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(54) Title: SYNTHESIS OF INORGANIC SiO_2 MICROCAPSULES CONTAINING PHASE CHANGE MATERIALS AND APPLICATIONS THEREIN

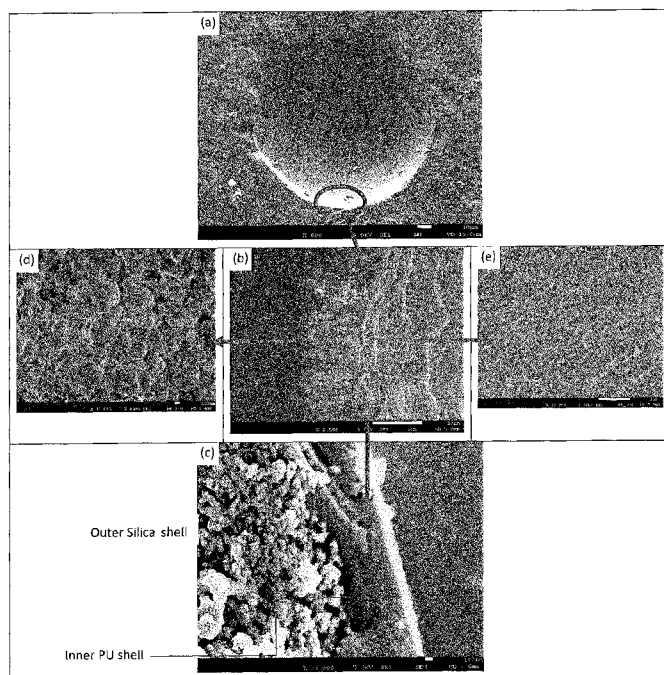


Fig. 2

(57) Abstract: Disclosed herein are microcapsules that encapsulate a phase change material, where the microcapsules have a dual-core structure with a first shell being made of an organic polymeric material, in particular polyurea surrounded by a second inorganic material shell, in particular silica. Also disclosed herein is a process to manufacture said microcapsules and applications thereof.



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Synthesis of Inorganic SiO₂ Microcapsules Containing Phase Change Materials and Applications Therein

Field of Invention

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This invention relates generally to microcapsules and a method of using Microencapsulated Phase Change Materials (MEPCMs) as core materials. More specifically, it relates to a method for microencapsulation of an organic phase change material (e.g. octadecane or paraffins) in a hybrid shell having an inorganic silicon dioxide (SiO₂) portion and an organic portion by means of an interfacial polymerization and electrostatic force process in an oil-in-water emulsion system. This invention also provides a process for manufacturing cool-paint coatings and said cool-paint coatings.

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Background

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It has been reported in many countries that the economic loss related to the wastage of energy is about 5% of general domestic product (GDP), which is a very significant proportion of a nation's costs. As such, ways to save energy and reduce emissions associated with energy production are critical issues in economic society. Energy-saving materials that can both store and release energy (i.e. reversible energy saving materials) have become a significant focus of research in both the scientific and industrial communities.

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The economic loss that occurs due to wasted energy can be minimized by improving the energy utilization rate and awareness of energy saving techniques. One approach to reducing energy wastage is the use of phase change materials (PCMs), which can both store heat energy by transforming from one matter phase (e.g. a solid) into another matter phase (e.g. a liquid or gas) and then release said energy by the reverse operation. However, the use of such materials commercially remains challenging.

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Applications of microcapsules are as varied as the material that can be microencapsulated, and there has been a long history of the use in the fields including but not limited to medicinal and biological preparation, fertilizers, flavorings, deodorizers, adhesives, surface coatings, foams, xerographic toners and carbonless copying systems. As such, the application of microcapsules to PCMs to provide microencapsulated phase change materials (MEPCMs) is considered a promising option for the utilization of said materials.

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Microcapsules for PCMs generally comprise a core material and a shell structure. The core material may be a gas, liquid or solid, and may be a single substance, or a mixture of substances in the form, for example, of a solution or a suspension. The core material is encapsulated by the outer shell structure, which is usually one of an organic or inorganic material. The microcapsule shell acts as a container that serves to isolate the core phase changing material from the surrounding environment and thus protects the core material when the phase change happens (i.e. from solid to liquid). When the temperature is high, the MEPCMs absorb heat from the surrounding ambient environment and the core's phase state changes (e.g. from solid to liquid). This phase change can be reversed when the ambient temperature drops, thereby allowing the MEPCMs to release heat to their surroundings, with an accompanying phase state change (e.g. from liquid to solid). Ideally, the shell of the MEPCM capsules still retain almost their original state even after going through a large number of heating and cooling cycles.

Microcapsules can be made by a variety of techniques such as those described in *Microencapsulation: Methods and Industrial Applications*, 2nd Edition; B. Simon, Taylor & Francis, 2006. Among the various approaches, interfacial polymerization is one of the most popular methods to prepare microcapsules. Interfacial polymerization includes producing an oil-in-water emulsion system by dispersing a water immiscible material into aqueous continuous phase with the assistance of surfactant, and the target core materials are often included in the discontinuous phase with oil phase reactants. Reactants that form the microcapsule wall are then added to the aqueous phase. A polymerization reaction to form the shell then takes place between the reactants, forming a polymer wall at the interface between the aqueous and oil phases, with core material being encapsulated.

One possible means of utilising PCMs is through the use of microencapsulated phase change materials (MEPCMs). Such MEPCMs have a number of potential applications - one of which being in the formation of temperature-adjusting cooling paint coatings. Such paint coatings would appear to provide an efficient means of energy storage and release. The addition of MEPCMs microcapsules into paint may result in a paint coating equipped with two means of temperature-adjustment. Firstly, the MEPCM microcapsules act to gradually absorb ambient heat from the environment during the day (undergoing a phase change from solid to liquid or gas), thereby reducing the amount of heat transferred to the coated object, such as a building. Hence, the coating reduces the energy needed to maintain the indoor temperature at comfortable level. Secondly, when the surrounding temperature drops at night, the MEPCM capsules, which stored the heat energy during the day, can release heat to the surroundings to adjust/maintain the indoor temperature at comfortable level. Thus, the

energy saving is quite appreciable, and so the need for large energy bills to effect the cooling of a building during the day and heating at night can be avoided.

A large number of PCM species have been encapsulated for temperature adjusting applications. However, the research undertaken to date has focused on the manufacture of shells using polymers or other organic materials. For example, the application of microencapsulation for manufacturing phase change materials has been adopted by BASF chemical company since 2010. However, most of the capsule shells consist of polymer or organic materials, which are usually flammable (especially at high temperature), and can be decomposed to release toxic gases, which can be harmful to health and the environment. Furthermore, polymer shells have a very low strength and so can be damaged easily (e.g. by mechanical shocks). These restrict the widespread application of polymer capsules.

There is currently a lot research focus on silica-based PCM capsules, which mainly relates to the synthesis of single silica shell capsules. For current single silica shell capsules, it has been found that they are brittle and easily broken, making them unsuitable for practical use. The use of a silica-polymer dual shell structures, the thickness of polymer shell is normally in the micrometer scale, which leads to the significant restriction of heat transfer and so these materials are unsuitable for use MEPCMs.

The research on inorganic based materials for phase change materials remains largely unexplored, and only a few publications have appeared. U.S. Pat. No. 7919184 B2 discloses phase change materials encapsulated with a metal shell or hybrid shell (polymer and metal), and the diameter distribution of such capsules ranges from about 10nm to 1000nm to eliminate the problem of abrasion as well as blockage of heat exchange passages. However, the capsule size is too small and that limits the application of these capsules. CN. Pat. No. 100494305 C application discloses a preparation method for a microcapsule wall made of a silica material that microencapsulates a phase change material. However, at the emulsion stage, an alkali metal salt was added as an additive, and also a stabilizer added to equilibrate the emulsion system, since the capsules could be affected by any induced impurities. However, there is no evidence to verify if the capsules have a significant durability property.

There are a number of examples of applying microencapsulation for PCM materials. U.S. Pat. No. 20110259544 A1 describes an apparatus for storing thermal energy. In one embodiment, the apparatus is provided including at least one phase change material and a capsule containing the at least one phase change material, where the encapsulation material

and phase change material are selected to store and discharge thermal energy at temperatures of greater than 400 degrees without capsule failure. U.S. Pat. No. 6270836 discloses a method by interfacial polymerization in the synthesis of alkanes as the core material, with polyurea/polyurethane as shell microcapsules, and such microencapsulated phase change material has a certain resistance to leaks. However, since the wall is organic material, which is easily flammable, with the potential threat of combustion, therefore its uses in civil construction materials carries a certain risk. U.S. Pat. No. 4504402 A describes the microencapsulation of phase change composition by using a pellet-shaped product of about 1/8 inch to 1 inch in size, formed out of an outer seamless shell member which defines a cavity that permanently encases a phase change composition. Other examples of application of microencapsulation for PCM materials can be found in U.S. Pat. No. 6703127 B2 and U.S. Pat. No. US 6514362 B1.

A silica-based MEPCM capsule system is described in *New approach for sol-gel synthesis of microencapsulated n-octadecane phase change material with silica wall using sodium silicate precursor* (Energy, 2014, 1-11). PCM capsules that are encapsulated in a silica-based material are synthesized, which microcapsules are then characterized using Differential Scanning Calorimetry (DSC) to investigate the durability of said capsules. However, even though the silica-MEPCMs capsules were successfully synthesized, they revealed that the durability of capsules is not acceptable due to the significant curve-shift in the DSC curves provided therein after only 100 heating-cooling cycles, suggesting that the material was not stable.

Thus, one of the most essential evaluation factors for MEPCMs is long term stability. Inadequate long term stability of the PCMs and the container material (i.e. the shell of the microcapsule) is a problem that has limited widespread use of these materials as latent heat stores. This poor stability is mainly due to two factors: poor stability of the material properties due to thermal cycling; and probable corrosion between the core-PCM and the container (i.e. the shell material). In addition, should an MEPCM capsule be damaged it is probable that the core contents are then diffused to the surrounding matrix, leading to a reduction (if not entire loss) of effectiveness over time. Therefore, there remains a need for effective MEPCMs that can be manufactured simply on an industrial scale for applications that include the temperature control of a building over an extended period of time.

Summary of Invention

In this invention, core material-PCM as a temperature adjustor, is encapsulated in silica shell based microcapsules *via* interfacial polymerization and electrostatic interaction. In addition, electrostatic force between oppositely charged molecules also plays an important role in formation of the capsule shell. That is, the positively charged and negatively charged molecules in the reaction mixture are attracted to one another *via* electrostatic force to form a new shell covering the existing capsules.

It has been surprisingly found that a particular combination of materials and process provides an unexpectedly stable microencapsulated phase change material. Thus, in a first aspect of the invention, there is provided a microcapsule encapsulating a phase change material comprising:

a core encapsulated by a first shell and a second shell, where the first shell is sandwiched between the second shell and the core, wherein:

the core comprises a phase change material that undergoes a phase change at from 0°C to 200°C;

the first shell is an organic polymeric material; and

the second shell is an inorganic material.

