previously achieved upon exposure to T_3, the completely colorless state will be retained until exposure to a temperature equal to or lesser than T_4.

Said another way, the color-changing system (3) may be in the completely colored state or the completely colorless state at a temperature between T_2 and T_4, depending upon whether the color-changing system (3) approaches that temperature from a lower or higher temperature or depending upon whether the color-changing system (3) is being heated from a lower temperature or cooled from a higher temperature.

As to particular embodiments, the colored state or the colorless state can be retained upon exposure to temperatures between about 20 Celsius degrees to about 100 Celsius degrees or between about 50 Celsius degrees to about 100 Celsius degrees from the temperature at which the colored state or the colorless state was achieved. In other words, the length of segment EF shown in Figure 3, which represents the temperature range width indicating the degree of hysteresis or hysteresis range or hysteresis window ΔH, can be in a range of between about 20 Celsius degrees to about 100 Celsius degrees or between about 50 Celsius degrees to about 100 Celsius degrees.

Transition Temperature

As to particular embodiments, in addition to having a color-memory property, the color changing system (3) can also have a narrow transition between the colorless state and the colored state, or between the colored state and the colorless state.

Again referring primarily to Figure 3, a narrow transition between the colorless state and the colored state means that the difference between the coloration initiation temperature (T_4) and the complete coloration temperature (T_1) is relatively small, whereby this difference may be referred to as $\Delta_{T4\text{-}T1}$.

Notably, $\Delta_{T4\text{-}T1}$ can be related to the sensitivity of the temperature sensor (1), whereby a smaller difference between the coloration initiation temperature (T_4) and the complete coloration temperature (T_1) can equate to greater sensitivity, whereby it may be advantageous to have a more sensitive, and accordingly more accurate, temperature sensor (1).

Likewise, again referring primarily to Figure 3, a narrow transition between the colored state and the colorless state means that the difference between the decoloration initiation temperature (T_2) and the complete decoloration temperature (T_3) is relatively small, whereby this difference may be referred to as $\Delta_{T3\text{-}T2}$.

As with $\Delta_{T4\text{-}T1}$, $\Delta_{T3\text{-}T2}$ can be related to the sensitivity of the temperature sensor (1), whereby a smaller difference between the decoloration initiation temperature (T_2) and the complete decoloration temperature (T_3) can equate to greater sensitivity, whereby it may be advantageous to have a more sensitive, and accordingly more accurate, temperature sensor (1).

As to particular embodiments, the difference between the coloration initiation temperature and the complete coloration temperature ($\Delta_{T4\text{-}T1}$) and/or the difference between the decoloration initiation temperature and the complete decoloration temperature ($\Delta_{T3\text{-}T2}$) can be not greater than about 4 Celsius degrees.

As to particular embodiments, the difference between the coloration initiation temperature and the complete coloration temperature (Δ_{T4-T1}) and/or the difference between the decoloration initiation temperature and the complete decoloration temperature (Δ_{T3-T2}) can be not greater than about 3 Celsius degrees.

As to particular embodiments, the difference between the coloration initiation temperature and the complete coloration temperature (Δ_{T4-T1}) and/or the difference between the decoloration initiation temperature and the complete decoloration temperature (Δ_{T3-T2}) can be not greater than about 2 Celsius degrees.

As to particular embodiments, the difference between the coloration initiation temperature and the complete coloration temperature (Δ_{T4-T1}) and/or the difference between the decoloration initiation temperature and the complete decoloration temperature (Δ_{T3-T2}) can be not greater than about 1 Celsius degree.

As to particular embodiments, $T_4 = T_1$ and/or $T_3 = T_2$.

Microcapsules

As to particular embodiments, the reversible color-changing system (3) can be contained, meaning that the dye (4), the developer (5), and the solvent (6) are continuously kept within a physical proximity which allows interaction between the components. Additionally, by being contained, the color-changing system (3) can be separated from the external environment, which may damage or destroy the color-changing system (3).

As stated above, as to particular embodiments, the color-changing system (3) can be encapsulated within a capsule or microcapsule (9) to provide a corresponding encapsulated or microencapsulated color-changing system (3), whereby the capsule or microcapsule (9) can have a diameter in a range of between about 500 nanometers to about 50 microns, depending upon the embodiment. As to particular embodiments, the microcapsules (9) can have a mean diameter of between about 1 micron to about 3 microns.

The capsule or microcapsule wall which forms the corresponding capsule or microcapsule (9) around the color-changing system (3) can be formed from any of a numerous and wide variety of polymers, such as melamine formaldehyde resin (CAS No.: 9003-08-01); polyurethane resin (CAS No.: 9009-54-5); acrylic resin, epoxy resin, CYMEL® 385 resin, gelatin, or the like.

Coating

As to particular embodiments of the temperature sensor (1), the encapsulated or microencapsulated color-changing system (3) can be incorporated into a coating. As but one illustrative example, the encapsulated or microencapsulated color-changing system (3) can be incorporated into an ink.

As to particular embodiments, the ink can be selected from the group including or consisting of: flexographic inks, gravure inks, offset inks, screen inks, and metal decoration inks. The ink can be water-based, solvent-based, UV-curable, wet, dry, or combinations thereof, depending upon the application.

As but only a few illustrative examples, the ink can comprise: an acrylic solution, an acrylic emulsion, a sulfonated polyester, a polyester resin, an epoxy resin, an acrylated monomer or oligomer, an alkyd resin, or the like.

As to particular embodiments, the ink can be specifically formulated for application to a substrate via printing, such as medium-speed printing or high-speed printing onto a substrate configured as a label, tag, or packaging material.

Substrate

As to particular embodiments of the temperature sensor (1), the encapsulated or microencapsulated color-changing system (3) can be coupled to a substrate, which can be formed from any of a numerous and wide variety of materials. As but a few illustrative examples, the substrate can include paper, paper products, wood, fiber, metal, glass, ceramic, plastic, thermoplastic materials, thermoset materials, or the like, or combinations thereof.

Additionally, as to particular embodiments, the temperature sensor (1) can, but need not necessarily, further include a cover which covers the encapsulated or microencapsulated color-changing system (3) coupled to the substrate, thus disposing the encapsulated or microencapsulated color-changing system (3) between the substrate and the cover.

The cover may be used for aesthetic reasons or for safety reasons, for example when it may be desirable to prevent contact between elements of the temperature sensor (1) and the temperature-sensitive product (8).

The precise shapes and conformations of the substrate and the cover may not be critical. However, some embodiments lend themselves to easier manufacture and assembly. For example, in one embodiment, the substrate and the cover can have the form of a sheet (i.e., the substrate and the cover are configured as two sheets opposed adjacent one another). The substrate and the cover can have approximately the same thickness or different thicknesses, such as each being a plastic film having a thickness of about 2 to 50 mils.

The materials from which each of the substrate and the cover are made can be substantially immaterial, other than the substrate should be sufficient to support the encapsulated or microencapsulated color-changing system (3) and the cover should be sufficient to cover the encapsulated or microencapsulated color-changing system (3). By way of example, each of the substrate and the cover can be a polyester film having a thickness of about 2 to 10 mils. Preferably, at least one of the substrate and the cover can be transparent.

At least one of the substrate and the cover can have a viewing portion adapted to permit detection of the color change associated with formation of the colored dye-developer complex (7), for example by visual observation of the temperature sensor (1) (i.e., not requiring disassembly of the temperature sensor (1)). Alternatively, the temperature sensor (1) can be disassembled to determine whether the colored dye-developer complex (7) formed. As to particular embodiments, at least one of the substrate and the cover can be sufficiently transparent or translucent such that the color change can be detected by direct visual observation of the viewing portion.

As to particular embodiments, one or both of the substrate and the cover can act as a packaging material or package, or a component thereof, for containing a temperature-sensitive product (8). The substrate, the cover, or both can be an integral part of the packaging material (i.e., unitary with the packaging material such that removal of the substrate or the cover would compromise the integrity of the packaging material and its function of separating its interior from the external environment). Alternatively, the substrate, the cover, or both can be separable (e.g., tearable, detachable, or peelable) from the packaging material.

As to particular embodiments, the capsules or microcapsules (9) which contain the color-changing system (3) can be bound to the substrate, to the cover, or to both, either directly or by way of a binding agent.

Alternatively, as to other particular embodiments, the capsules or microcapsules (9) which contain the color-changing system (3) can be kept proximate to, but not necessarily bound to any surface of, the substrate or the cover.

