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METHODS OF MANUFACTURING THE  
HEAT STORAGE MATERIALS**(30) **Foreign Application Priority Data**

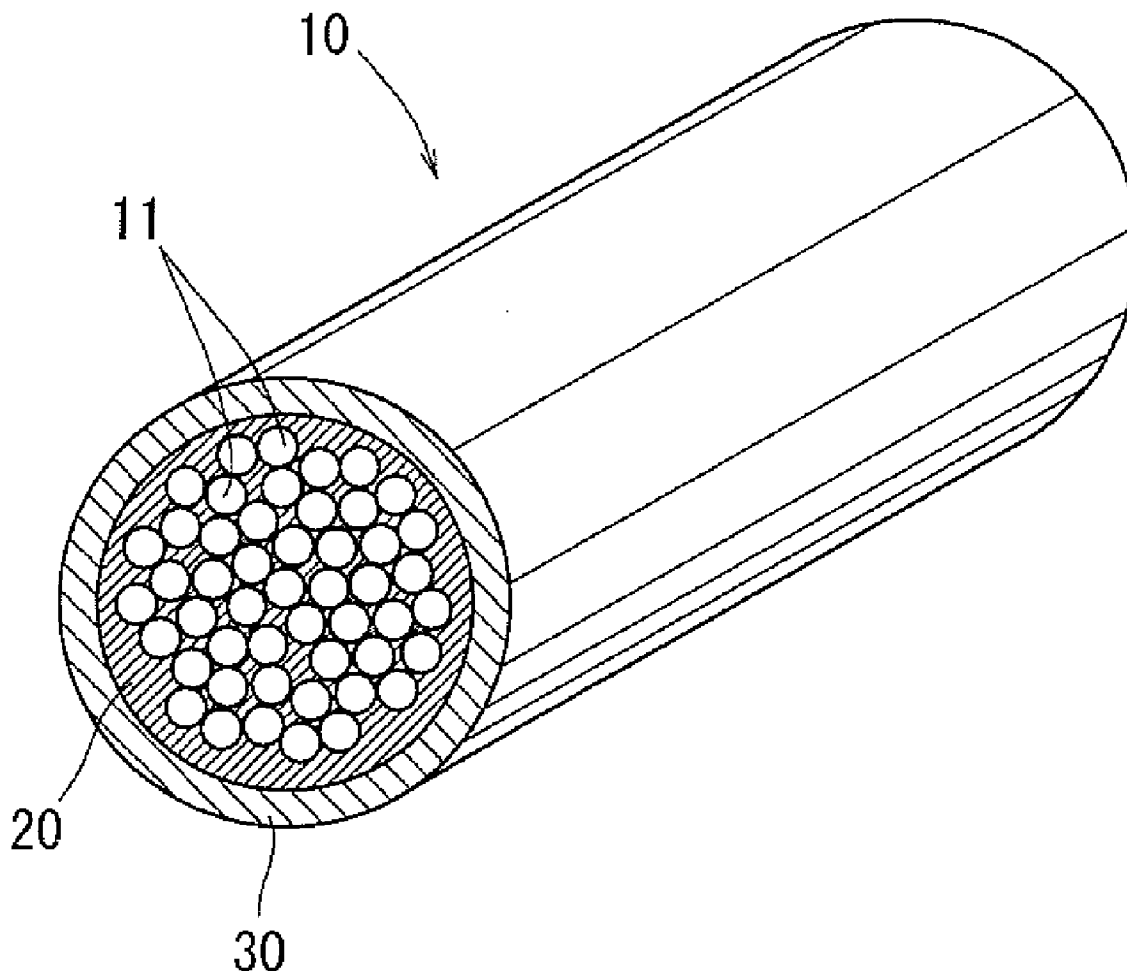
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**ALEXANDRIA, VA 22314 (US)**(57) **ABSTRACT**

The present invention includes a heat storage granule having a plurality of microcapsules mixed with a binder and granulated into the heat storage granule. Each of the microcapsules may have an outer case and a phase change material contained therein. The outer case may be made of synthetic resin. The phase change material can absorb and dissipate latent heat in response change in temperature. The heat storage granule may have a cover layer that has heat conductivity and resistance against alcohol, both of which may be higher than those of a thermosetting resin or a thermoplastic resin.