In embodiments of the first aspect of the invention:

(a) the phase change material may undergo a phase change at from 5°C to 150°C;

(b) the phase change material may be an organic material. For example, the organic material may be a C₁₄-C₄₅ paraffinic hydrocarbon (e.g. C₁₄, C₁₈, C₂₂-C₄₅ hydrocarbon, such as octadecane);

(c) the organic polymeric material may comprise functional groups that are cationic in aqueous media, optionally wherein the functional groups are cationic in aqueous media at a pH of from 2.0 to 5.0, such as from 2.5 to 4.0, such as 3.0 (e.g. the organic polymeric material may comprise a polyurea, such as a polyurea formed from a polyimine and an organic diisocyanate, optionally wherein the organic polymeric material may comprise a polyurea formed by the reaction between hexamethylene diisocyanate and polyethylenimine (e.g. the weight average molecular weight of the polyethylenimine may be from 800 Daltons to 3,000 Daltons, such as from 1,000 Daltons to 2,000 Daltons, such as 1,300 Daltons);

(d) the inorganic material may be silica;

(e) the microcapsule may have an average size of from 50 μm to 500 μm , such as from 75 μm to 450 μm , 100 to 400 μm ;

(f) the first shell may have a thickness of from 75 to 250 nm (e.g. from 100 to 200 nm);

5 (g) the second shell may comprise spheres of the inorganic material having a diameter of from 100 to 500 nm (e.g. from 150 to 450 nm);

(h) the core material may comprise from 60 to 85 wt% of the microcapsule (e.g. from 65 to 80 wt%, such as 75 wt% of the microcapsule);

(i) the core may further comprise carbon nanotubes.

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In a second aspect of the invention, there is provided a formulation comprising a microcapsule encapsulating a phase change material as defined in the first aspect of the invention and in any technically sensible combination of its embodiments, where the formulation is a paint formulation, a cement formulation or a concrete formulation.

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In a third aspect of the invention, there is provided a process of making a microcapsule encapsulating a phase change material as defined in the first aspect of the invention and in any technically sensible combination of its embodiments, comprising the steps of:

20 (a) providing an aqueous emulsion comprising a first organic material that is water-immiscible, a phase change material and a surfactant;

(b) adding a second organic material to the aqueous emulsion to form polymeric pre-microcapsules having a core comprising the phase change material and an organic polymeric shell, through the reaction of the first and second organic materials together in a polymerisation reaction; and

25 (c) adding an inorganic monomeric material to the polymeric pre-microcapsules to form an inorganic shell around each polymeric pre-microcapsules under conditions that cause polymerisation of the inorganic monomeric material to provide a microcapsule encapsulating a phase change material, wherein:

30 the conditions of step (c) cause self-assembly of the inorganic shell on the organic polymeric shell due to attractive electrostatic interactions between the organic polymeric shell and the inorganic monomeric material; and

the phase change material undergoes a phase change at from 0°C to 200°C.

In embodiments of the third aspect of the invention:

35 (a) the surfactant may be a non-ionic surfactant (e.g. the non-ionic surfactant may be selected from one or more of the group consisting of arabic gum polyethylene oxide

lauryl ether 30, sorbitan oleate, sorbitan 80, and polyoxyethylene sorbitol Yu monooleate 80 mixture);

(b) the phase change material may undergo a phase change at from 5°C to 150°C;

5 (c) the phase change material may be an organic material (e.g. the organic material may be a C₁₄-C₄₅ paraffinic hydrocarbon (e.g. a C₁₄, C₁₈, C₂₂-C₄₅ paraffinic hydrocarbon, such as octadecane);

(d) the first and second organic materials, following reaction together, provide an organic polymeric material comprising functional groups that are cationic in aqueous media
10 optionally wherein the functional groups are cationic at a pH of from 2.0 to 5.0, such as from 2.5 to 4.0, such as 3.0 (e.g. the first organic material may be an organic diisocyanate and the second organic material may be a polyimine (e.g. the first organic material may be an hexamethylene diisocyanate and the second organic material may be a polyethyienimine, optionally wherein the weight average molecular weight of the polyethyienimine may be from
15 800 Daltons to 3,000 Daltons, such as from 1,000 Daltons to 2,000 Daltons, such as 1,300 Daltons));

(e) the inorganic monomeric material may be a silica precursor (e.g. Si(OH)₄ monomer);

(f) the microcapsule provided in step (c) of the third aspect of the invention may
20 have an average size of from 50 to 500 µm, such as from 75 to 450 µm, 100 to 400 µm;

(g) the organic polymeric shell may have a thickness of from 75 to 250 nm (e.g. from 100 to 200 nm);

(h) the inorganic shell comprises spheres of the polymerised inorganic monomeric material having a diameter of from 100 to 500 nm (e.g. from 150 to 450 nm);

25 (i) the phase change material comprises from 60 to 85 wt% of the microcapsule (e.g. from 65 to 80 wt%, such as 75 wt% of the microcapsule);

(j) in step (a) of the third aspect of the invention, the aqueous emulsion comprising a first organic material that is water-immiscible, a phase change material and a surfactant may be provided by:

30 (i) providing an aqueous solution of a surfactant under stirring at a stirring speed of from 200 to 4000 RPM (e.g. from 400 to 2000 RPM, such as from 600 to 2000 RPM); and

(ii) providing a mixture of the first organic material and the phase change material and adding it to the stirred aqueous solution of the surfactant, optionally
35 wherein step (ii) may be conducted at a temperature of from 30 to 60 °C, such as 50 °C;

(k) step (b) of the third aspect of the invention may be conducted at a temperature of from 30 to 60 °C, such as 50 °C;

(l) step (c) of the third aspect of the invention may be conducted at a pH of from 2.0 to 5.0, such as from 2.5 to 4.0, such as 3.0;

5 (m) step (c) of the third aspect of the invention may be conducted at a pH of from 2.0 to 5.0, such as from 2.5 to 4.0, such as 3.0;

(n) before step (a), the phase change material may be mixed with carbon nanotubes and the pre-mixed material used as the phase change material.

10 Further aspects and embodiments of the invention are described in the numbered clauses below.

1. A MEPCM microcapsule comprising

- 15 a. a core material made of phase change materials such as octadecane, or more specifically, paraffin;
- b. an intermediate shell made of polymer such as polyurea; and
- c. an outer shell made of inorganic SiO₂.

2. A method of synthesizing a MEPCM microcapsule of (1), comprising the steps of:

- 20 a. producing an oil-in-water emulsion system by dispersing a water immiscible material into an aqueous continuous phase with the assistance of a surfactant;
- b. adding a target core material into a discontinuous phase;
- c. adding reactants that form a microcapsule wall into the aqueous phase such that a polymerization reaction takes place between the reactants, forming a polymer wall
- 25 at the interface between the aqueous and organic phases, with core material being encapsulated; and
- d. permitting electrostatic forces between opposite charged molecules i.e. different charge among reaction molecules, positive charge and negative charge molecules
- 30 to attract each other together via electrostatic force to form a new shell covering on the existing capsules, where

it is noted that steps 2a-2c above relate to interfacial polymerization, while step 2d relates to an electrostatic force process.

35 3. A paint for outdoor structures such as buildings, having the microcapsules of (1) distributed throughout the paint matrix, such that the temperature of the structure which is painted, is regulated.

4. A method for making a paint for outdoor structures such as buildings, by dispersing the microcapsules of (1) evenly throughout the paint matrix.

5 Drawings

Figs. 1(a) shows a typical scanning electron microscopy (SEM) image of shell thickness and diameter of an individual capsule prepared in this invention, in this case a microcapsule of Example 2; Fig. 1(b) shows typical SEM images of prepared microcapsules (also of Example 2) - by facilely adjusting specific parameters (e.g. stirring speed) it is possible to fabricate microcapsules having a desired size and shell thickness according to the practical requirement. The white bar represents 100 μm in Figs. 1(a) and 1(b).

The image in Fig. 2(a) shows a SEM image of an individual microcapsule cross section of Example 2, where the white bar represents 10 μm . Fig. 2(b) shows a magnified portion of Fig. 2(a) providing more detail of the shell cross-section, where the white bar represents 10 μm . Fig. 2(c) shows a magnified portion of Fig. 2(b) at the interface of the inner polymer and outer silica shells, where the white bar represents 100 nm. Fig. 2(d) shows a magnified portion of Fig. 2(b), providing a magnified image of the outer silica shell, where the white bar represents 100 nm. Fig. 2(e) shows a magnified portion of Fig. 2(b), providing a magnified image of the inner polymer shell, where the white bar represents 1 μm .

Fig. 3 is a graph showing the diameter distribution of silica-octadecane capsules under various agitation rates for Examples 1 to 3.

Fig. 4 is the DSC curves of the durability testing for silica MEPCMs obtained from Example 2.

Fig. 5 is a SEM image taken after the 150 heating-cooling cycles.

Fig. 6 depicts the morphology of silica-octadecane/CNTs capsules by SEM: (a) overview of capsules; (b) individual capsule; (c) cross section of individual capsule; and (d) magnification of CNTs in the core.

Fig. 7 is a comparison DSC curves of silica-octadecane/CNTs capsules and silica-octadecne capsules (as a control sample).

Fig. 8 is a schematic depiction of the test apparatus used to test the thermal insulation provided by silica-octadecane microcapsules in a modified cement board.

Fig. 9 depicts experimental curves of the top surface temperature (Top-) and bottom surface temperature (Bottom-) for cement boards having a different wt% content of the microcapsules of the current invention and the internal temperature of the thermally insulated box (Box-) under 800W/m^2 irradiation for 15 min: (a) C-10-5wt%, (b) C-10-15wt% and (c) C-10-25wt%, respectively, with each being compared to data generated under the same conditions by a control sample C-10, while (d) depicts the average peak temperature of different positions (top, bottom and inside box) of C-10, C-10-5wt%, C-10-15wt% and C-10-25wt%, respectively.

Description

This invention develops a facile way for encapsulation of different types of PCMs, including but not limited to paraffin, where the range of melting temperature starts from 0°C to 200°C (e.g. 5°C to 150°C). Therefore, these MEPCMs can be applied to different fields due to the wide operating temperature range of the encapsulated PCMs. This process involves encapsulating a PCM, as the core material, into silica shell microcapsules *via* an *interfacial* polymerization reaction to form an organic polymeric shell and subsequently an electrostatic force in an oil-in-water emulsion system to form an inorganic shell on the organic polymeric shell. The microcapsules are designed to increase thermal conductivity and durability. Also the inorganic shell (e.g. an inorganic silica shell) can be used to increase the specific thermal conductivity as well as mechanical properties of the microcapsules. As a non-limiting example application, cool paint coatings may be manufactured by dispersing the PCM-filled microcapsules into commercial paint coatings, and the resulting cool-paint coatings display good temperature-adjusting performance.

In order to overcome the problems mentioned above, a dual shell structure was developed in this invention comprising an outer shell of an inorganic material and an inner shell of an organic polymeric material (e.g. a silica-polyurea dual shell structure) to encapsulate a PCM. Thus, there is disclosed a microcapsule encapsulating a phase change material comprising a core encapsulated by a first shell and a second shell, where the first shell is sandwiched between the second shell and the core, wherein the core comprises a phase change material that undergoes a phase change at from 0°C to 200°C ; the first shell is an organic polymeric material; and the second shell is an inorganic material.