Container Component as Substrate

As to particular embodiments, the encapsulated or microencapsulated color-changing system (3) can be coupled to a substrate configured as a container component of a container which can contain the temperature-sensitive product (8).

As to particular embodiments, the container component can include or be formed from at least one thermoplastic material, such as a thermoplastic polymer, or a thermoplastic resin. Following, the container component can include at least one thermoplastic material and the encapsulated or microencapsulated color-changing system (3).

As to particular embodiments, the container component can include or be formed from at least one thermoset material, such as a thermosetting polymer, a thermosetting resin, or a thermosetting plastic. Following, the container component can include at least one thermoset material and the encapsulated or microencapsulated color-changing system (3).

As to particular embodiments, the thermoplastic material and/or the thermoset material can include a material that can be processed below about 232°C (about 450°F). As but a few illustrative examples, the thermoplastic material and/or the thermoset material can include low density polyethylene (LDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE), polypropylene (PP, OPP, BOPP), polystyrene (PS), high impact polystyrene (HIPS), styrene acrylonitrile (SAN), acrylonitrile butadiene styrene (ABS), polycarbonate (PC), polyurethane (PU), silicones (PDMS), polyvinyl chloride (PVC), polyethylene terephthalate (PET), crystalline polystyrene, epoxy, epoxy resins, and polyepoxides, of the like, or combinations thereof.

As to particular embodiments, the container component can include or be formed from the encapsulated or microencapsulated color-changing system (3) in admixture with at least a portion of the thermoplastic material.

As to particular embodiments, the container component can include or be formed from the encapsulated or microencapsulated color-changing system (3) incorporated into at least a portion of the thermoplastic material.

As to particular embodiments, the container component can include or be formed from the encapsulated or microencapsulated color-changing system (3) integrated with at least a portion of the thermoplastic material.

As to particular embodiments, the container component can include or be formed from the encapsulated or microencapsulated color-changing system (3) suspended in at least a portion of the thermoplastic material.

As to particular embodiments, the container component can include or be formed from the encapsulated or microencapsulated color-changing system (3) substantially homogenously suspended in at least a portion of the thermoplastic material.

As to particular embodiments, the container component can include or be formed from the encapsulated or microencapsulated color-changing system (3) embedded in at least a portion of the thermoplastic material.

As to particular embodiments, the container component can include or be formed from the encapsulated or microencapsulated color-changing system (3) substantially homogenously embedded in at least a portion of the thermoplastic material.

In contrast to the above, as to particular embodiments, the encapsulated or microencapsulated color-changing system (3) can be applied to an external surface of the container component.

As to particular embodiments, the encapsulated or microencapsulated color-changing system (3) can be printed on an external surface of the container component.

As to particular embodiments, the encapsulated or microencapsulated color-changing system (3) can be incorporated into an ink which can be printed on an external surface of the container component.

As to particular embodiments, the container component can be configured as a closure, such as a cap or a lid.

Regarding production, the thermoplastic material can be formed into an embodiment of a container component according to known methods for producing plastic products, including (but not limited to) injection molding, compression molding, and extrusion.

Additionally, concerning production of a container component including an admixture of the encapsulated or microencapsulated color-changing system (3) and the thermoplastic material, the encapsulated or microencapsulated color-changing system (3) can be incorporated into the container component according to known methods for producing plastic products including two

or more constituents. As to particular embodiments, the encapsulated or microencapsulated color-changing system (3) can be incorporated as a masterbatch or mixed or admixed or integrated with the thermoplastic material prior to formation of the container component.

The amount of the encapsulated or microencapsulated color-changing system (3) incorporated into the container component may not be particularly limited, so long as the desired thermochromic effect can be achieved. As to particular embodiments, the encapsulated or microencapsulated color-changing system (3) can be present in the container component in an amount of about 1% to about 50% by weight, based on the weight of the container component.

Low Temperature Indicator

As to particular embodiments, the instant temperature sensor (1) can be used as a low temperature indicator, a cool temperature indictor, or a freeze indicator, whereby the preselected temperature threshold (2) can be a temperature at which a temperature-sensitive product (8) becomes undesirably cool or freezes.

Following, if the temperature-sensitive product (8) and reliably-associated temperature sensor (1) are exposed to the temperature threshold (2), the colored dye-developer complex (7) will form and remain stable even upon an increase in temperature to effectively record exposure of the temperature-sensitive product (8) to the temperature threshold (2).

Now referring primarily to Figure 1A through Figure 1C, and Figure 3, one illustrative example of a low temperature indicator is illustrated, whereby upon exposure to the temperature threshold (2), the color-changing system (3) can undergo a color change and be completely colored at T_1. Following, the completely colored state can be retained upon an increase in temperature, as the colored dye-developer complex (7) remains stable until temperature T_2 is reached.

As to particular embodiments, the temperature threshold (2) may, but need not necessarily, be a temperature not higher than about 2° Celsius, and T_2 may, but need not necessarily, be a temperature not lower than ambient, and not lower than about 45° Celsius.

As to particular embodiments, the temperature threshold (2) may, but need not necessarily, be a temperature of about 2° Celsius, and T_2 may, but need not necessarily, be a temperature of about 45° Celsius. Notably, this example has a hysteresis window (ΔH) of 43 Celsius degrees.

As to particular embodiments, the temperature threshold (2) may be a temperature between about -20° Celsius and about 20° Celsius.

As to particular embodiments, the esters shown in Formulas I through VI may be useful for embodiments of the temperature sensor (1) configured as a low temperature indicator, a cool temperature indictor, or a freeze indicator.

High Temperature Indicator

As to particular embodiments, the instant temperature sensor (1) can be used as a high temperature indicator, a warm temperature indictor, or a thaw indicator, whereby the preselected temperature threshold (2) can be a temperature at which a temperature-sensitive product (8) becomes undesirably warm or thaws.

Following, if the temperature-sensitive product (8) and reliably-associated temperature sensor (1) are exposed to the temperature threshold (2), the dye (4) and developer (5) will dissociate and remain dissociated even upon a decrease in temperature to effectively record exposure of the temperature-sensitive product (8) to the temperature threshold (2).

Now referring primarily to Figure 2A, as to particular embodiments of the temperature sensor (1) which function as a high temperature indicator, activation of the color-changing system (3) may be required prior to use. For example, the color-changing system (3) may be activated by exposure to an activation temperature (10) which results in association of the dye (4) and the developer (5) to form the colored dye-developer complex (7). Following, upon exposure to a temperature threshold (2) which results in dissociation of the dye (4) and the developer (5) and accordingly, dissociation of the colored dye-developer complex (7), a color change to colorless can occur.

As to particular embodiments, the activation temperature (10) can be significantly lower than the lowest temperature typically achievable by a conventional refrigerator. Thus, after recordation of a color change from colored to colorless, exposure to a conventional refrigerator will not induce formation of the colored dye-developer complex (7).

As to particular embodiments, the activation temperature (10) can be significantly lower than the lowest temperature typically achievable by a conventional freezer. Thus, after recordation of a color change from colored to colorless, exposure to a conventional freezer will not induce formation of the colored dye-developer complex (7).

As to particular embodiments, the activation temperature (10) can be a temperature achievable with freeze spray, cold spray, vapocoolant, refrigerant spray, gas duster, or the like,

which may be able to achieve a temperature of lower than about -20° Celsius, for example a temperature of about -50° Celsius.

Now referring primarily to Figure 2B through Figure 2D, and Figure 3, one illustrative example of a high temperature indicator is illustrated, whereby upon exposure to the temperature threshold (2), the color-changing system (3) can undergo a color change and be completely colorless at T_3 (as shown in Figure 2C). Following, the completely colorless state can be retained upon a decrease in temperature from T_3 (as shown in Figure 2D), as the dye (4) and developer (5) remain dissociated until temperature T_4 is reached.

As to particular embodiments, the temperature threshold (2) may, but need not necessarily, be a temperature not lower than about 8° Celsius, and T_4 may, but need not necessarily, be a temperature not higher than about -1° Celsius.

As to particular embodiments, the temperature threshold (2) may, but need not necessarily, be a temperature of about 8° Celsius, and T_4 may, but need not necessarily, be a temperature of about -1° Celsius. Notably, this example has a hysteresis window (ΔH) of 9 Celsius degrees.

As to particular embodiments, the temperature threshold (2) may, but need not necessarily, be a temperature not lower than about 8° Celsius, and T_4 may, but need not necessarily, be a temperature not higher than about -5° Celsius.