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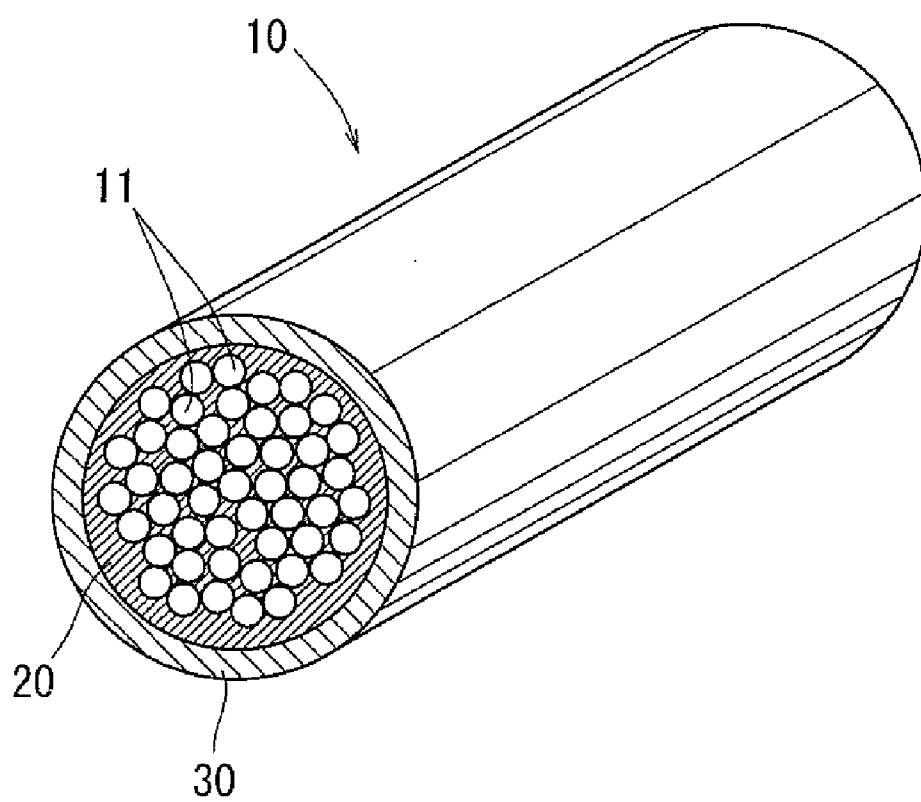


FIG. 1

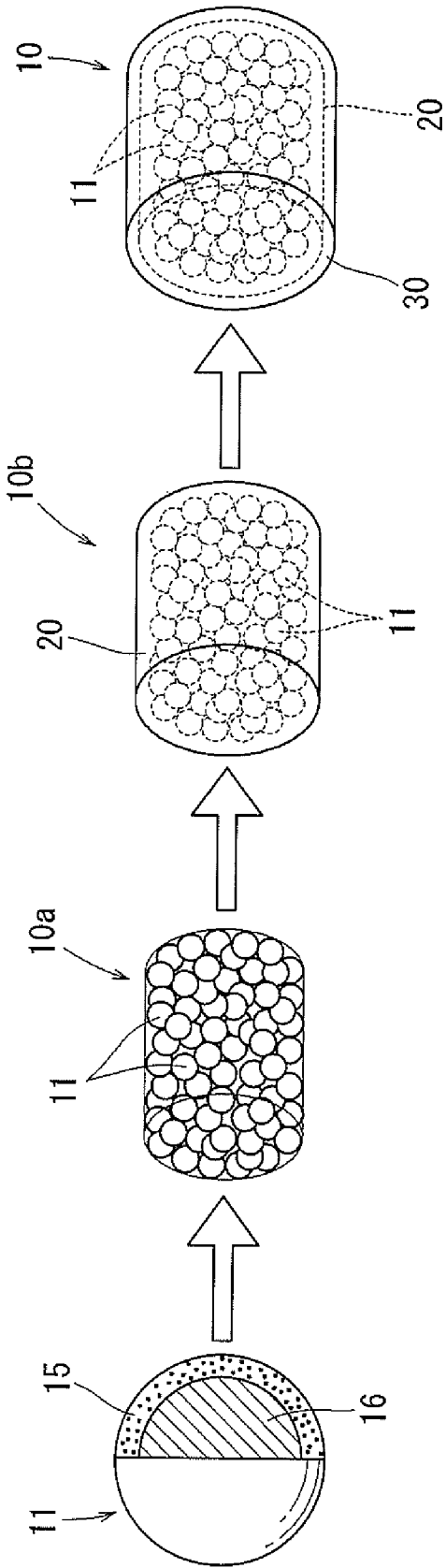


FIG. 2 (d)