PCMs that can be used herein include various organic and inorganic substances. Examples of PCMs include, but are not limited to, hydrocarbons (e.g., straight-chain alkanes or paraffinic hydrocarbons, branched-chain alkanes, unsaturated hydrocarbons, halogenated hydrocarbons, and alicyclic hydrocarbons), hydrated salts (e.g., calcium chloride hexahydrate, calcium bromide hexahydrate, magnesium nitrate hexahydrate, lithium nitrate trihydrate, potassium fluoride tetrahydrate, ammonium alum, magnesium chloride hexahydrate, sodium carbonate decahydrate, disodium phosphate dodecahydrate, sodium sulfate decahydrate, and sodium acetate trihydrate), waxes, oils, water, fatty acids, fatty acid esters, dibasic acids, dibasic esters, 1-halides, primary alcohols, secondary alcohols, tertiary alcohols, aromatic compounds, clathrates, semi-clathrates, gas clathrates, anhydrides (e.g., stearic anhydride), ethylene carbonate, methyl esters, polyhydric alcohols (e.g., 2,2-dimethyl-1,3-propanediol, 2-hydroxymethyl-2-methyl-1,3-propanediol, ethylene glycol, polyethylene glycol, pentaerythritol, dipentaerythritol, pentaglycerine, tetramethylol ethane, neopentyl glycol, tetramethylol propane, 2-amino-2-methyl-1,3-propanediol, monoaminopentaerythritol, diaminopentaerythritol, and tris(hydroxymethyl)acetic acid), sugar alcohols (erythritol, D-mannitol, galactitol, xylitol, D-sorbitol), polymers (e.g., polyethylene, polyethylene glycol, polyethylene oxide, polypropylene, polypropylene glycol, polytetramethylene glycol, polypropylene malonate, polyneopentyl glycol sebacate, polypentane glutarate, polyvinyl myristate, polyvinyl stearate, polyvinyl laurate, polyhexadecyl methacrylate, polyoctadecyl methacrylate, polyesters produced by polycondensation of glycols (or their derivatives) with diacids (or their derivatives), and copolymers, such as polyacrylate or poly(meth)acrylate with alkyl hydrocarbon side chain or with polyethylene glycol side chain and copolymers including polyethylene, polyethylene glycol, polyethylene oxide, polypropylene, polypropylene glycol, or polytetramethylene glycol), metals, and mixtures thereof.

The selection of a PCM is typically dependent upon the transition temperature that is desired for a particular application that is going to include the PCM. The transition temperature is the temperature or range of temperatures at which the PCM experiences a phase change from solid to liquid or liquid to solid. For example, a PCM having a transition temperature near room temperature or normal body temperature can be desirable for clothing applications. A phase change material according to some embodiments of the invention can have a transition temperature in the range of about 0° C. to about 200°C. In other embodiments of the invention, the transition temperature may be from 5°C to 150°C, such as from 15°C to 100° C or from 30° C to 75° C.

Paraffinic PCMs may be a paraffinic hydrocarbon, that is, hydrocarbons represented by the formula C_nH_{n+2} , where n can range from about 10 to about 46 carbon atoms, such as from 14 to 45 carbon atoms. PCMs useful in the invention include paraffinic hydrocarbons having 13 to 28 carbon atoms. Specific paraffinic hydrocarbons that may be used in embodiments of the invention are listed below in Table 1, along with their melting point.

Compound Name	Number of Carbon Atoms	Melting Point (° C.)
n-Octacosane	28	61.4
n-Heptacosane	27	59.0
n-Hexacosane	26	56.4
n-Pentacosane	25	53.7
n-Tetracosane	24	50.9
n-Tricosane	23	47.6
n-Docosane	22	44.4
n-Heneicosane	21	40.5
n-Eicosane	20	36.8
n-Nonadecane	19	32.1
n-Octadecane	18	28.2
n-Heptadecane	17	22.0
n-Hexadecane	16	18.2
n-Pentadecane	15	10.0
n-Tetradecane	14	5.9

Table 1

Methyl ester PCMs may be any methyl ester that has the capability of absorbing or releasing thermal energy to reduce or eliminate heat flow within a temperature stabilizing range.

Examples of methyl esters that may be suitable for use in embodiments of the current invention, includes, but is not limited to methyl palmitate methyl formate, methyl esters of fatty acids such as methyl caprylate, methyl caprate, methyl laurate, methyl myristate, methyl palmitate, methyl stearate, methyl arachidate, methyl behenate, methyl lignocerate and fatty acids such as caproic acid, caprylic acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, lignoceric acid and cerotic acid; and fatty acid alcohols such as capryl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, arachidyl alcohol, behenyl alcohol, lignoceryl alcohol, ceryl alcohol, montanyl alcohol, myricyl alcohol, and geddyl alcohol.

In embodiments of the invention mentioned herein, the phase change material may be an organic material. In particular embodiments that may be mentioned herein the PCM may be a Paraffinic PCM, such as octadecane. The PCM may comprises from 60 to 85 wt% of the entire weight of the microcapsule (e.g. from 65 to 80 wt%, such as 75 wt% of the microcapsule).

Paraffin is (or paraffinic hydrocarbons are) a low price commercial product that has high latent heat potential organic phase change material. Therefore, its use in this invention can enable the fabrication of the microencapsulated PCMs to be reasonably and easily scaled up.

As mentioned herein, the core of the microcapsules may further comprise/contain carbon nanotubes in addition to the phase change material. Advantages associated with the inclusion of carbon nanotubes into the core may include yet greater mechanical stability and a reduction in the hysteresis phenomenon typically experienced with phase change materials. This is discussed in more detail in the Examples section.

As mentioned herein, the microcapsule shells are formed from a unique dual-shell structure that is strong and flexible, where the inner shell (i.e. first shell) is formed from an organic polymeric material and the outer shell (i.e. second shell) is formed from an inorganic material.

In particular embodiments of the invention, the first shell may be formed from an organic polymeric material that comprises functional groups that are cationic in aqueous media. When used herein the term "functional groups that are cationic in aqueous media" refers to a functional group in an organic molecule that may carry a positive charge over a range of pH values when in an aqueous environment (e.g. from pH 1.0 to pH 10.0, such as from pH 1.5 to pH 8.0 or from pH 2.0 to pH 7.0, such as from pH 2.5 to 4.0, such as 3.0). The first shell may have a thickness of from 75 to 250 nm (e.g. from 100 to 200 nm).

Suitable organic polymeric materials comprises functional groups that are cationic in aqueous media include but are not limited to polyurea, gelatine, chitosan, polyethylenimine, poly(L-lysine), polyamidoamine, poly(amino-co-ester)s, and poly[2-(N,N-dimethylamino)ethyl methacrylate]. A particular organic polymeric material that may be mentioned herein may be a polyurea, for example a polyurea formed from a polyimine and an organic diisocyanate. In certain embodiments of the invention, the polyurea may be formed by the reaction between hexamethylene diisocyanate and polyethyienimine. In such embodiments, the weight

average molecular weight of the polyethylenimine may be from 800 Daltons to 3,000 Daltons, such as from 1,000 Daltons to 2,000 Daltons, such as 1,300 Daltons.

In particular embodiments of the invention, the second shell may be formed from silica. The second shell may be formed from spheres of the inorganic material having a diameter of from 100 to 500 nm (e.g. from 150 to 450 nm).

The microcapsules mentioned herein may have an average size (e.g. diameter) ranging from 50 μm to 500 μm , such as from 75 μm to 450 μm , 100 to 400 μm .

Unless otherwise stated the sizes, thicknesses and diameters mentioned herein may be measured using ImageJ software based upon a suitable image of the microcapsule, such as a scanning electron microscope image.

In an embodiment of the invention, the dual-shell structure of the microcapsule may be a silica-polyurea dual shell capsule. These are strong and flexible due to the dual shell structure, and they can retain their structural integrity and prevent leakage when subjected to an external force or phase change process, i.e. from solid to liquid or liquid to solid. The thickness of the polyurea membrane of the dual structure is thin enough (about 100-200 nm, as shown in Fig. 2(c) that the polyurea membrane appears almost to have no influence on the heat transfer to the PCM material through the shells of the microcapsule, but this membrane provides strength and flexibility to the microcapsule, as well as playing an important role in promoting the formation of the silica shell.

The microcapsules described herein may be used to produce temperature-adjusting coatings. The invented PCMs-based temperature-adjusting coatings possess a number of advantages over existing temperature-adjusting coatings. The resulting PCMs-based temperature-adjusting coatings possess a number of advantages over existing temperature-adjusting coatings. First of all, as shown by DSC characterization (see Example 4), the MEPCMs capsules of the current invention are shown to have significant durability, robustness and have notable impermeability, this may in part be due to the microparticles of the current invention having a compact shell structure as shown in Fig. 2. As discussed in Example 4, comparing the first heating-cooling cycle to the 150th heating-cooling cycle does not show any significant variation. Hence, the enthalpy (energy storage capacity) of the microcapsules remains constant, which demonstrates that the silica-MEPCMs capsules can be subjected to hundreds of heating and cooling cycles and still provide excellent results and long-term durability. Thus, the microcapsules disclosed herein perform more stably and

reliably than other reported microcapsules, which tend to start to leak after a short period of time. In addition, these advantages minimize the impact of the introduction of extra materials to the host matrix (such as paint, cement or concrete), and from another aspect saves energy, which is of considerable economic importance. Therefore, these MEPCMs can be applied to a range of different fields due to the wide operating temperature range achievable for these PCMs, while still retaining their durability and integrity.

Secondly, considering the polymer shell is flammable and easily broken, inorganic silica-based capsules are nominated, where such a special stable property of silica-based capsules will serve to prevent the PCM liquid from spilling out of capsules due to the high compactness of silica shell, and providing a firm *container* for further long-term performance. Thirdly, the raw materials used to manufacture the PCMs are commercially available and hence the preparation of temperature-adjusting coatings is convenient and time efficient. Fourthly, the properties of the microparticles make it easy to manufacture facilely.

The microcapsules disclosed herein are designed to increase the thermal conductivity and durability. Also disclosed herein is a PCM that utilizes an inorganic silica shell to increase the specific thermal conductivity as well as mechanical properties of the microparticles. As a non-limiting example of an application, cool paint coatings can be manufactured by dispersing the PCM-filled microcapsules into a commercial paint coating, and the resulting cool-paint coating displays good temperature-adjusting performance. Thus, there is also disclosed a paint formulation comprising a microcapsule encapsulating a phase change material as disclosed hereinbefore.

Furthermore, in order to benefit from the temperature-adjusting capacity of the PCM-encapsulated microcapsules disclosed herein, the microcapsule based phase change material may be distributed (e.g. randomly dispersed) throughout a host commercial paint matrix, and this can be applied (e.g. by brushing) the resulting mixed function paint onto the wall of a building. During daytime, the function of capsules in the coating is triggered, such that the PCM absorbs the heat and the core-material PCM phase status changes from solid to liquid, thereby inhibiting heat transfer, which would otherwise have gone through the wall into the interior of the building resulting in an increase in temperature. At night, when the ambient temperature reduces gradually, the PCM phase status changes from liquid to solid, and hence, heat will be released to the surroundings, including into the interior of the building.

Therefore, the MEPCMs capsules act as a smart temperature adjusting material due to its reversible phase change function and durability. That is, during the phase change period, the inorganic silica capsule shell acts as a robust container and protects the PCMs from leaking out and so maintains the whole constant enthalpy of the microcapsules. As will be appreciated, the currently disclosed microcapsules also allow controllable efficiency of thermal conductivity by adjusting the core-shell ratio and shell thickness. Thus, the microcapsules described herein can be randomly dispersed in paint, wet cement and wet concrete in order to yield cool-paint coatings, cement and concrete, which can be used for adjusting and/or controlling the temperature of a building in a cost-effective and durable manner.

When used herein, "formulation" may be used to refer to a product in a state with or without a solvent present. For example, when applied to a "paint formulation", the formulation covers a paint formulation containing a solvent to enable it to be applied to, for example, a wall, but it also covers the dried formulation following application to said wall. The same hold true for other formulations mentioned herein, such as cement formulations and concrete formulations.

Also disclosed herein is a method that provides a facile way for encapsulating different types of PCMs, including but not limited to paraffinic hydrocarbons as discussed herein before (e.g. octadecane), where the range of melting temperature of the PCM may range from 0 °C to 200°C (e.g. from 5 °C to 150°C). This method is a process of making a microcapsule encapsulating a phase change material as defined hereinbefore, comprising the steps of:

(a) providing an aqueous emulsion comprising a first organic material that is water-immiscible, a phase change material and a surfactant;

(b) adding a second organic material to the aqueous emulsion to form polymeric pre-microcapsules having a core comprising the phase change material and an organic polymeric shell, through the reaction of the first and second organic materials together in a polymerisation reaction; and

(c) adding an inorganic monomeric material to the polymeric pre-microcapsules to form an inorganic shell around each polymeric pre-microcapsules under conditions that cause polymerisation of the inorganic monomeric material to provide a microcapsule encapsulating a phase change material, wherein:

the conditions of step (c) cause self-assembly of the inorganic shell on the organic polymeric shell due to attractive electrostatic interactions between the organic polymeric shell and the inorganic monomeric material; and

the phase change material undergoes a phase change at from 0°C to 200°C.