As to particular embodiments, the temperature threshold (2) may, but need not necessarily, be a temperature of about 8° Celsius, and T_4 may, but need not necessarily, be a temperature of about -5° Celsius. Notably, this example has a hysteresis window (ΔH) of 13 Celsius degrees.

As to particular embodiments, the temperature threshold (2) may be a temperature between about -20° Celsius and about 20° Celsius.

As to particular embodiments, the esters shown in Formulas VII through IX may be useful for embodiments of the temperature sensor (1) configured as a high temperature indicator, a warm temperature indictor, or a thaw indicator.

Dual Temperature Indicator

As to particular embodiments, the instant temperature sensor (1) can include a plurality of populations of encapsulated or microencapsulated color-changing systems (3), whereby each

population has a characteristic preselected temperature threshold (2) to which it reacts to provide a color change.

For example, the temperature sensor (1) can include (i) a first color-changing system (11) useful as a low temperature indicator (thus, having a relatively low temperature threshold (2)) and (ii) a second color-changing system (12) useful as a high temperature indicator (thus, having a relatively high temperature threshold (2)), whereby the components of the color-changing systems (11)(12) can be the same or different, depending upon the application. This dual temperature indicator may be employed to provide an indication of exposure to at least two temperature thresholds (2), which may be useful to determine if a temperature-sensitive product (8) was maintained within a preselected temperature range between the two temperature thresholds (2).

Prior to use, the second color-changing system (12) can be activated (as described above and as shown in Figure 4A) and accordingly, can be in a colored state. Subsequently, the temperature sensor (1) can initially display both a colored state (via the activated second color-changing system (12)) and a colorless state (via the first color-changing system (11)) when at a temperature above T_4 and below T_2.

In use, if the temperature sensor (1) is exposed to a temperature at or below the temperature threshold (2) of the first color-changing system (11), namely below T_1, both the first and second color-changing systems (11)(12) will be in a completely colored state, as shown in Figure 4B. Further, if the temperature sensor (1) is exposed to a temperature at or above the temperature threshold (2) of the second color-changing system (12), namely above T_3, both the first and second color-changing systems (11)(12) will be in a completely colorless state, as shown in Figure 4C. After exposure to at least one of the temperature thresholds (2), it will not be possible for the temperature sensor (1) to display both a completely colored state and a completely colorless state, thereby providing evidence of exposure to at least one of the temperature thresholds (2).

As but one illustrative example, a particular embodiment of the dual temperature indicator can indicate exposure to temperatures outside a range of about 2° Celsius to about 8° Celsius. Said another way, this embodiment of the dual temperature indicator can function as (i) a low temperature indicator with a temperature threshold (2) of about 2° Celsius and (ii) a high temperature indicator with a temperature threshold (2) of about 8° Celsius.

It is herein contemplated that embodiments of the instant dual temperature indicator may be useful as tamper indicators, especially if the first and second color-changing systems (11)(12) are disposed on a substrate such that they cannot be thermally separated. As but one illustrative

example, this may be accomplished by arranging the first and second color-changing systems (11)(12) adjacent one another or interposed between one another.

Regarding tampering, embodiments of the dual temperature indicator may be particularly useful with sealed items which may be subjected to unauthorized opening and resealing, whereby this tampering may not have been previously detectable.

For example, one method of unauthorized opening of a sealed item may involve heating the sealing adhesive to a temperature at which it ceases to act as an adherent, thereby allowing access to the previously-sealed item; following, the item may then be resealed. Alternatively, another method of unauthorized opening may involve freezing the sealing adhesive to a temperature at which it ceases to act as an adherent, thereby again allowing access to the previously-sealed item; heating the adhesive may then allow it to regain its adhesive properties such that the unauthorized access may not detectable. In these instances, the instant dual temperature indicator would provide a visual indication of both the heating and cooling of the sealing adhesive, thus providing visual evidence of tampering.

Additional Indicators

As to particular embodiments, the instant temperature sensor (1) can include other indicators (e.g., a time indicator, a pressure indicator, a moisture indicator, etc.) associated with it, so that the temperature-sensing functionality of the temperature sensor (1) can be combined with corresponding time-sensing functionality, pressure-sensing functionality, moisture-sensing functionality, etc.

Barcode

As to particular embodiments, the instant temperature sensor (1) can be configured as a human-readable textual message or a machine-readable message. Regarding the latter, as to particular embodiments, the temperature sensor (1) can be configured as a barcode or a matrix barcode, which can typically be read by a scanner.

As to particular embodiments, the barcode can be colored and machine-readable at temperatures less than the temperature threshold (2), and colorless at temperatures greater than the temperature threshold (2), thus rendering the barcode unreadable.

Example 1

The subject matter of this disclosure is now described with reference to the following example. Of note, this example is provided for the purpose of illustration only, and the subject matter is not limited to this example, but rather encompasses all variations which are evident as a result of the teachings provided herein.

A particular embodiment of a microencapsulated reversible thermochromic color-changing system can be made, according to methods taught in United States Patent No. 8,883,049, United States Patent No. 9,175,175, and United States Patent No. 9,695,320, by combining (i) about 5-15% w/w crystal violet lactone as the dye, (ii) about 5-15% w/w 4-[2-ethyl-1-(4-hydroxyphenyl)hexyl]phenol as the developer, (iii) about 55-65% w/w of a mixture of the solvents shown in Formulas III and IV present in a 1:1 ratio, and (iv) about 15-25% w/w melamine resin, whereby the latter forms the microcapsule wall upon microencapsulation of the dye, developer, and solvent. As to particular embodiments, this microencapsulated reversible thermochromic color-changing system can exhibit a coloration initiation temperature at about 0° Celsius and a complete coloration temperature at about -2° Celsius, thus having a narrow transition between the colorless state and the colored state and namely, a difference of only about 2 Celsius degrees between the coloration initiation temperature and the complete coloration temperature. Additionally, this microencapsulated reversible thermochromic color-changing system can change from colored to colorless at about 50° Celsius.

Following, the microencapsulated reversible thermochromic color-changing system can be incorporated into an ink vehicle, for example in an amount of about 35-45% w/w.

As can be easily understood from the foregoing, the basic concepts of the present invention may be embodied in a variety of ways. The invention involves numerous and varied embodiments of a temperature sensor and methods for making and using such a temperature sensor.

As such, the particular embodiments or elements of the invention disclosed by the description or shown in the figures or tables accompanying this application are not intended to be limiting, but rather exemplary of the numerous and varied embodiments generically encompassed by the invention or equivalents encompassed with respect to any particular element thereof. In addition, the specific description of a single embodiment or element of the invention may not explicitly describe all embodiments or elements possible; many alternatives are implicitly disclosed by the description and figures.

It should be understood that each element of an apparatus or each step of a method may be described by an apparatus term or method term. Such terms can be substituted where desired to make explicit the implicitly broad coverage to which this invention is entitled. As but one example, it should be understood that all steps of a method may be disclosed as an action, a means for taking that action, or as an element which causes that action. Similarly, each element of an apparatus may be disclosed as the physical element or the action which that physical element facilitates. As but one example, the disclosure of a "combination" should be understood to encompass disclosure of the act of "sensing" -- whether explicitly discussed or not -- and, conversely, were there effectively disclosure of the act of "sensing", such a disclosure should be understood to encompass disclosure of a "sensor" and even a "means for sensing". Such alternative terms for each element or step are to be understood to be explicitly included in the description.

In addition, as to each term used it should be understood that unless its utilization in this application is inconsistent with such interpretation, common dictionary definitions should be understood to be included in the description for each term as contained in the Random House Webster's Unabridged Dictionary, second edition, each definition hereby incorporated by reference.

All numeric values herein are assumed to be modified by the term "about", whether or not explicitly indicated. For the purposes of the present invention, ranges may be expressed as from "about" one particular value to "about" another particular value. When such a range is expressed, another embodiment includes from the one particular value to the other particular value. The recitation of numerical ranges by endpoints includes all the numeric values subsumed within that range. A numerical range of one to five includes for example the numeric values 1, 1.5, 2, 2.75, 3, 3.80, 4, 5, and so forth. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint. When a value is expressed as an approximation by use of the antecedent "about," it will be understood that the particular value forms another embodiment. The term "about" generally refers to a range of numeric values that one of skill in the art would consider equivalent to the recited numeric value or having the same function or result. Similarly, the antecedent "substantially" means largely, but not wholly, the same form, manner or degree and the particular element will have a range of configurations as a person of ordinary skill in the art would consider as having the same function or result. When a particular element is expressed as an approximation by use of the antecedent "substantially," it will be understood that the particular element forms another embodiment.