FIG. 2 (c)

FIG. 2 (b)

FIG. 2 (a)

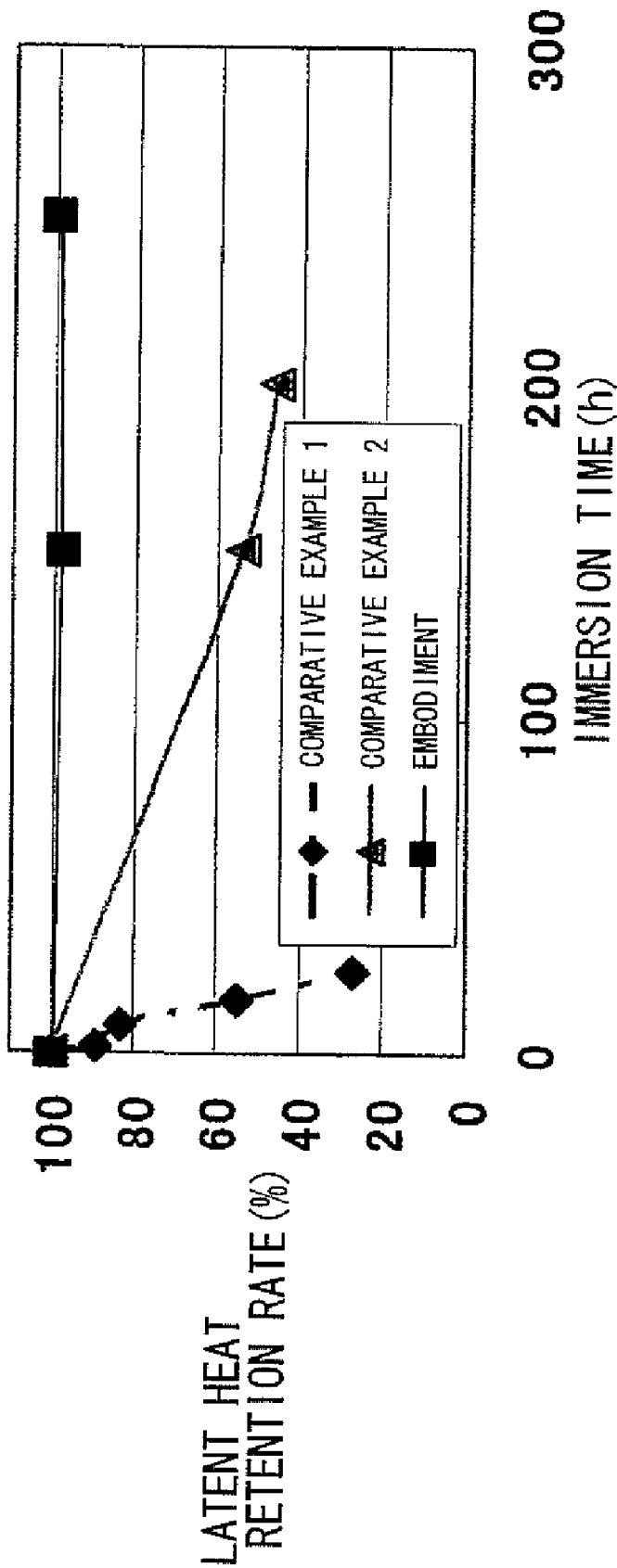


FIG. 3

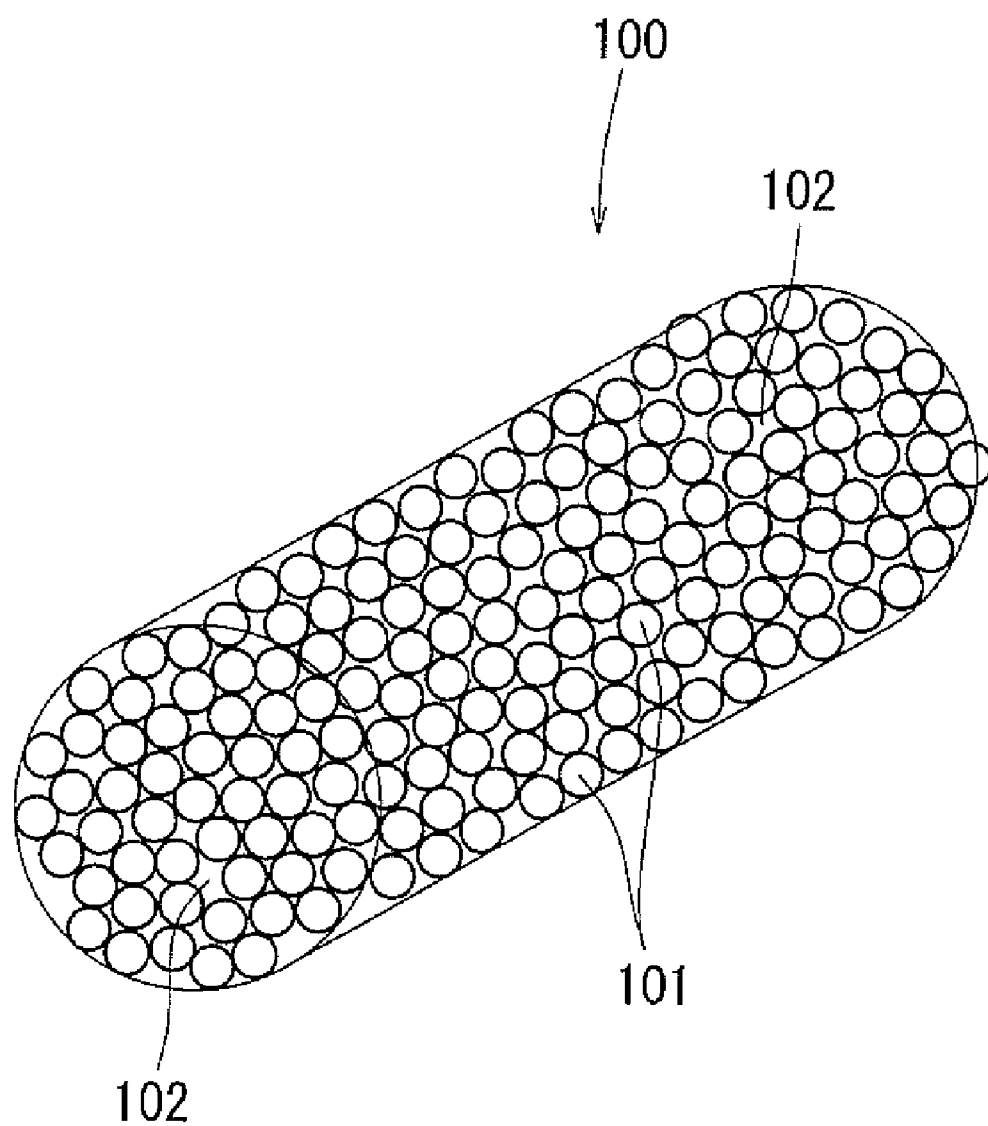


FIG. 4  
PRIOR ART

## HEAT STORAGE MATERIALS AND METHODS OF MANUFACTURING THE HEAT STORAGE MATERIALS

[0001] This application claims priority to Japanese patent application serial number 2008-137450, the contents of which are incorporated herein by reference.

### BACKGROUND OF THE INVENTION

#### [0002] 1. Field of the Invention

[0003] The present invention relates to heat storage materials that can be disposed within canisters of fuel vapor processing apparatus for inhibiting fuel vapor produced within a fuel tank from dissipating to the atmosphere, and in particular to heat storage materials in forms of granules. Each of the granules has microcapsules each having an outer case and a phase change material that is contained within the outer case and can absorb and dissipate latent heat in response change in temperature. The microcapsules are mixed with a binder and are formed into the granules. The present invention also relates to methods of manufacturing the heat storage materials.