Thus, the process enables a specific PCM (from those described hereinbefore), as the core material, to be encapsulated into a dual shell microparticle *via* an interfacial polymerization reaction and electrostatic force in an oil-in-water emulsion system. The outer shell is inorganic (e.g. silica), while the inner shell is made from an organic polymeric material as described hereinbefore. During the formation of the microcapsule, the organic polymeric material may be cationic and the inorganic material may be anionic (or *vice versa*), which enables that electrostatic force between oppositely charged molecules to play an important role in the formation of the capsule shell. That is, the positively charged and negatively charged molecules in the reaction mixture are attracted to one another *via* electrostatic force to form a new shell covering the existing inner organic polymeric capsule.

Without wishing to be bound by theory, it is believed that the formation of the oil-in-water emulsion system affects the ultimate size of the microcapsules obtained, as the stirring/agitation of the emulsion plays a role in determining the size of the emulsion droplets (a core of PCM surrounded by the first organic material). This can be inferred from the worked examples provided hereinbelow. Given this, the aqueous emulsion comprising a first organic material that is water-immiscible, a phase change material and a surfactant may be provided by:

- (i) providing an aqueous solution of a surfactant under stirring at a stirring speed of from 200 to 4000 RPM (e.g. from 400 to 2000 RPM, such as 600 to 2000 RPM); and
- (ii) providing a mixture of the first organic material and the phase change material and adding it to the stirred aqueous solution of the surfactant to form an emulsion.

These agitation conditions may also provide the organic polymeric shell with a thickness of from 75 to 250 nm (e.g. from 100 to 200 nm). For example, when the pre-microcapsule is formed in step (b) by a polyurea formed from hexamethylene diisocyanate and polyethylenimine with a weight average molecular weight of 1,300 Daltons, a speed of 600 RPM in the process of steps (i) and (ii) corresponds to the eventual production of microcapsules having an average size of 500 μm , a speed of 1,200 RPM in steps (i) and (ii) corresponds to the eventual production of microcapsules having an average size of 100 μm , and a speed of 2,000 RPM in steps (i) and (ii) corresponds to the eventual production of microcapsules having an average size of 50 μm .

It will be appreciated that step (ii) may be conducted at ambient temperature, but may also be conducted at an elevated temperature, such as a temperature suitable for causing a polymerisation required in step (b). For example, step (ii) may be conducted at a

temperature of from 30 to 60 °C, such as 50 °C. Alternatively, step (ii) may be conducted at ambient temperature and the resulting emulsion may then be heated up to a suitable temperature to enable the reaction required in step (b) to be conducted (e.g. 30 to 60 °C, such as 50 °C).

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The phase change material may comprise from 60 to 85 wt% of the finally-produced microcapsule by weight (e.g. from 65 to 80 wt%, such as 75 wt% of the microcapsule). When carbon nanotubes are used in conjunction with the phase change material, they may constitute from 0.01 to 0.05 wt% (e.g. 0.025 wt%) of the total amount of phase change material present in the capsules. In other words, when present, carbon nanotubes are counted as part of the weight of the phase change material and so constitute from 0.006 to 0.0425 wt% of the finally-produced microcapsule by weight.

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A suitable surfactant that may be mentioned herein for use in the process described above may be a non-ionic surfactant. Suitable non-ionic surfactants that may be mentioned in embodiments of the invention include, but are not limited to, arabic gum polyethylene oxide lauryl ether 30, sorbitan oleate, sorbitan 80, and polyoxyethylene sorbitol Yu monooleate 80 mixture and combinations thereof. The non-ionic surfactant may act as an emulsifying agent.

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The first and second organic materials mentioned in the process above may react together to provide an organic polymeric material comprising functional groups that are cationic in aqueous media. The functional groups may be cationic at a pH as described hereinbefore (e.g. they may be cationic at a pH of from 2.0 to 5.0, such as from 2.5 to 4.0, such as 3.0). The first organic material may be an organic diisocyanate and the second organic material may be a polyimine that react together to provide a polyurea. For example, the first organic material may be an hexamethylene diisocyanate and the second organic material may be a polyethylenimine (e.g. the weight average molecular weight of the polyethylenimine is from 800 Daltons to 3,000 Daltons, such as from 1,000 Daltons to 2,000 Daltons, such as 1,300 Daltons).

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In embodiments of the invention that may be mentioned herein, the inorganic monomeric material may be a silica precursor, such as $\text{Si}(\text{OH})_4$ monomer, which may be prepared by hydrolysis of a silica ester (e.g. trimethoxymethylsilane).

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Under the process described herein, the inorganic shell that is deposited may comprise spheres of the polymerised inorganic monomeric material having a diameter of from 100 to

500 nm (e.g. from 150 to 450 nm). The polymerised inorganic monomeric material may be silica.

The average size (i.e. diameter) of the microcapsules provided in step (c) of the process above may be from 50 to 500 μm , such as from 75 to 450 μm , 100 to 400 μm .

In a specific embodiment of the process described hereinbefore, microencapsulation of paraffinic hydrocarbons (and other PCMs) can be realized through an interfacial polymerization reaction between Hexamethylene diisocyanate (HDI), Polyethylenimine (PEI) (to form a polyurea) and then a subsequent electrostatic force attraction between the polyurea and a pre-hydrolyzed silicate ester (i.e. monomeric $\text{Si}(\text{OH})_4$). This may be accomplished by the formation of a surfactant solution (e.g. using an arabic gum aqueous solution) under mechanical agitation at ambient temperature. To this pH-adjusted (and stirred) solution is slowly added in a drop-wise manner an organic solution formed by mixing paraffin (i.e. a paraffinic hydrocarbon) with HDI to form an organic solution. The addition of the organic solution to the pH-adjusted solution develops an oil-in-water emulsion solution. The emulsion system can then be heated to a set temperature and the polymerization reaction can then be initiated by the addition of PEI. After stabilization of the polymer, pre-hydrolyzed silicate ester solution can be added, and its pH value is adjusted by addition of HCl solution to a set value (e.g. from pH 2.0 to pH 5.0, such as pH 3.0). Finally, the system is returned to room temperature to initiate the condensation reaction of pre-hydrolyzed silicate ester based on electrostatic force. The reaction is stopped after a set period of time, and the resultant microcapsules are washed, filtered using deionized water and dried for further analysis and application.

In this embodiment, the yield of the microencapsulation process is around 60 wt%, and the core content in the microcapsules is approximately 75 wt%. The resultant microcapsules have an average diameter of 50 – 500 μm , depending on the particular reaction conditions used for the preparation. The average diameter of prepared microcapsules is greatly influenced by reaction conditions such as agitation rate.

In certain embodiments, the core of the formed microcapsules may contain both a phase change material and carbon nanotubes. When present, carbon nanotubes may be pre-mixed with the phase change material in a manner to ensure that they are uniformly dispersed within said phase change material before the process outlined above is begun. This may be accomplished in the manner discussed in more detail below in the examples.

This invention discloses a method to facilely encapsulate phase change materials (PCMs) into silica-based microcapsules *via* an interfacial polymerization reaction and electrostatic force in an oil-in-water emulsion. The microcapsules can be incorporated into any matrix materials that the microcapsules can be dispersed, so this invention can be used to manufacture a broad range of materials that possess temperature-adjusting function. Specifically, this invention may also be applied to the formation of materials for energy saving applications.

In order that the invention may be readily understood and put into practical effect, particular embodiments will now be described by way of the following non-limiting examples.

Examples

Methods

Images were captured using a scanning electron microscope. The average size of the microcapsules was obtained through measuring the SEM images of the microcapsules by using ImageJ software.

Materials

Arabic gum, hexamethylene diisocyanate (HDI), polyethyienimine (PEI, $M_w \sim 1300$), octadecane, trimethoxymethylsilane (MTTS) and hydrochloric acid solution (HCl, 0.1N) were purchased from Sigma Aldrich (Singapore). Aqueous solution of pH=3.0 was prepared using HCl solution. All chemicals were used directly without further purification.

Example 1

At ambient temperature, 30 ml of deionized water and 0.93 g of a 3 wt% aqueous solution of arabic gum were mixed in a 500 ml beaker. The beaker was suspended in a temperature-controlled water bath on a programmable hot plate with an external temperature probe. The solution was agitated with a digital mixer (Caframo) driving a three-bladed propeller at 600 RPM. The mixture was heated to 50 °C at a heating rate of 5 °C/min. After 50 °C was reached, 5g octadecane (a type of PCM) and 1g hexamethylene diisocyanate (HDI) were then slowly added into the above aqueous solution to generate an emulsion. After 10 min of emulsification, 10 g of a 1 wt% aqueous solution of polyethyienimine (average M_n : 1200, average M_w : 1300) was added drop wise into the emulsion and the reaction was agitated at 150 RPM for 2 hours at 50 °C. Subsequently, both the stirrer and hot plate were switched off

and the resultant pre-microcapsules were washed with deionized water three times (about 100 ml each time) using a separating funnel. After washing, the treated pre-microcapsules were re-dispersed into a 500ml beaker which was loaded with 30ml of a prepared pH=3 aqueous HCl solution.

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At the same time, the pre-hydrolysed trimethoxymethylsilane (MTTS) was prepared as follows. MTTS (2g) and HCl solution (pH=3; 4g) were mixed together and suspended in a water bath, the mixture was then heated to 35 °C at a heating rate of 5 °C/min. After reaching 35 °C, the reaction was continued for 1h at 35 °C under agitation at 700 RPM and provided a transparent solution containing $\text{Si}(\text{OH})_4$ monomer for further use.

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Subsequently, the pre-hydrolyzed MTTS was slowly added into the pre-microcapsules solution. Based on electrostatic force, monomeric $\text{Si}(\text{OH})_4$ deposited onto the surface of the oil droplets to further form a Si-O-Si (silica) net structure shell following agitation of the reaction mixture at 150 RPM for 24 hours. Ultimately, the resultant microcapsules with diameter of about 500 μm were washed with deionized water three times (about 100 ml each time) and collected for air-drying at room temperature in fume hood for 24 hours before further analysis.

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20 Example 2

At ambient temperature, 30 ml of deionized water and 0.93 g of a 3 wt% aqueous solution of arabic gum were mixed in a 500 ml beaker. The beaker was suspended in a temperature-controlled water bath on a programmable hot plate with an external temperature probe. The solution was agitated with a digital mixer (Caframo) driving a three-bladed propeller. Under agitation at 1200 RPM, the mixture was heated to 50 °C at a heating rate of 5 °C/min. Once 50 °C was attained, 5g octadecane (a type of PCM) and 1g hexamethylene diisocyanate (HDI) were then slowly added into the above aqueous solution to generate an emulsion. After 10 min of emulsification, 10 g of a 1 wt% aqueous solution of polyethylenimine (average M_n : 1200, average M_w : 1300) was added drop wise into the emulsion solution. Under agitation at 150 RPM, the reaction was continued for 2 hours at 50 °C. Subsequently, both the stirrer and hot plate were switched off and the resultant pre-microcapsules were washed with deionized water three times (about 100 ml each time) by using a separating funnel. The washed and treated pre-microcapsules were then re-dispersed in 500ml beaker which was loaded with 30ml of a pre-prepared HCl solution (pH=3 , as measured by a pH meter).