Moreover, for the purposes of the present invention, the term "a" or "an" entity refers to one or more of that entity unless otherwise limited. As such, the terms "a" or "an", "one or more" and "at least one" can be used interchangeably herein.

Thus, the applicant(s) should be understood to claim at least: i) each of the temperature sensors herein disclosed and described, ii) the related methods disclosed and described, iii) similar, equivalent, and even implicit variations of each of these devices and methods, iv) those alternative embodiments which accomplish each of the functions shown, disclosed, or described, v) those alternative designs and methods which accomplish each of the functions shown as are implicit to accomplish that which is disclosed and described, vi) each feature, component, and step shown as separate and independent inventions, vii) the applications enhanced by the various systems or components disclosed, viii) the resulting products produced by such systems or components, ix) methods and apparatuses substantially as described hereinbefore and with reference to any of the accompanying examples, x) the various combinations and permutations of each of the previous elements disclosed.

The background section of this patent application, if any, provides a statement of the field of endeavor to which the invention pertains. This section may also incorporate or contain paraphrasing of certain United States patents, patent applications, publications, or subject matter of the claimed invention useful in relating information, problems, or concerns about the state of technology to which the invention is drawn toward. It is not intended that any United States patent, patent application, publication, statement or other information cited or incorporated herein be interpreted, construed or deemed to be admitted as prior art with respect to the invention.

The claims set forth in this specification, if any, are hereby incorporated by reference as part of this description of the invention, and the applicant expressly reserves the right to use all of or a portion of such incorporated content of such claims as additional description to support any of or all of the claims or any element or component thereof, and the applicant further expressly reserves the right to move any portion of or all of the incorporated content of such claims or any element or component thereof from the description into the claims or vice-versa as necessary to define the matter for which protection is sought by this application or by any subsequent application or continuation, division, or continuation-in-part application thereof, or to obtain any benefit of, reduction in fees pursuant to, or to comply with the patent laws, rules, or regulations of any country or treaty, and such content incorporated by reference shall survive during the entire pendency of this application including any subsequent continuation, division, or continuation-in-part application thereof or any reissue or extension thereon.

Additionally, the claims set forth in this specification, if any, are further intended to describe the metes and bounds of a limited number of the preferred embodiments of the invention and are not to be construed as the broadest embodiment of the invention or a complete listing of embodiments of the invention that may be claimed. The applicant does not waive any right to develop further claims based upon the description set forth above as a part of any continuation, division, or continuation-in-part, or similar application.

V. CLAIMS

1. A temperature sensor comprising:

a reversible thermochromic color-changing system comprising:

a dye;

a developer; and

a solvent;

wherein upon exposure to a preselected temperature threshold, association or disassociation of said dye and said developer results in a visible color change; and

wherein said color-changing system comprises a color-memory property which facilitates retention of said color change to record said exposure to said temperature threshold.

2. The temperature sensor of claim 1, wherein said dye comprises a leuco dye.

3. The temperature sensor of claim 2, wherein said leuco dye reversibly changes between a substantially colorless state and a visibly colored state.

4. The temperature sensor of claim 3, wherein said color-changing system comprises:

a coloration temperature at which said leuco dye changes to said colored state; and

a decoloration temperature at which said leuco dye changes from said colored state;

wherein said coloration temperature differs from said decoloration temperature.

5. The temperature sensor of claim 4, wherein said color-changing system comprises:

a coloration temperature at which said leuco dye changes to said colored state; and

a decoloration temperature at which said leuco dye changes to said colorless state;

wherein said coloration temperature differs from said decoloration temperature.

6. The temperature sensor of claim 5, wherein said coloration temperature is less than said decoloration temperature.

7. The temperature sensor of claim 6, wherein said color-memory property facilitates retention of said color change upon an increase in temperature from said coloration temperature.

8. The temperature sensor of claim 7, wherein said color-memory property facilitates retention of said colored state upon an increase in temperature from said coloration temperature.

9. The temperature sensor of claim 8, wherein said color-memory property facilitates retention of said color change upon an increase in temperature from a freezing point of said color-changing system.

10. The temperature sensor of claim 9, wherein said color-memory property facilitates retention of said colored state upon an increase in temperature from said freezing point.

11. The temperature sensor of claim 6, wherein said color-memory property facilitates retention of said color change upon a decrease in temperature from said decoloration temperature.

12. The temperature sensor of claim 11, wherein said color-memory property facilitates retention of said colorless state upon a decrease in temperature from said decoloration temperature.

13. The temperature sensor of claim 12, wherein said color-memory property facilitates retention of said color change upon a decrease in temperature from a melting point of said color-changing system.

14. The temperature sensor of claim 13, wherein said color-memory property facilitates retention of said colorless state upon a decrease in temperature from said melting point.

15. The temperature sensor of claim 6, wherein said coloration temperature differs from said decoloration temperature by at least about 40 Celsius degrees.

16. The temperature sensor of claim 6, wherein said coloration temperature differs from said decoloration temperature by at least about 45 Celsius degrees.

17. The temperature sensor of claim 6, wherein said coloration temperature differs from said decoloration temperature by at least about 50 Celsius degrees.

18. The temperature sensor of claim 6, wherein said color-changing system comprises a narrow transition between said colorless state and said colored state.

19. The temperature sensor of claim 18, wherein said color-changing system comprises a narrow transition between a coloration initiation temperature and a complete coloration temperature.

20. The temperature sensor of claim 19, wherein the difference between said coloration initiation temperature and said complete coloration temperature is not greater than about 4 Celsius degrees.

21. The temperature sensor of claim 19, wherein the difference between said coloration initiation temperature and said complete coloration temperature is not greater than about 3 Celsius degrees.

22. The temperature sensor of claim 19, wherein the difference between said coloration initiation temperature and said complete coloration temperature is not greater than about 2 Celsius degrees.

23. The temperature sensor of claim 19, wherein the difference between said coloration initiation temperature and said complete coloration temperature is not greater than about 1 Celsius degrees.

24. The temperature sensor of claim 6, wherein said color-changing system comprises a narrow transition between said colored state and said colorless state.

25. The temperature sensor of claim 24, wherein said color-changing system comprises a narrow transition between a decoloration initiation temperature and a complete decoloration temperature.

26. The temperature sensor of claim 25, wherein the difference between said decoloration initiation temperature and said complete decoloration temperature is not greater than about 4 Celsius degrees.

27. The temperature sensor of claim 25, wherein the difference between said decoloration initiation temperature and said complete decoloration temperature is not greater than about 3 Celsius degrees.

28. The temperature sensor of claim 25, wherein the difference between said decoloration initiation temperature and said complete decoloration temperature is not greater than about 2 Celsius degrees.

29. The temperature sensor of claim 25, wherein the difference between said decoloration initiation temperature and said complete decoloration temperature is not greater than about 1 Celsius degrees.

30. The temperature sensor of claim 1, wherein said solvent comprises an ester.

31. The temperature sensor of claim 30, wherein said ester comprises a diphenylmethyl ester.

32. The temperature sensor of claim 30, wherein said ester has Formula I.

33. The temperature sensor of claim 30, wherein said ester has Formula II.

34. The temperature sensor of claim 30, wherein said ester has Formula III.

35. The temperature sensor of claim 30, wherein said ester has Formula IV.

36. The temperature sensor of claim 30, wherein said ester has Formula V.

37. The temperature sensor of claim 30, wherein said ester has Formula VI.

38. The temperature sensor of claim 30, wherein said ester has Formula VII.

39. The temperature sensor of claim 30, wherein said ester has Formula VIII.

40. The temperature sensor of claim 30, wherein said ester has Formula IX.

41. The temperature sensor of claim 30, wherein said ester has Formula X.

42. The temperature sensor of claim 30, wherein said ester has Formula XI.

43. The temperature sensor of claim 30, wherein said ester has Formula XII.

44. The temperature sensor of claim 30, wherein said ester has Formula XIII.

45. The temperature sensor of claim 1, wherein said solvent comprises a mixture of two or more esters.

46. The temperature sensor of claim 45, wherein one said ester comprises a diphenylmethyl ester and another said ester comprises another diphenylmethyl ester.