#### [0004] 2. Description of the Related Art

[0005] A known canister for a fuel vapor processing apparatus includes an adsorption material, such as activated carbon, for adsorbing and capturing fuel vapor in order to prevent the fuel vapor from dissipating into the atmosphere. The fuel vapor may be produced due to evaporation of gasoline fuel stored within a fuel tank when a vehicle equipped with the fuel tank is stopped. The canister has a tank port communicating within an upper space of the fuel tank, an atmospheric port having one end open into the atmosphere, and a purge port for the flow of the fuel vapor desorbed (purged) from the adsorption material. When fuel vapor is produced due to increase in temperature of the fuel tank during driving of a vehicle engine or during stopping of the vehicle, the fuel vapor may be adsorbed by the adsorption material as it flows into the canister via the tank port and then flows further toward the atmospheric port. Therefore, it is possible to prevent the fuel vapor from being discharged to the atmosphere. The fuel vapor adsorbed by the adsorption material can be desorbed (purged) by the flow of outside air that may be introduced into the canister via the atmospheric port by a negative pressure of an air intake pipe of the engine or by a suction pump that is controlled to be driven independently of the engine. Therefore, the adsorption material can be regenerated.

[0006] The fuel vapor may be liquefied when it is adsorbed by the adsorption material, and the liquefied fuel may be gasified again when it is desorbed from the adsorption material. Therefore, when the fuel vapor is adsorbed, the temperature of the adsorption material may be increased due to condensation heat or by an exothermic reaction. On the contrary, when the fuel vapor is desorbed, the temperature of the adsorption material may be decreased due to evaporation heat or by an endothermic reaction. On the other hand, the adsorption material has a porous structure and has such a property that an adsorption capacity increases as the temperature decreases while the adsorption capacity decreases as the temperature increases. Therefore, in order to improve the adsorption and desorption performances of the adsorption material, it may be preferable to inhibit change in temperature of the

adsorption material by inhibiting dissipation and absorption of heat, which may be caused as the phase of the fuel changes.

[0007] Japanese Laid-Open Publication No. 2005-233106 has proposed a canister that has a heat storage material contained therein together with an adsorption material. The heat storage material can serve to inhibit change in temperature of the adsorption material by using latent heat. Japanese Laid-Open Publication No. 2006-233962 has proposed a heat storage material for use with a canister. In the above Publication No. 2005-233106, pellet-like heat storage members (molded heat storage members) are used as the heat storage material. A granulation process of a mixture of microcapsules and a binder manufactures the heat storage members. Each of the microcapsules includes an outer case made of melamine resin or the like and a phase change material sealingly contained in the outer case and made of paraffin, such as tetradecane and pentadecane, having a relatively low melting point. By putting the heat storage material into the canister in addition to the adsorption material, potential increase in temperature of the adsorption material that may be caused by adsorbing the fuel vapor can be inhibited by latent heat (melting heat) produced when the phase change material contained within the heat storage material changes from the solid phase to the liquid phase. On the other hand, potential decrease in temperature of the adsorption material that may be caused by desorbing the fuel can be inhibited by latent heat (solidification heat) produced when the phase change material contained within the heat storage material changes from the liquid phase to the solid phase. Hence, the adsorption and desorption performances of the adsorption material may be improved.

[0008] The above Publication No. 2006-233962 proposed to cover outer surfaces of microcapsules of the heat storage material by a material that has heat conductivity higher than that of an adsorption material and can prevent the fuel vapor from passing therethrough, in order to prevent a phase change material contained in the microcapsules from causing change in a melting point due to passage of the fuel vapor through outer cases of the microcapsules. More specifically, this publication proposed to put the phase change material or the microcapsules sealing containing the phase change material into pellet-like metal cases (e.g., claims 6 and 7 and paragraph [0060] to [0062]), to put the phase change material or microcapsules sealing containing the phase change material into pellet-like cases made of resin film having metal foil laminated therewith (e.g., claim 8 and paragraphs [0063] and [0064]), and to put a microcapsule-type heat storage material, which has a metal material plated or deposited on an outer surface of each of the microcapsules, directly within the canister without granulation using a binder (e.g., claim 9, paragraph [0065]). As the metal that does not permit passage of the fuel vapor, aluminum, copper, iron and stainless steel are proposed.