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At the same time, the pre-hydrolysed trimethoxymethylsilane (MTTS) was prepared as follows. MTTS (2g) and HCl solution (pH=3; 4g) were mixed together and suspended in a water bath, the mixture was then heated to 35 °C at a heating rate of 5 °C/min. After reaching 35 °C, the reaction was continued for 1h at 35°C under agitation at 700 RPM and provided a transparent solution containing Si(OH)_4 monomer for further use.

Subsequently, the pre-hydrolyzed MTTS was slowly added into the pre-microcapsules solution. Based on electrostatic force, monomeric Si(OH)_4 deposited onto the surface of the oil droplets to further form a Si-O-Si (silica) net structure shell following agitation of the reaction mixture at 200 RPM for 24 hours. Ultimately, the resultant microcapsules with diameter of about 100 μm were washed with deionized water three times (about 100 ml each time) and collected for air-drying at room temperature in fume hood for 24 hours before further analysis.

Fig. 1 shows the individual and overview microcapsules of Example 2. As can be seen in Fig. 1a, a well-defined microcapsule with a hierarchical structure of the surface was obtained. In addition, the diameter of the capsules is uniform as shown in Fig. 1b.

Fig. 2 shows the detailed structure of a capsule shell of Example 2, in which, Figs. 2(a)-(c) show the shell structure at different magnifications, with the silica-PU dual shell structure clearly visible in Fig. 2(c). Figs. 2(d)-(e) show the high magnification images of the outer and inner shell of an individual silica MEPCMs capsule, and they clearly demonstrate that both sides are dense and compact. From Fig. 2(d), it can be seen that a large quantity of nano-silica particles contact tightly. Fig. 2(e) shows the structure of the inner capsule shell.

A silica-PU dual shell structure can be seen clearly in Fig. 2(c), and as Fig. 2(d) shows, the outer shell is densely compact in terms of huge amount of nanometer scale silica spheres (diameter: 100~500 nm). This typical structure makes the whole capsule shell more compacted and dense to inhibit the core-PCMs from spilling out of the capsules, i.e. enhance impermeability of the microcapsules. A similar structure appears in the inner shell as shown in Fig. 2(e), where large quantities of linear columnar polymer combine together to form a tight net structure. The inorganic silica is robust, but also easily brittle material and polymer shell has a good toughness property, so the embodiments of the current invention combine these two properties in a dual-shell structure, possessing strength and toughness.

Example 3

At ambient temperature, 30 ml of deionized water and 0.93 g of a 3 wt% aqueous solution of arabic gum were mixed in a 500 ml beaker. The beaker was suspended in a temperature-controlled water bath on a programmable hot plate with an external temperature probe. The solution was agitated with a digital mixer (Caframo) driving a three-bladed propeller. Under agitation at 2000 RPM, the mixture was heated to 50 °C at a heating rate of 5 °C/min. Once 50 °C was attained, 5g octadecane (a type of PCM) and 1g hexamethylene diisocyanate (HDI) were then slowly added into the above aqueous solution to generate an emulsion. After 10 min of emulsification, 10 g of a 1 wt% aqueous solution of polyethylenimine (average M_n : 1200, average M_w : 1300) was added drop wise into the emulsion solution. Under agitation at 150 RPM, the reaction was continued for 2 hours at 50 °C. Subsequently, both the stirrer and hot plate were switched off and the resultant pre-microcapsules were washed with deionized water three times (about 100 ml each time) by using a separating funnel. The washed and treated pre-microcapsules were then re-dispersed in 500ml beaker which was loaded with 30ml of a pre-prepared HCl solution (pH=3 , as measured by a pH meter).

At the same time, the pre-hydrolysed trimethoxymethylsilane (MTTS) was prepared as follows. MTTS (2g) and HCl solution (pH=3; 4g) were mixed together and suspended in a water bath, the mixture was then heated to 35 °C at a heating rate of 5 °C/min. After reaching 35 °C, the reaction was continued for 1h at 35 °C under agitation at 700 RPM and provided a transparent solution containing $\text{Si}(\text{OH})_4$ monomer for further use.

Subsequently, the pre-hydrolyzed MTTS was slowly added into the pre-microcapsules solution. Based on electrostatic force, monomeric $\text{Si}(\text{OH})_4$ deposited onto the surface of the oil droplets to further form a Si-O-Si (silica) net structure shell following agitation of the reaction mixture at 300 RPM for 24 hours. Ultimately, the resultant microcapsules with diameter of about 50 μm were washed with deionized water three times (about 100 ml each time) and collected for air-drying at room temperature in fume hood for 24 hours before further analysis.

Agitation results for Examples 1 to 3

In order to study the effect of agitation rate on the microcapsule size, three different agitation rates for the formation of the polymer shell, 600 RPM, 1200 RPM and 2000 RPM, were carried out as shown in Figure 3. This figure shows that the microcapsule size can be

controlled under different agitation rates and it can be concluded that the diameters of microcapsules can be effectively controlled by careful selection of the agitation rate used to form the polymeric inner shell of the microcapsules.

5 Example 4

Long-term performance assessment of MEPCMs

Following the procedures described above in Examples 1-3 (or adaptations therefrom), pure silica-based MEPCMs capsules in white powder form can be prepared. 10 mg of the
10 microcapsules was taken using a precision balance as a sample for the characterization of the durability and reliability of capsules by using Differential Scanning Calorimetry (DSC) testing, where various ramp rates were investigated ranging from 0.05 to 10°C/min.

Specifically, a DSC analysis using 150 DSC cycles at a ramp rate at 10°C/min using 10 mg
15 of silica-MEPCMs capsules was used to evaluate the durability of the microcapsules. The treated capsules may also be inspected by scanning electron microscope (SEM) to examine the structure and morphology to figure out if any change has happened comparing with the original MEPCMs capsules.

20 DSC analysis was conducted using the microcapsules of Example 2.

Fig. 4 demonstrates the long term performance of the silica MEPCMs capsules obtained in Example 2. After running 150 heating-cooling cycles, only a slight shift was observed when comparing the condition after multiple cycles to the condition after the first heating-cooling
25 cycle. This indicates the resulting silica MEPCMs capsules have notable thermal stability and anti-fatigue properties, perhaps due to the dense and well integrated capsule shells which inhibits the core-PCM from spilling out from the capsules. Furthermore, it is revealed that the thermal conductivity elevated after the first heating-cooling cycle in terms of multi cycles that shift forward to the opposite running direction. As a result, comparing each of the
30 multi cycle curves, they approximately overlapped each other, which indicated that good durability silica-MEPCMs capsules were fabricated successfully.

In addition, Fig. 5 is a SEM image taken after the 150 heating-cooling cycles and no discernable difference can be seen between the microcapsules of Fig. 5 and the
35 microcapsules of Fig. 1(b), which is an SEM image of similar scale of the microcapsules of Example 2 before exposure to 150 heating-cooling cycles.

Example 5

The PCM material may be supplemented by carbon nanotubes (CNTs). An example of this is provided below.

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General Procedure to Admix CNTs with PCM

1. A certain amount of octadecane (e.g. 5g) was heated at 50 °C for 15 min to ensure conversion to liquid phase.
- 10 2. One droplet of Span 80, as a dispersant, was added into liquid octadecane, after that, ultrasonic treatment was applied for 5 min at 50 °C;
3. A certain amount of CNTs (e.g. 0.025wt%, CNTs/PCM=0.025:1) was introduced into the mixture/solution of step 2. The mixture solution was then subjected to ultrasonic treated for 1 hour at 50 °C to provide a uniform dispersal of the CNTs in the mixture
15 solution (liquid octadecane with dispersant Span 80).

The obtained composite material (CNTs/octadecane) can be used as the core material for further fabrication of CNTs modified silica-PCM capsules by analogy to the processes of Examples 1 to 3.

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CNT-Containing Microcapsules

Silica-octadecane/CNTs capsules were synthesized successfully using the general procedure above and by analogy to the process described in Examples 1 to 3. The
25 CNTs:PCM ratio was 0.025:1.

As can be seen in Figure 6(a), which shows a selection of the resultant microcapsules, the silica-octadecane/CNTs microcapsules have a uniform diameter of about 150 μm. Figure 6(b) provides a closer view of an individual microcapsule and it can be seen that the very
30 rough outer shell is formed from nano-silica particles as is the case for the other materials described herein. Figure 6(c) verifies that the core/shell structure contains an outer shell of silica, with a polymer inner shell and an octadecane/CNTs core. As disclosed in Figure 1c the outer shell has a thickness of about 10 μm.

35 Figure 6(d) shows CNTs in the core along with octadecane. The diameter of the CNTs is about 100 nm and their length is about a few microns, which can be ascribed to the ultrasonic treatment where the CNTs cleaved into shorter lengths. In addition, as can be

seen, there is a reticular formation of CNTs mixed together with octadecane (area where the arrow points). This special structure can effectively increase the rate of heat flow of octadecane, meaning that the heat exchange rate and the temperature sensitivity can be improved due to the function of CNTs. Without wishing to be bound by theory, it is believed that the CNTs may help to transmit heat more effectively and efficiently into the octadecane in the core of the microcapsules.

Figure 7 shows DSC curves of silica-octadecane/CNTs microcapsules and silica-octadecane microcapsules (control sample). As can be seen, the DSC curve of the silica-octadecane/CNTs microcapsules was high and narrow compared to that of the control sample. This revealed that both the melting point and the solidification point of the CNT-containing core were ahead of that of the control sample. That is, the melting point was lower than that of the control sample and the solidification point was higher than that of the control sample. This remarkable function reduces the occurrence of the hysteresis phenomenon, meaning that the introduction of the CNTs appears to enable the microcapsules to more quickly track changes in the ambient temperature.

These results show that both the melting point and solidification point of the silica-octadecane/CNTs microcapsules were much closer to the ideal value of octadecane than that of the control sample. It is known that the ideal value of phase change temperature for certain applications (e.g. for buildings) is 28 °C. That is to say, the introduction of the CNTs additive remitted/reduced the hysteresis of octadecane in the phase change process.

Example 6

Preparation of Cement Board Samples

By analogy to the process described in Example 1 to 3, a 300 µm silica microcapsule having a polymer inner shell and an octadecane core was formed by using an agitation rate of 800 RPM for the step of forming the polymeric inner shell around the octadecane core.

Four portions of wet cement were formed using 200g cement and 60g H₂O were mixed together. After that, various amounts of the 300 µm silica microcapsules were added into one of the portions of the wet cement with mechanical mixing (0 wt%, 5 wt%, 15 wt% and 25 wt%) to provide a uniform dispersal of the microcapsules within the cement matrix (when the microcapsules are present). The resulting slurries were then poured into a mold (dimension: 215×85×30 mm) and vibrated gently to remove entrapped air and to achieve good

compaction. Each sample was then covered with a plastic wrap and cured at ambient temperature for 24 h before demolding. Each sample was cured in moist conditions (humidity 90 %) for another 29 days before further analysis.

5 *Thermal insulation performance of silica-octadecane capsules modified cement samples*

Figure 8 depicts a test machine 100 that was formed comprising an insulated thermal box 110 with a cradle 120 for the cement blocks 130 manufactured above and a lamp 140 (halogen 100W) set 30 cm above the block 130 when in the cradle 120, this provided a solar radiation of 800 W/m² on the top surface of the cement block 130 as measured using a solar power meter. Thermal sensors 150 were attached to the top and bottom of the cement block and to the inside of the thermally insulated box at a position set apart from the bottom of the cement block in its cradle. The sensors were attached to a computer that monitored the temperature change in real time once the lamp was switched on and continued to do so once the lamp was switched off after 15 minutes. The thermal insulation property of each of the four cement boards was then evaluated based on the resultant curves provided by the different test locations. The test conditions involved a room temperature of 25 °C, relative humidity of 55% and a pressure of 1007.00 millibar (100700 Pascals).