47. The temperature sensor of claim 46, wherein one said ester has Formula III and another said ester has Formula IV.

48. The temperature sensor of claim 45, wherein one said ester has Formula VII and another said ester has Formula VIII.

49. The temperature sensor of claim 1, wherein said solvent comprises a ketone.

50. The temperature sensor of claim 49, wherein said ketone has Formula XIV.

51. The temperature sensor of claim 1, wherein said color-changing system is contained such that said dye, said developer, and said solvent are encapsulated together.

52. The temperature sensor of claim 51, wherein said color-changing system is encapsulated within a capsule to provide an encapsulated color-changing system.

53. The temperature sensor of claim 52, wherein said color-changing system is encapsulated within a microcapsule to provide a microencapsulated color-changing system.

54. The temperature sensor of claim 1, wherein said color-changing system is incorporated into a coating.

55. The temperature sensor of claim 1, wherein said color-changing system is incorporated into an ink.

56. A method for visually determining whether a temperature-sensitive product has been exposed to a preselected temperature threshold, comprising:

reliably associating a temperature sensor with said temperature-sensitive product, said temperature sensor comprising:

a reversible thermochromic color-changing system comprising:

a dye;

a developer; and

a solvent;

wherein upon exposure to said temperature threshold, association or disassociation of said dye and said developer results in a visible color change; and

wherein said color-changing system comprises a color-memory property which facilitates retention of said color change to record said exposure to said temperature threshold.

57. The method of claim 56, further comprising visually observing said temperature sensor.

58. The method of claim 57, wherein visual detection of said color change indicates that said temperature-sensitive product was exposed to said temperature threshold.

59. The method of claim 58, wherein visual detection of the absence of said color change indicates that said temperature-sensitive product was not exposed to said temperature threshold.

60. A method for indicating whether a temperature-sensitive product has been exposed to a preselected temperature threshold, comprising:

reliably associating a temperature sensor with said temperature-sensitive product, said temperature sensor comprising:

a reversible thermochromic color-changing system comprising:

a dye;

a developer; and

a solvent;

wherein upon exposure to said temperature threshold, association or disassociation of said dye and said developer results in a visible color change; and

wherein said color-changing system comprises a color-memory property which facilitates retention of said color change to record said exposure to said temperature threshold.

61. The method of claim 60, further comprising detecting whether or not said color change occurred.

62. The method of claim 61, wherein detection of said color change indicates that said temperature-sensitive product was exposed to said temperature threshold.

63. The method of claim 60, wherein detection of the absence of said color change indicates that said temperature-sensitive product was not exposed to said temperature threshold.

64. A method of using a temperature sensor, comprising:

reliably associating said temperature sensor with a temperature-sensitive product, said temperature sensor comprising:

a reversible thermochromic color-changing system comprising:

a dye;

a developer; and

a solvent;

wherein upon exposure to said temperature threshold, association or disassociation of said dye and said developer results in a visible color change; and

wherein said color-changing system comprises a color-memory property which facilitates retention of said color change to record said exposure to said temperature threshold.

65. The method of claim 64, further comprising detecting whether or not said color change occurred.

66. The method of claim 65, wherein detection of said color change indicates that said temperature-sensitive product was exposed to said temperature threshold.

67. The method of claim 66, wherein detection of the absence of said color change indicates that said temperature-sensitive product was not exposed to said temperature threshold.

68. The method of claim 65, further comprising visually observing said temperature sensor to detect whether or not said color change occurred.

69. A method of making a temperature sensor, comprising:

containing a reversible thermochromic color-changing system comprising:

a dye;

a developer; and

a solvent;

wherein upon exposure to a preselected temperature threshold, association or disassociation of said dye and said developer results in a visible color change; and

wherein said color-changing system comprises a color-memory property which facilitates retention of said color change to record said exposure to said temperature threshold.

70. The method of claim 69, wherein said dye comprises a leuco dye.

71. The method of claim 70, wherein said solvent comprises an ester.

72. The method of claim 71, wherein said ester comprises a diphenylmethyl ester.

73. The method of claim 71, wherein said ester has Formula I.

74. The method of claim 71, wherein said ester has Formula II.

75. The method of claim 71, wherein said ester has Formula III.

76. The method of claim 71, wherein said ester has Formula IV.

77. The temperature sensor of claim 71, wherein said ester has Formula V.

78. The temperature sensor of claim 71, wherein said ester has Formula VI.

79. The temperature sensor of claim 71, wherein said ester has Formula VII.

80. The temperature sensor of claim 71, wherein said ester has Formula VIII.

81. The temperature sensor of claim 71, wherein said ester has Formula IX.

82. The method of claim 69, wherein said solvent comprises a mixture of two or more esters.

83. The temperature sensor of claim 82, wherein one said ester comprises a diphenylmethyl ester and another said ester comprises another diphenylmethyl ester.

84. The temperature sensor of claim 83, wherein one said ester has Formula III and another said ester has Formula IV.

85. The temperature sensor of claim 82, wherein one said ester has Formula VII and another said ester has Formula VIII.

86. The method of claim 69, further comprising encapsulating said color-changing system to provide a contained color-changing system.

87. The method of claim 86, further comprising microencapsulating said color-changing system.

88. The method of claim 87, further comprising incorporating said contained color-changing system into a coating.

89. The method of claim 88, further comprising incorporating said contained color-changing system into an ink.

90. The method of claim 89, further comprising printing said ink on a substrate.

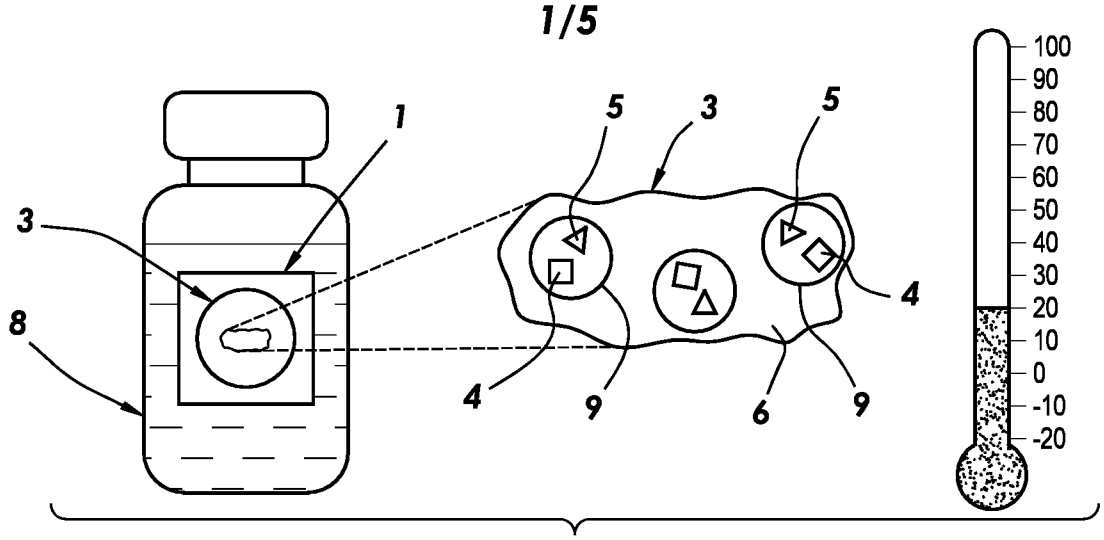


FIG.1A

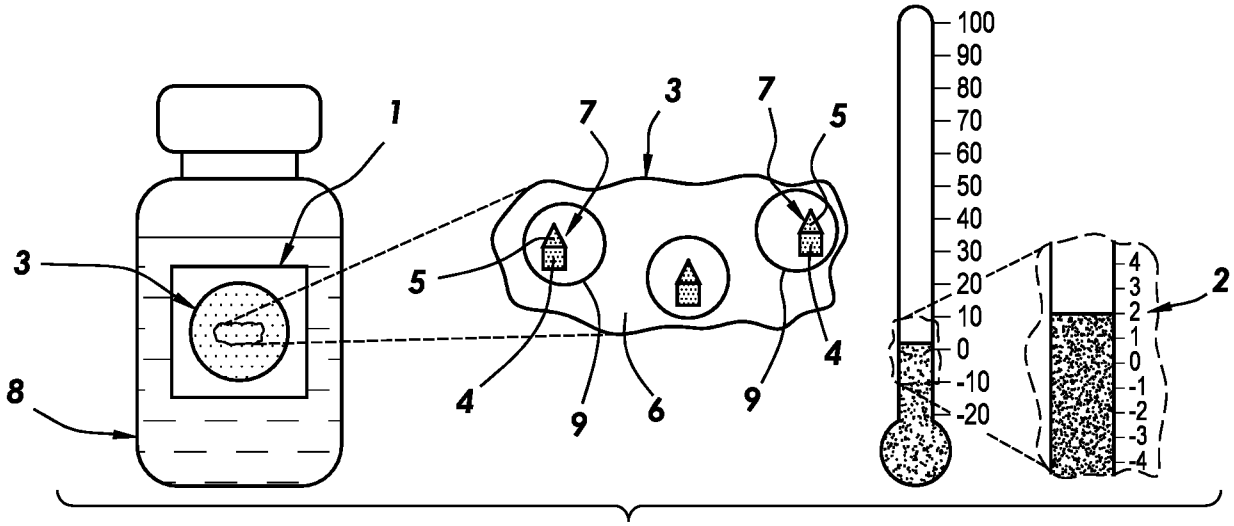


FIG.1B

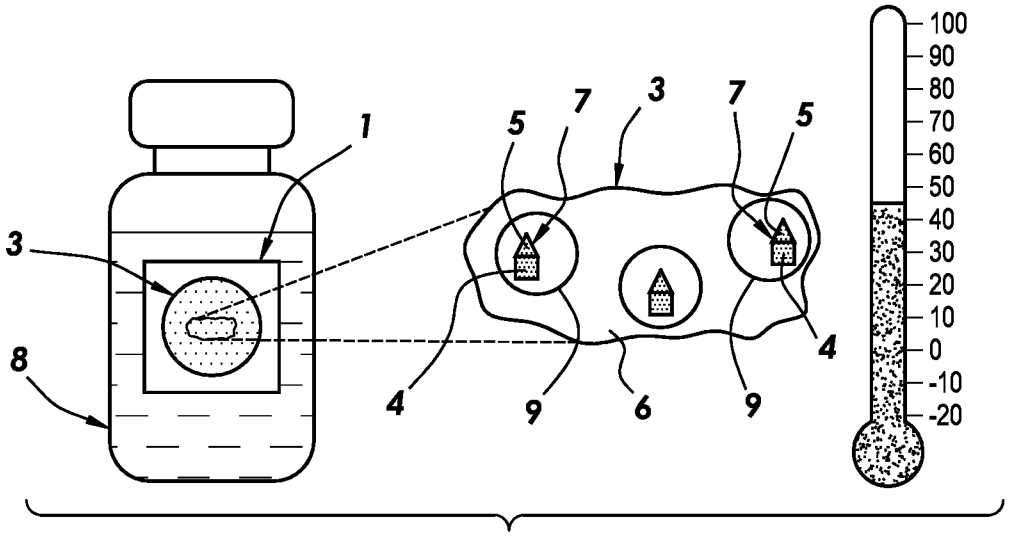


FIG.1C

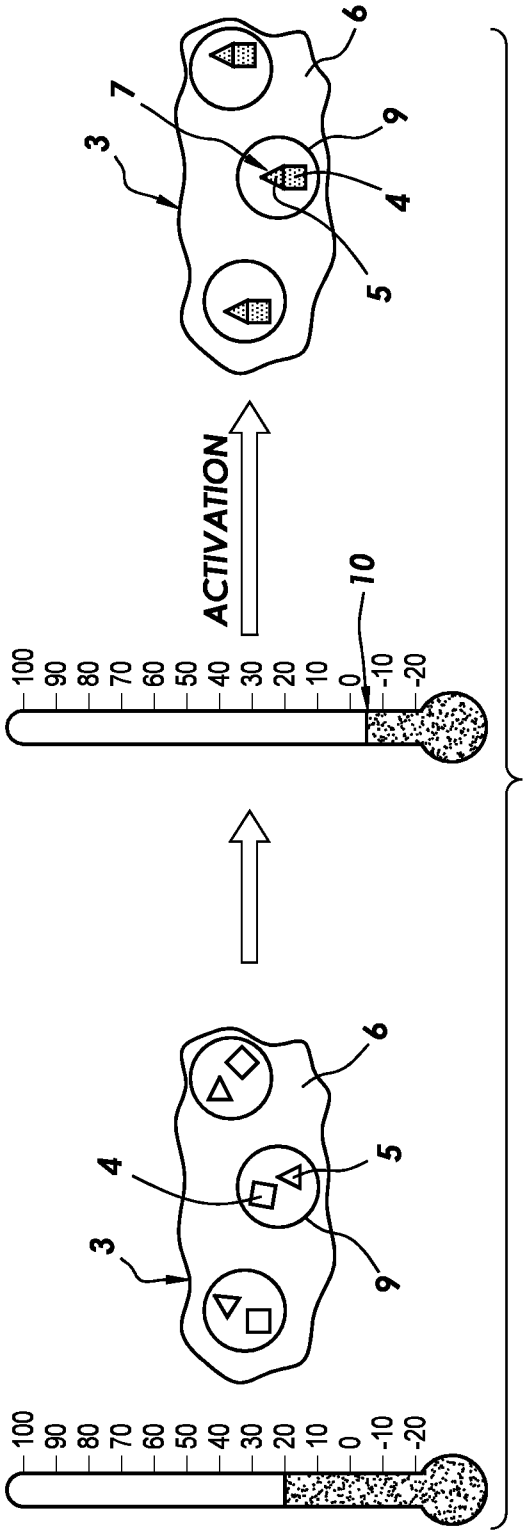

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FIG.2A

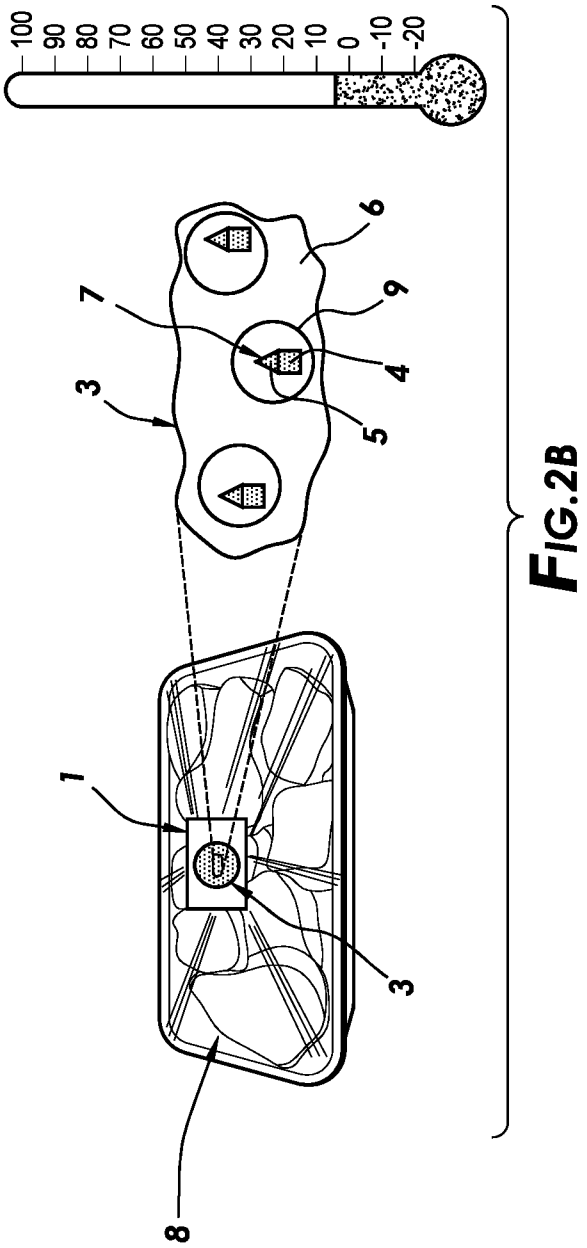
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FIG.2B