20 Table 1 shows the abbreviated legends used in Figure 9 for each of the samples tested in the thermal insulation test.

Legend	Description
C-10	10 mm cement board
C-10-5wt%	10 mm cement board with 5wt% 300 µm silica-octadecane capsules
C-10-15wt%	10 mm cement board with 15wt% 300 µm silica-octadecane capsules
C-10-25wt%	10 mm cement board with 25wt% 300 µm silica-octadecane capsules

Table 1

Figure 9(a) shows the temperature history curves of sample C-10-5wt%, control sample C-10 and the internal chamber (Box). For sample C-10-5wt%, the temperature difference between the top and bottom surface of C-10-5wt% was about 4 °C following 15 min of radiation, showing that a temperature gradient had been established. The maximum internal box air temperature for sample C-10-5wt% was about 28.8 °C following 15 min radiation. However, for control sample C-10, the bottom surface temperature increased linearly in line

with the top surface temperature and the temperature difference was about 3.5 °C, which was less than that of C-10-5wt%. The maximum internal air temperature in the box was 29.1 °C. Thus, even with only 5wt% of the microcapsules present in the cement, there was a slight, but significant reduction in the maximal box temperature of around 0.3 °C. This can be ascribed to the silica-octadecane capsules embedded in cement board.

Figure 9(b) shows the temperature history curves of sample C-10-15wt% against control sample C-10 and the internal chamber of the box. As shown, the bottom surface temperature of sample C-10-15wt% rose slowly under light radiation of about 14 min, the temperature was no more than 28 °C (ideal melting point of octadecane). The hysteresis time is almost equivalent to 2 times than that of the sample C-10-5wt%. However, after the bottom surface temperature reached 28 °C the bottom surface temperature increased sharply in parallel with the top surface temperature under the continuous light radiation, indicating that octadecane in the cement board melted thoroughly and that the heat storage capacity had reached saturation. Therefore, the variation of bottom surface temperature of sample C-10-15wt% was similar to that of control sample C-10. However, the temperature difference between the top and bottom surface temperatures was approximately 8 °C at 15 min of radiation and the maximal internal thermal box temperature was 27.4 °C. Compared with the maximal temperature of control sample and sample C-10-5wt%, the maximal internal box temperature was reduced by 1.7 °C and 1.4 °C, respectively. As can be seen, in the case where the other parameters remain unchanged, an increase of silica-octadecane microcapsule content can effectively reduce the internal temperature of the thermal box.

Figure 9(c) shows the temperature history curves of sample C-10-25wt% compared to the control sample C-10 and the internal chamber (Box). The bottom surface temperature of the sample C-10-15wt% was always no more than 28 °C under the light radiation of about 15 min and the hysteresis time was about 3 times than that of sample C-10-5wt%. It is important to note that the bottom surface temperature of the sample C-10-25wt% was still below 28 °C after 15 minutes of light radiation (which is when the light was turned off), while the top surface temperature was much higher than that of bottom surface (a difference of about 13 °C following 15 min of radiation). Following radiation, some of the heat flow spread to the surrounding environment as well as passing through the cement board to increase the bottom surface temperature. Hence, when the top and bottom surface temperatures reached a balance, the bottom surface's temperature did not continue to show a significant increase when the top and bottom surface temperatures overlapped at around 25 minutes in contrast to the 5 wt% and 15 wt% samples above. The maximal internal thermal box temperature was 26.5 °C for the 25 wt% sample, which is a reduction of around 2.6 °C compared to the

control sample, and this temperature difference compared to the control was the largest among these three samples.

Figure 9(d) shows the average peak temperatures of the top and bottom of the samples C-10, C-10-5wt%, C-10-15wt%, C-10-25wt% and the internal chamber for each sample. As can be seen, the temperatures of samples C-10-5wt%, C-10-15wt% and C-10-25wt% were always lower than those obtained using control sample C-10. In addition, the temperatures obtained decreased with increasing capsule content. This is ascribed to the thermal storage function of the PCM, which can effectively delay and/or mitigate the rising rate of temperature.

In summary, it was concluded that the thermal insulation performance of the capsules content 25% was the best. However, the capsule content is not the only consideration. For example, for application in buildings, the strength of the cement board should be high enough to ensure safety and to match building regulations. While not tested here, it is speculated that the strength of cement board will be probably be reduced by using a large content of cement capsules. As such, it would be important to balance the temperature efficiencies provided by the use of the microcapsules described herein against other requirements of the particular product that the microcapsules are placed in.

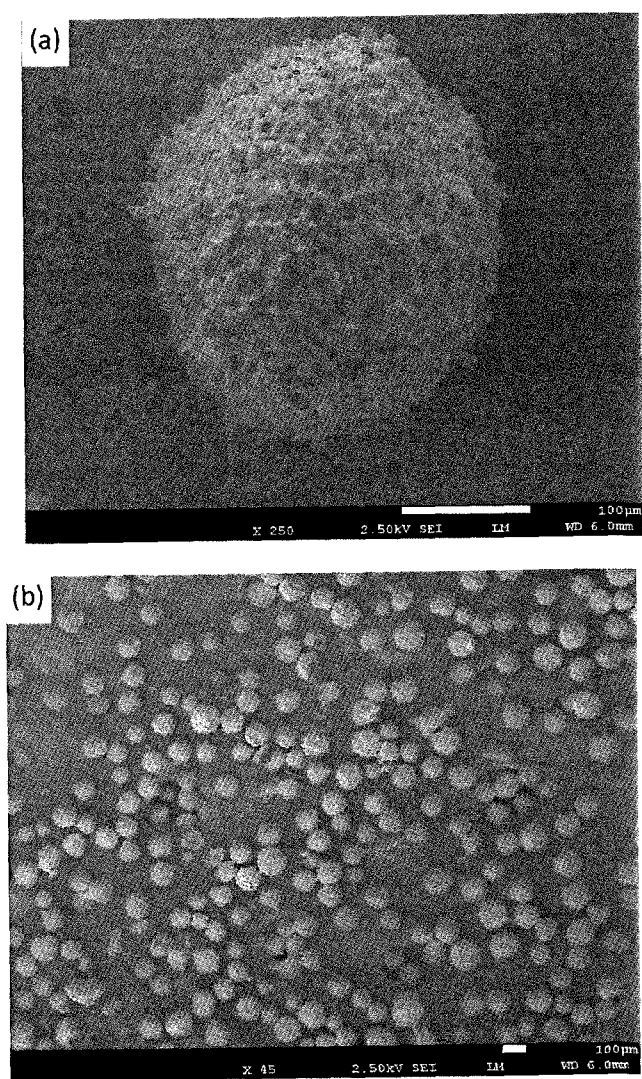
Claims

1. A microcapsule encapsulating a phase change material comprising:
a core encapsulated by a first shell and a second shell, where the first shell is sandwiched between the second shell and the core, wherein:
the core comprises a phase change material that undergoes a phase change at from 0°C to 200°C;
the first shell is an organic polymeric material; and
the second shell is an inorganic material.
2. The microcapsule of Claim 1, wherein the phase change material undergoes a phase change at from 5°C to 150°C.
3. The microcapsule of Claim 1 or Claim 2, wherein the phase change material is an organic material.
4. The microcapsule of Claim 3, wherein the organic material is a C₁₄-C₄₅ paraffinic hydrocarbon (e.g. a C₁₄, C₁₈, C₂₂-C₄₅ hydrocarbon, such as octadecane).
5. The microcapsule of any one of the preceding claims, wherein the core further comprises carbon nanotubes.
6. The microcapsule of any one of the preceding claims, wherein the organic polymeric material comprises functional groups that are cationic in aqueous media, optionally wherein the functional groups are cationic in aqueous media at a pH of from 2.0 to 5.0, such as from 2.5 to 4.0, such as 3.0.
7. The microcapsule of Claim 6, wherein the organic polymeric material comprises a polyurea (e.g. a polyurea formed from a polyimine and an organic diisocyanate).
8. The microcapsule of Claim 7, wherein the organic polymeric material comprises a polyurea formed by the reaction between hexamethylene diisocyanate and polyethylenimine, optionally wherein the weight average molecular weight of the polyethylenimine is from 800 Daltons to 3,000 Daltons, such as from 1,000 Daltons to 2,000 Daltons, such as 1,300 Daltons.

9. The microcapsule of any one of the preceding claims, wherein the inorganic material is silica.
10. The microcapsule of any one of the preceding claims, wherein the microcapsule has an average size of from 50 μm to 500 μm , such as from 75 μm to 450 μm , 100 to 400 μm .
11. The microcapsule of any one of the preceding claims, wherein the first shell has a thickness of from 75 to 250 nm (e.g. from 100 to 200 nm).
12. The microcapsule of any one of the preceding claims, wherein the second shell comprises spheres of the inorganic material having a diameter of from 100 to 500 nm (e.g. from 150 to 450 nm).
13. The microcapsule of any one of the preceding claims, wherein the core material comprises from 60 to 85 wt% of the microcapsule (e.g. from 65 to 80 wt%, such as 75 wt% of the microcapsule).
14. A formulation comprising a microcapsule encapsulating a phase change material as defined in any one of Claims 1 to 13, wherein the formulation is a paint formulation, a cement formulation or a concrete formulation.
15. A process of making a microcapsule encapsulating a phase change material as defined in any one of Claims 1 to 13, comprising the steps of:
- (a) providing an aqueous emulsion comprising a first organic material that is water-immiscible, a phase change material and a surfactant;
 - (b) adding a second organic material to the aqueous emulsion to form polymeric pre-microcapsules having a core comprising the phase change material and an organic polymeric shell, through the reaction of the first and second organic materials together in a polymerisation reaction; and
 - (c) adding an inorganic monomeric material to the polymeric pre-microcapsules to form an inorganic shell around each polymeric pre-microcapsules under conditions that cause polymerisation of the inorganic monomeric material to provide a microcapsule encapsulating a phase change material, wherein:
 - the conditions of step (c) cause self-assembly of the inorganic shell on the organic polymeric shell due to attractive electrostatic interactions between the organic polymeric shell and the inorganic monomeric material; and
 - the phase change material undergoes a phase change at from 0°C to 200°C.

16. The process of Claim 15, wherein the surfactant is a non-ionic surfactant.
17. The process of Claim 16, wherein the non-ionic surfactant is selected from one or more of the group consisting of arabic gum polyethylene oxide lauryl ether 30, sorbitan oleate, sorbitan 80, and polyoxyethylene sorbitol Yu monooleate 80 mixture.
18. The process of any one of Claims 15 to 17, wherein the phase change material undergoes a phase change at from 5°C to 150°C.
19. The process of any one of Claims 15 to 18, wherein the phase change material is an organic material.
20. The process of Claim 18, wherein the organic material is a C₁₄-C₄₅ paraffinic hydrocarbon (e.g. a C₁₄, C₁₈, C₂₂-C₄₅ paraffinic hydrocarbon, such as octadecane).
21. The process of any one of Claims 15 to 20, wherein before step (a) the phase change material is pre-mixed with carbon nanotubes.
22. The process of any one of Claims 15 to 21, wherein the first and second organic materials, following reaction together, provide an organic polymeric material comprising functional groups that are cationic in aqueous media, optionally wherein the functional groups are cationic at a pH of from 2.0 to 5.0, such as from 2.5 to 4.0, such as 3.0.
23. The process of Claim 22, wherein the first organic material is an organic diisocyanate and the second organic material is a polyimine, optionally wherein the first organic material may be an hexamethylene diisocyanate and the second organic material may be a polyethylenimine (e.g. the weight average molecular weight of the polyethylenimine is from 800 Daltons to 3,000 Daltons, such as from 1,000 Daltons to 2,000 Daltons, such as 1,300 Daltons).
24. The process of any one of Claims 15 to 23, wherein the inorganic monomeric material is a silica precursor (e.g. Si(OH)₄ monomer).
25. The process of any one of Claims 15 to 24, wherein the microcapsule provided in step (c) of Claim 14 has an average size of from 50 to 500 μm, such as from 75 to 450 μm, 100 to 400 μm.