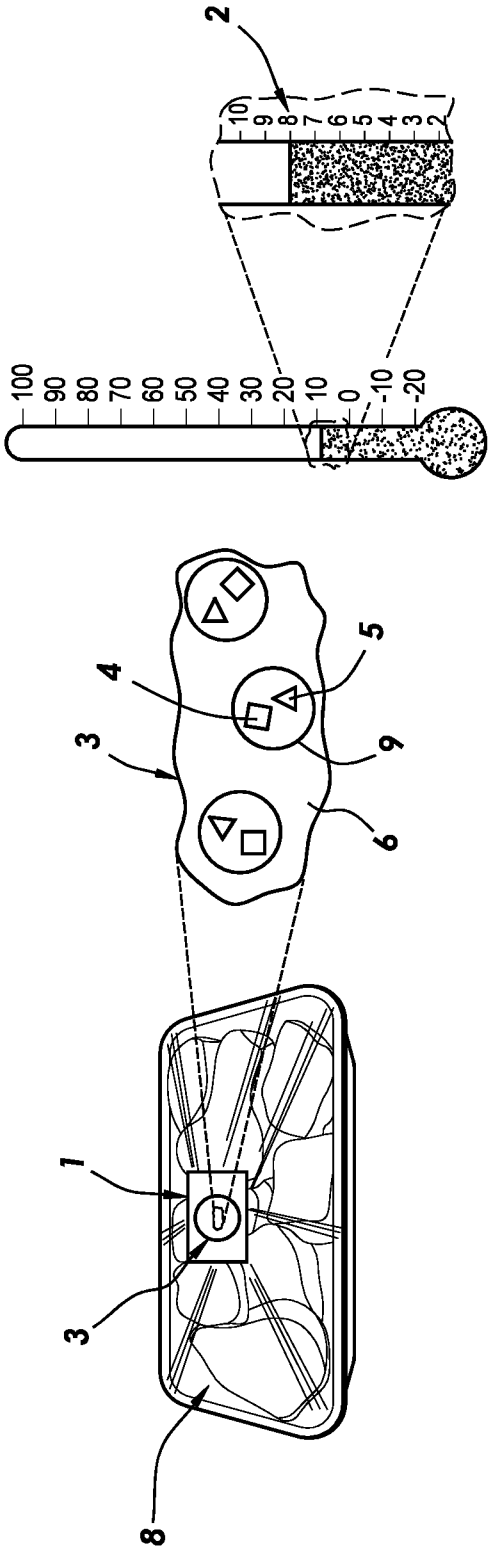
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FIG.2C

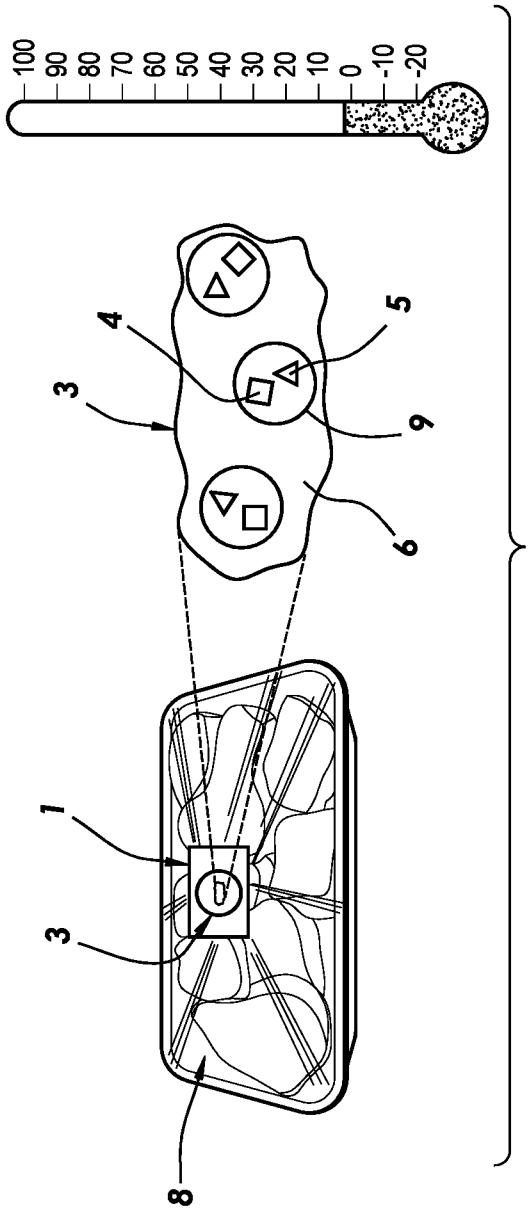
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FIG.2D