26. The process of any one of Claims 15 to 25, wherein the organic polymeric shell has a thickness of from 75 to 250 nm (e.g. from 100 to 200 nm).
27. The process of any one of Claims 15 to 26, wherein the inorganic shell comprises spheres of the polymerised inorganic monomeric material having a diameter of from 100 to 500 nm (e.g. from 150 to 450 nm).
28. The process of any one of Claims 15 to 27, wherein the phase change material comprises from 60 to 85 wt% of the microcapsule (e.g. from 65 to 80 wt%, such as 75 wt% of the microcapsule).
29. The process of any one of Claims 15 to 28, wherein in step (a) of Claim 14, the aqueous emulsion comprising a first organic material that is water-immiscible, a phase change material and a surfactant is provided by:
- (i) providing an aqueous solution of a surfactant under stirring at a stirring speed of from 200 to 4000 RPM (e.g. from 400 to 2000 RPM, such as 600 to 2000 RPM); and
 - (ii) providing a mixture of the first organic material and the phase change material and adding it to the stirred aqueous solution of the surfactant.
30. The process of Claim 29, wherein step (ii) is conducted at a temperature of from 30 to 60 °C, such as 50 °C.
31. The process of any one of Claims 15 to 30, wherein:
- (i) step (b) of Claim 15 is conducted at a temperature of from 30 to 60 °C, such as 50 °C; and/or
 - (ii) step (c) of Claim 15 is conducted at a pH of from 2.0 to 5.0, such as from 2.5 to 4.0, such as 3.0; and/or
 - (iii) step (b) of Claim 15 is conducted at a temperature of from 25 to 40 °C, such as 35 °C.