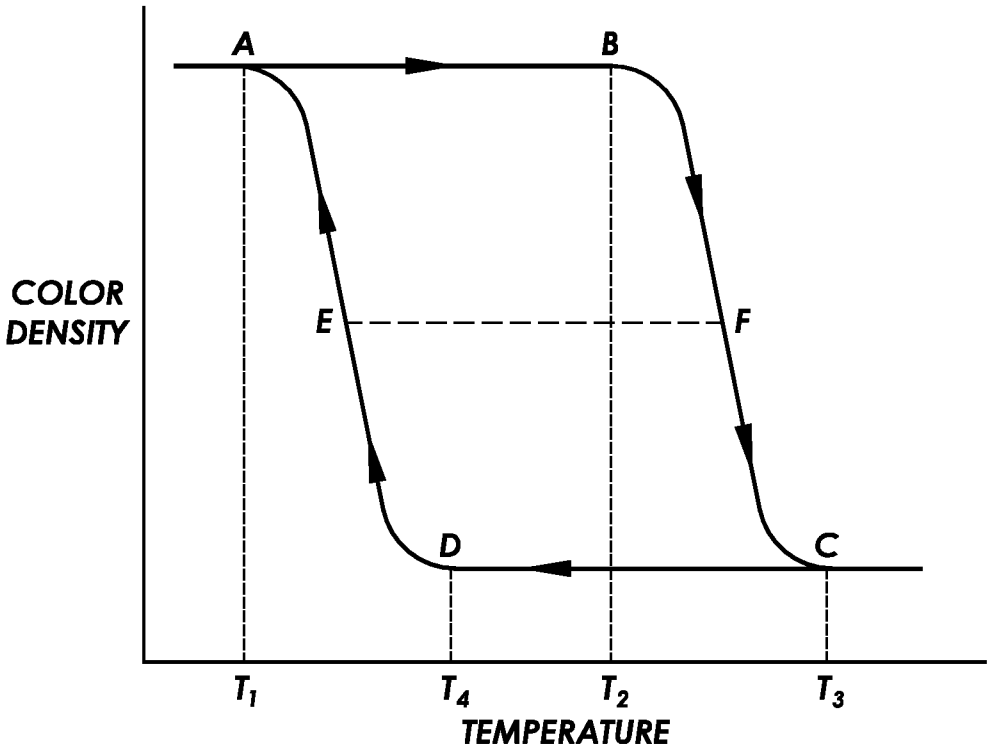

FIG.3

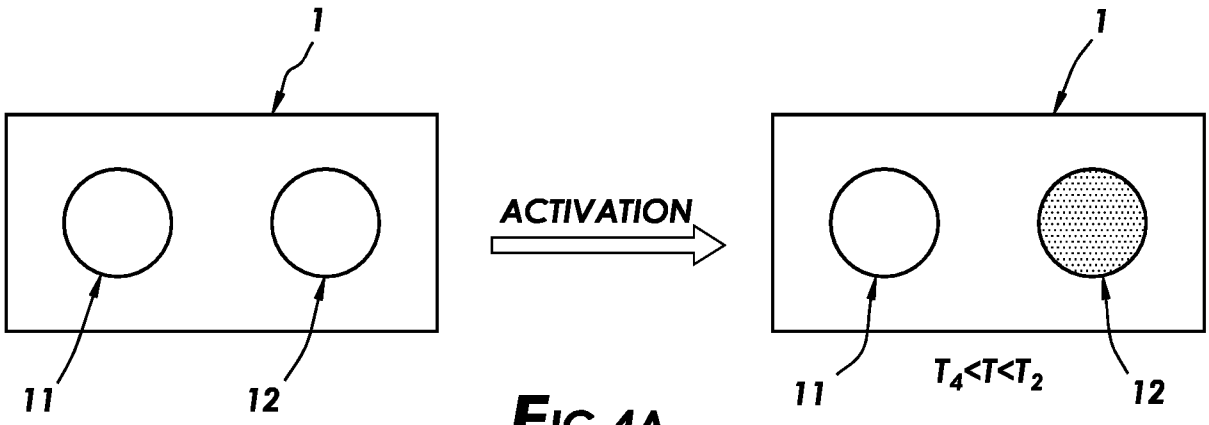

FIG.4A

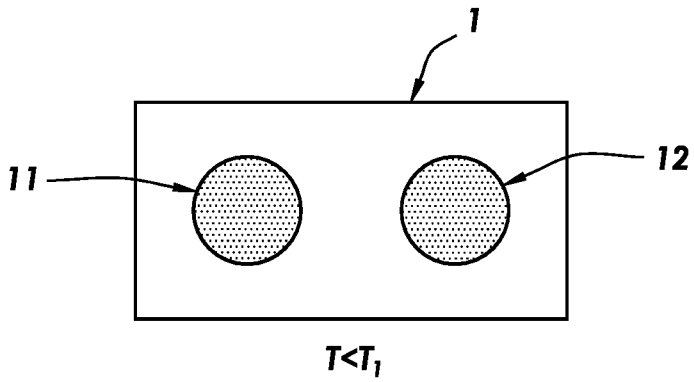

FIG.4B

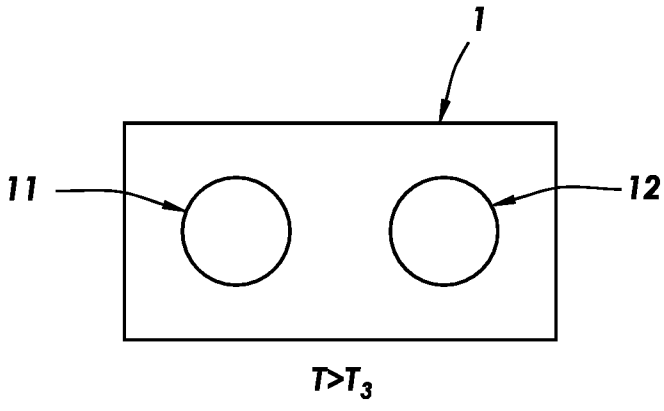

FIG.4C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 20/26073

A. CLASSIFICATION OF SUBJECT MATTER

IPC - A23L 3/015; A23L 5/40; G01L 11/00 (2020.01)

CPC - A23L 3/015; A23L 5/40; G01L 11/002; G01L 11/02; G01L 7/00

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)
See Search History document

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2004/0229754 A1 (Fujita) 18 November 2004 (18.11.2004) entirety of document especially [0001]; [0007]; [0011]-[0013]; [0016]-[0018]; [0021]-[0024]; [0032]; [0108]; [0117]; [0136]-[0138]; [0165] Fig. 1	1-30, 51-55 ---------- 31-32
Y	JP 2006/188660 A (Fujita) 20 July 2006 (20.07.2006) entirety of document especially para [0001]; [0011]	31-32
A	'Leuco Dye' Wikipedia 05 March 2018 (05.03.2018) retreived from <https://en.wikipedia.org/w/index.php?title=Leuco_dye&oldid=828934140>	2
A	US 2012/0141188 A1 (Fujita) 07 June 2012 (07.06.2012) entirety of document 1-31 51-55	1-32, 51-55
A	US 5,558,699 A (Nakashima et al) 24 September 1996 (24.09.1996) entirety of document	1-32, 51-55
A	US 5,281,570 A (Hasegawa et al) 25 January 1994 (25.01.1994) entirety of document	1-32, 51-55

☐ 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
"D" document cited by the applicant in the international application
"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	Date of mailing of the international search report
17 June 2020	26 AUG 2020
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Lee Young Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 20/26073

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
See Supplemental Page

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-32, 51-55

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US 20/26073

Continuation of:
Box III (lack of unity)

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I+: Claims 1-55 and 69-90 directed to a temperature sensor comprising: a reversible thermochromic color-changing system comprising: a dye; a developer; and a solvent; wherein upon exposure to a preselected temperature threshold, association or disassociation of said dye and said developer results in a visible color change; and wherein said color-changing system comprises a color-memory property which facilitates retention of said color change to record said exposure to said temperature threshold; and method of making temperature sensor. The temperature sensor will be searched to the extent that solvent comprises diphenylmethyl ester of formula I of claim 32. It is believed that claims 1-32 and 51-55 read on this first named invention, and thus these claims will be searched without fee to the extent that they encompass the combination, composition and method, described above. Applicant is invited to elect additional composition(s) and method(s), wherein each additional composition and method elected will require one additional invention fee. Applicants must specify the claims that encompass any additionally elected composition and method. Applicants must further indicate, if applicable, the claims which encompass the first named invention, if different than what was indicated above for this group. Failure to clearly identify how any paid additional invention fees are to be applied to the '+' group(s) will result in only the first claimed invention to be searched. Additionally, an exemplary election wherein different actual variables are selected is suggested. An exemplary election would be a temperature sensor where the solvent comprises diphenylmethyl ester of formula I of claim 33 (i.e., 1-31, 33 and 51-55).

Group II: Claims 56-63, directed to a method for visually determining whether a temperature-sensitive product has been exposed to a preselected temperature threshold.

Group III: Claims 64-68, directed to a method of using a temperature sensor, comprising: reliably associating said temperature sensor with a temperature-sensitive product, said temperature sensor.

The inventions listed as Groups I+-III do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features:

Group I+ includes the technical feature of a unique temperature sensor which is not required by any other invention of Group I+.

Group II includes the technical feature of a method for visually determining whether a temperature-sensitive product has been exposed to a preselected temperature threshold which is not required by any other invention of Group I+. and III.

Group III includes the technical feature OF a method of using a temperature sensor, comprising: reliably associating said temperature sensor with a temperature-sensitive product, said temperature sensor which is not required by any other invention of Group I+ and II.

Common technical features:

The inventions of Group I+ share the technical features of a temperature sensor comprising: a reversible thermochromic color-changing system comprising: a dye; a developer; and a solvent; wherein upon exposure to a preselected temperature threshold, association or disassociation of said dye and said developer results in a visible color change; and wherein said color-changing system comprises a color-memory property which facilitates retention of said color change to record said exposure to said temperature threshold.

Continued on Supplemental Page

Continuation of:
Box III (lack of unity)

These shared technical features, however, do not provide a contribution over the prior art as being anticipated by US 2004/0229754 A1 to Fujita (hereinafter 'Fujita') which discloses a temperature sensor comprising: (para [0001] This invention relates to a thermochromic coloring color-memory composition and a thermochromic coloring color-memory microcapsule pigment containing the same; para [0013] have the applicability to various fields such as of heat sensitive materials) a reversible thermochromic color-changing system (para [0001] More illustratively, it relates to a thermochromic coloring color-memory composition which displays reversible discoloration between coloring and decoloring; para [0013] the invention can generate reversible discoloration of coloring and decoloring showing a broad maximum hysteresis width (deltaH) regarding a color density-temperature curve) comprising: a dye; (para [0007] A requirement of the invention is a thermochromic coloring color-memory composition which comprises a homogeneous solubilized mixture of (A) an electron donative coloring organic compound, (B) an electron accepting compound and (C) an ester compound... which controls color reactions of the aforementioned (A) and (B); where electron donating coloring compound (A) is a dye, see specification pg 7 ln 5-15 As to particular embodiments, the leuco dye can be an electron-donating compound) a developer; (para [0007] ...(B) an electron accepting compound; where electron accepting compound (B) is a developer, see Specification pg 7 ln 5-15 As to particular embodiments... Further, the developer (5) can comprise an electron-accepting compound) and a solvent; (para [0007] A requirement of the invention is a thermochromic coloring color-memory composition which comprises a homogeneous solubilized mixture of (A)... (B)... and (C) an ester compound; where (C) is a solvent, see Example 1 para [0136] A thermochromic coloring color-memory composition was obtained by homogeneously and solubilizly dissolving... component (A)... component (B) and 50.0 parts of 4-benzyloxyphenylethyl caprate as the component (C); where 4-benzyloxyphenylethyl caprate has same structure as solvent seen in Specification Formula IX (m=4), see Specification pg 12 ln 4) wherein upon exposure to a preselected temperature threshold, association or disassociation of said dye and said developer results in a visible color change; (para [0007] (A) an electron donative coloring organic compound.... (B) an electron accepting compound... color reactions of the aforementioned (A) and (B); where the temperature-dependent color reactions see color changes shown in Figure 1, where Color Density (y-axis) increases or decreases as a function of temperature (x-axis)) and wherein said color-changing system comprises a color-memory property which facilitates retention of said color change to record said exposure to said temperature threshold (para [0011] It's another requirement is that the present composition has a color-memory ability; see Fig. 1, where the change of temperature from A to C yields no change in Color Density until temperatures lower than C are reached (see arrow). Where heating (D to B) retains changed color as composition is heated; see Example 1 para [0136]-[0137] A thermochromic coloring color-memory composition was obtained... This thermochromic coloring color-memory composition changed color from blue to colorless)

As said temperature sensor was known in the art at the time of the invention, these cannot be considered special technical features, that would otherwise unify the inventions of Groups I+, II and III. The inventions of Group I+, II and III thus lack unity under PCT Rule 13.