Figures**Fig. 1**

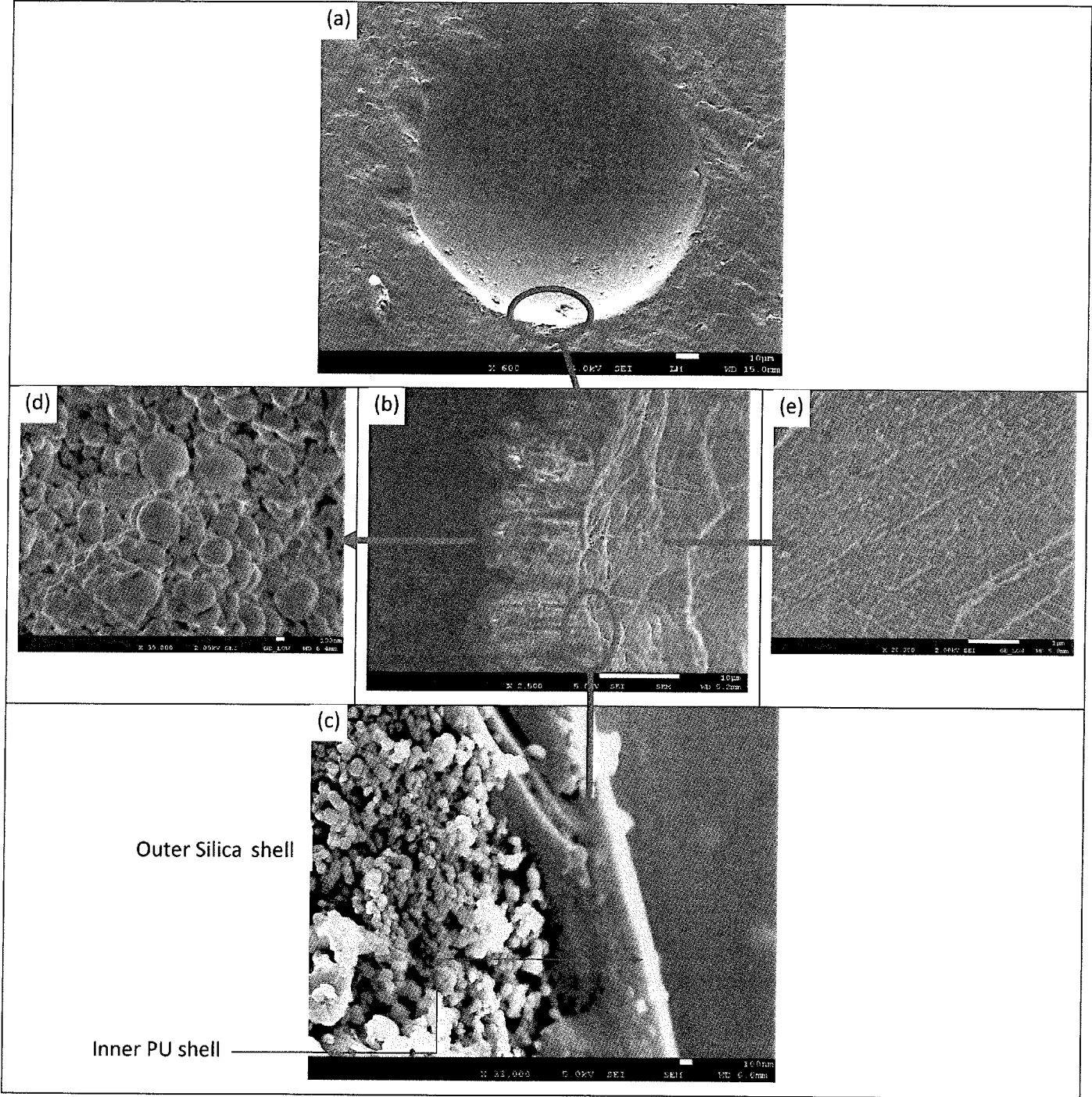


Fig. 2

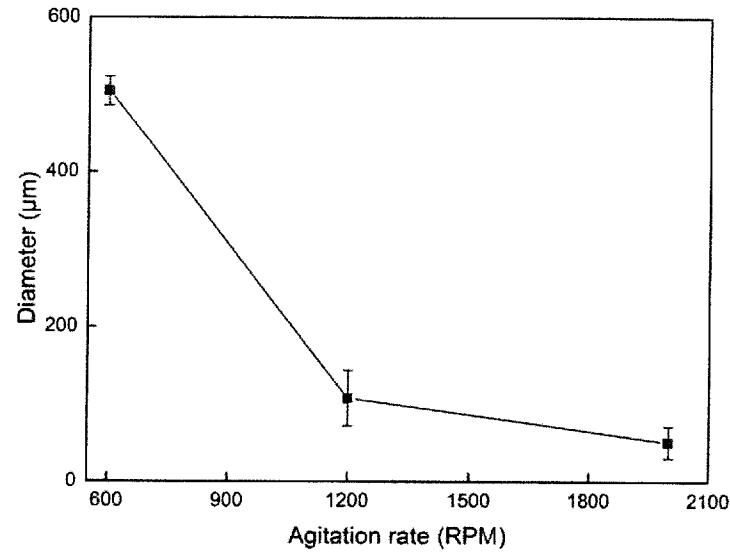


FIG. 3

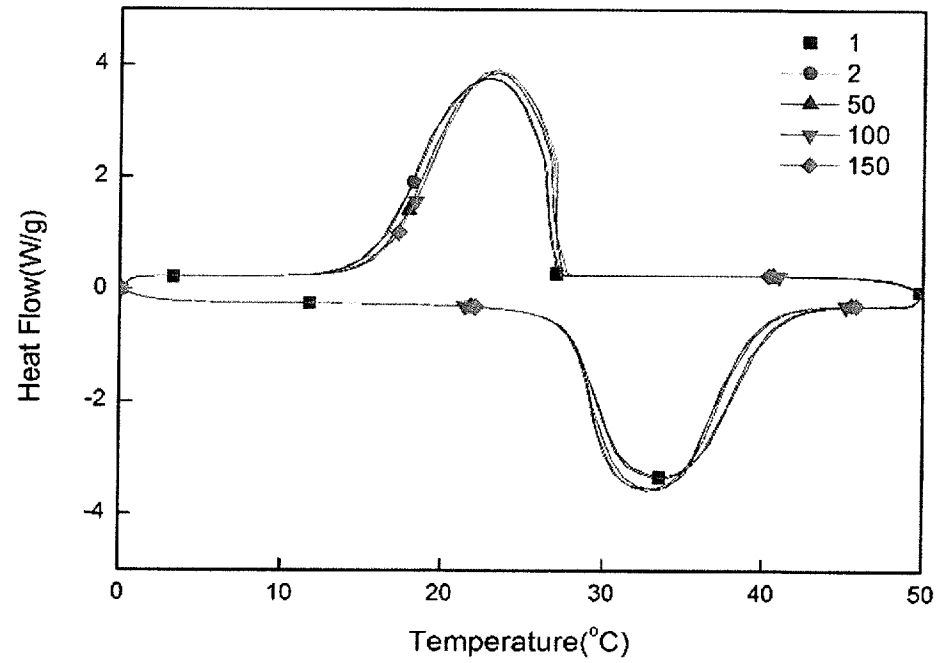


FIG. 4

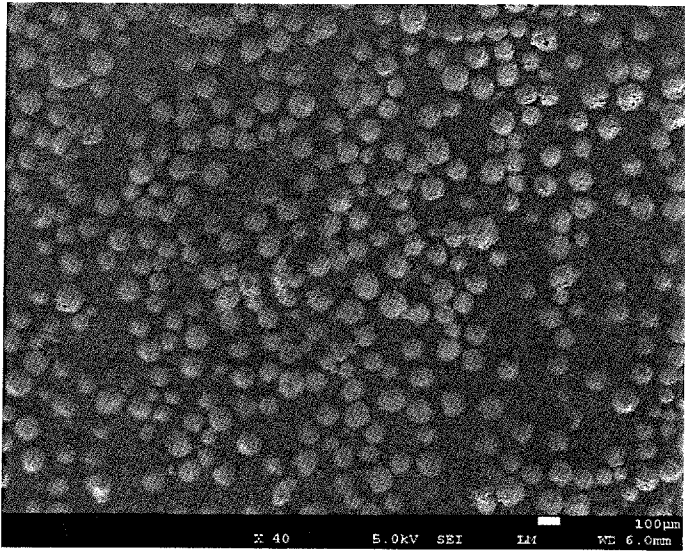


FIG. 5

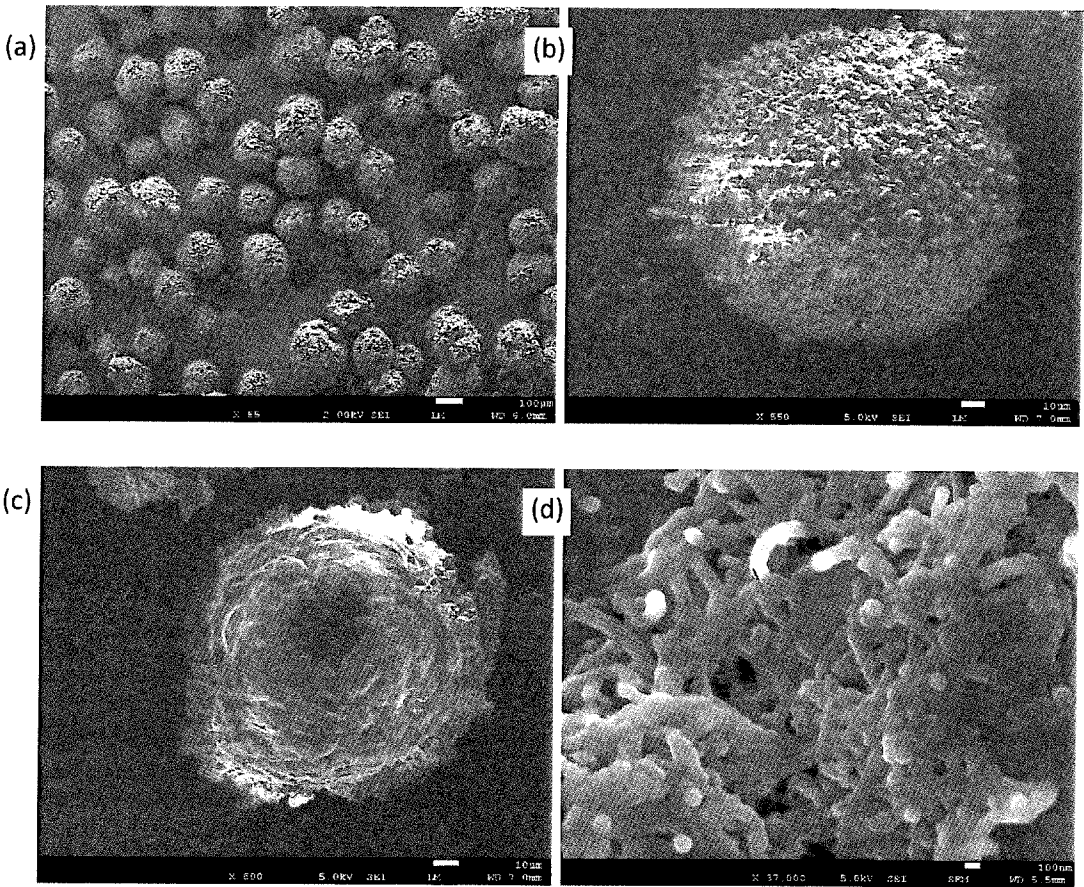


FIG. 6

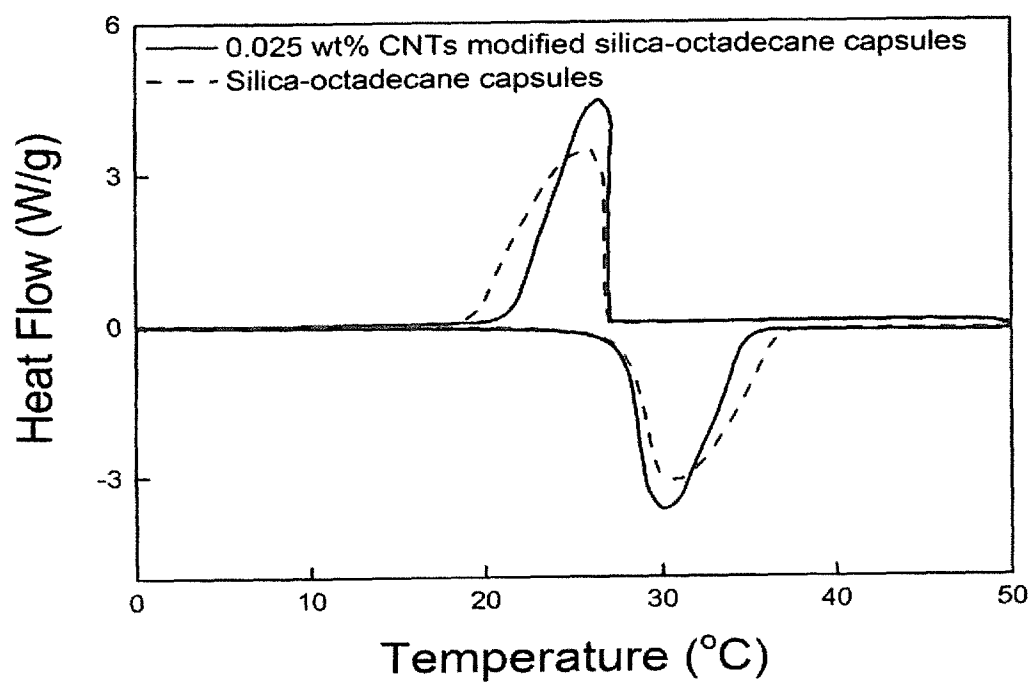


FIG. 7

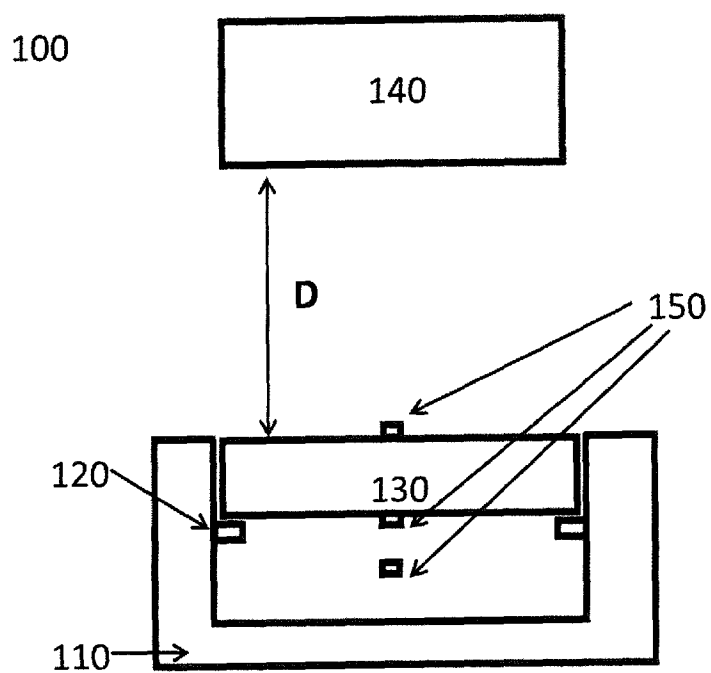


FIG. 8

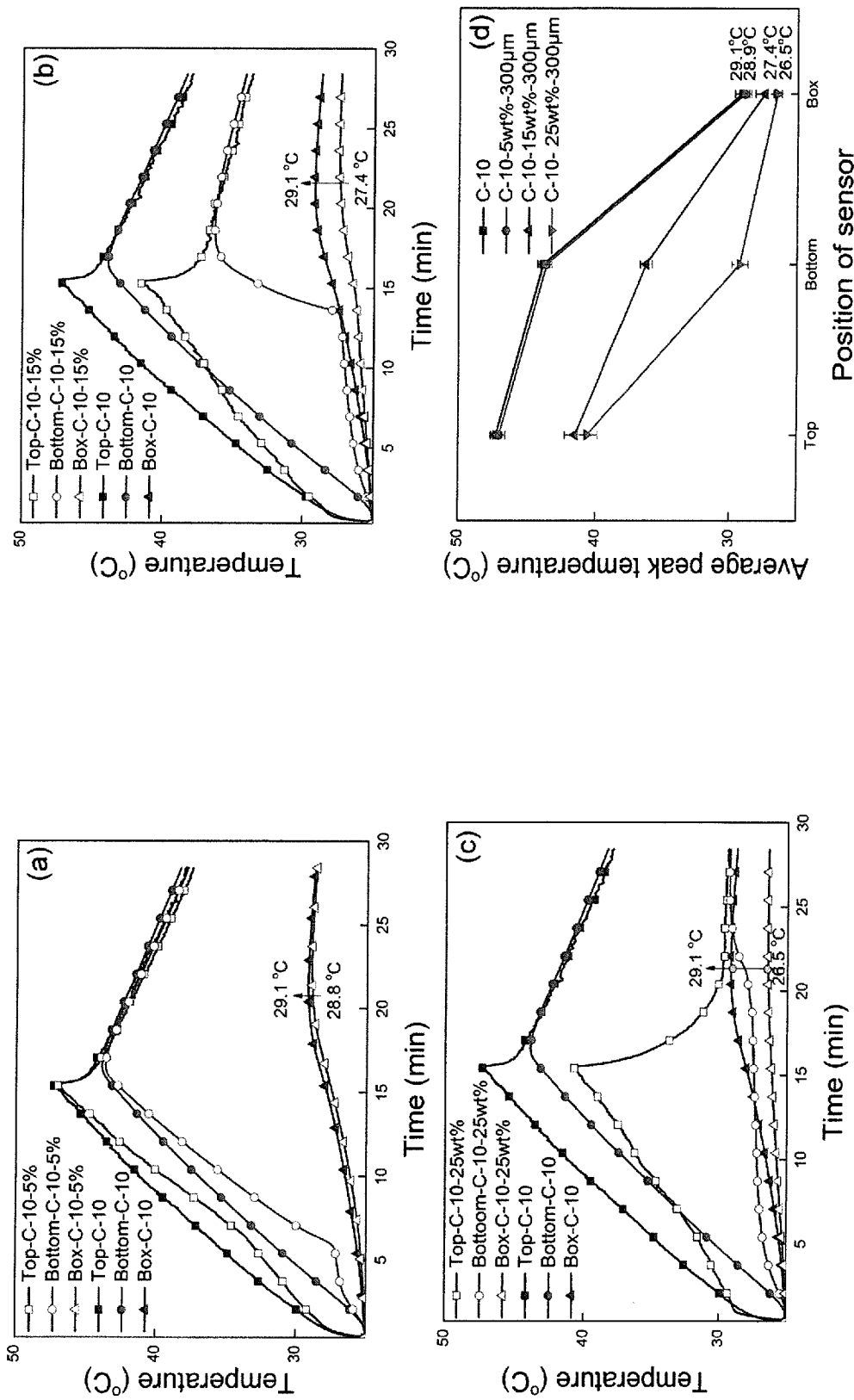


FIG. 9

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2016/050610

A. CLASSIFICATION OF SUBJECT MATTER

C09K 5/00 (2006.01) C09K 5/02 (2006.01)

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09K 5/02

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

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

English full text (FAMPAT) using keywords such as phase change, PCM, latent heat, capsule, encapsulate, core, shell, double, duo, dual, bilayer, first, second, multi, urea, polyethyleneimine, polymer, inorganic and similar terms.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 101555401 A (INSTITUTE OF CHEMISTRY, CHINESE ACADEMY OF SCIENCE) 14 October 2009 page 3, 3rd para; page 4, step (a); page 6, last para, page 7, 1st para; page 9, 1st para, last para; page 12, 2nd para; pages 16, 17, 20-21, page 25, 3rd para of the machine translation	1-31
X	CN 104031612 A (INSTITUTE OF CHEMISTRY, CHINESE ACADEMY OF SCIENCES) 10 September 2014 Pages 9, 10, 14 of the machine translation	1-14
X	CN 103285793 A (FUDAN UNIVERSITY) 11 September 2013 page 3, 1st para; page 4, para 3; example 1 at page 6, para 3; example 2 at page 7, para 2; example 3 at page 8, para 2 of the machine translation	1-14

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"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

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Date of the actual completion of the international search

28/02/2017 (day/month/year)

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2016/050610**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2014/188327 A1 (COMMISSARIAT A L'ENERGIE ATOMIQUE ET AUX ENERGIES ALTERNATIVES) 27 November 2014 & US 2016177156 A1 Whole document of the patent family member	-
P,X	WO 2016/100477 A1 (THE PROCTER & GAMBLE COMPANY) 23 June 2016 Whole document	1-31
P,X	WO 2016/100499 A1 (THE PROCTER & GAMBLE COMPANY) 23 June 2016 Whole document	1-31

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SG2016/050610

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 101555401 A	14/10/2009	NONE	NONE
CN 104031612 A	10/09/2014	NONE	NONE
CN 103285793 A	11/09/2013	NONE	NONE
WO 2014188327 A1	27/11/2014	EP2999764 A1	30/3/2016
		FR3005960 A1	28/11/2014
		US2016177156 A1	23/3/2016
WO 2016100477 A1	23/6/2016	US2016184196 A1	30/6/2016
WO 2016100499 A1	23/6/2016	US2016168510 A1	16/6/2016