[0009] In recent years, as one of countermeasures against global warming, there has been an international trend of legislating the use of plant-derived alcohol, including that called "biomass-ethanol" or "bio-ethanol", as fuel for automobiles by mixing it with conventional gasoline fuel. Gasoline mixed with ethanol may be called "gasohol." Bio-gasoline containing a few percent of ethyl tertiary-butyl ether (ETBE) mixed with normal gasoline is also being used. ETBE is obtained by the reaction between plant-derived ethanol and isobutene. It has been known that a botanical resource rich in carbohydrate or starchy material is suitable as ingredient of biomass-etha-

nol. Currently, molasses derived from sugarcane (mainly in South America), sugarcane (mainly in the United States), and sugar beet (mainly in Europe) are used mainly as the ingredient. Biomass-ethanol made from the other ingredient, such as sorghum (corn, kaoliang), Irish potato, sweet potato and wheat, is also being developed. This is based on an idea (carbon neutral) that these plants absorbed CO<sub>2</sub> in the air, and therefore, fuel made from these plants does not cause increase of the absolute amount of CO<sub>2</sub> over the entire globe even if the fuel is burnt and converted into CO<sub>2</sub>. When alcohol containing-fuel is used for a vehicle, fuel vapor may contain evaporated alcohol content.

**[0010]** The heat storage material of the above Publication No. 2005-233106 used outer cases made of melamine resin that has less resistance against alcohol. Therefore, if this heat storage material is used in connection with the operation for adsorbing and desorbing vaporized mixed fuel produced from alcohol-containing fuel, there is a possibility of causing problems, in particular when degraded alcohol-containing fuel is used. Thus, if alcohol-containing fuel is degraded, this may cause increase of organic acid and peroxide, which act to break cross-linkage of the melamine resin forming the outer cases of the microcapsules. Therefore, the degree of cross-linking of the melamine resin may be lowered to cause leakage of the phase change material contained in the microcapsules. If the phase change material flows out of the microcapsules, latent heat produced by the microcapsules may be reduced to the result that a suitable heat storage effect cannot be achieved and that the performance of the adsorption material is degraded. Although not clearly disclosed in the Publication No. 2005-233106, in general, in this kind of granulated heat storage material, in order to enable the phase change material to be effectively changed in phase in response to change in temperature of the adsorption material, an amount of a binder used for bonding the microcapsules together is set to be as small as possible for exposing at least a part of each of the microcapsules. More specifically, as shown in FIG. 4, the granulated heat storage material has a porous body **100** having spaces or voids **102** formed between microcapsules **101**.

**[0011]** According to the Publication No. 2006-233962, microcapsules each containing a phase change member is put into a metal container. Although this publication is not focused on the use for alcohol-containing fuel, the metal container may have more resistance against alcohol than melamine resin. Therefore, the above problem may not be so serious. However, in the case that microcapsules are put into a metal container formed into a pellet, a troublesome operation is necessary for putting the microcapsules into the metal container. Further, in the case that a surface of each of microcapsules is coated with a metal coating, it is not necessary for putting the microcapsules into a metal container. However, because the microcapsules are put directly into a canister, the microcapsules are filled close to each other, so that the air cannot easily flow through the canister. Therefore, adsorption and desorption efficiency of the canister may be lowered.

**[0012]** Therefore, there is a need in the art for a granulated heat storage material that can prevent or minimize a phase change material from flowing out of the heat storage material even in the case of application to alcohol-containing fuel.

#### SUMMARY OF THE INVENTION

**[0013]** One aspect according to the present invention includes a heat storage material that includes a heat storage

granule having a plurality of microcapsules mixed with a binder and granulated into the at least one heat storage granule. Each of the microcapsules may have an outer case and a phase change material contained therein. The outer case may be made of synthetic resin. The phase change material can absorb and dissipate latent heat in response change in temperature. The heat storage granule may have a cover layer that has heat conductivity and resistance against alcohol, both of which may be higher than those of a thermosetting resin or a thermoplastic resin.

**[0014]** Another aspect according to the present invention includes a method of manufacturing a heat storage material. The method may include granulating a mixture of a plurality of microcapsules and a binder into a plurality of porous heat storage granules each having spaces or voids between the microcapsules; providing an underlying layer on each of the porous heat storage granules, so that the voids within at least a surface layer part of each of the porous heat storage granules are filled with the underlying layer; and providing a cover layer on a surface of each of the porous heat storage granules having the underlying layer.

**[0015]** A further aspect of the present invention includes another method of manufacturing a heat storage material. The method may include the steps of granulating a mixture of a plurality of microcapsules and a liquid binder into a plurality of non-porous heat storage granules; and providing a cover layer on a surface of each of the heat storage granules.

**[0016]** A further aspect of the present invention includes a heat storage granule including a granule body and a carbon cover layer or a metal cover layer. The heat storage granule may include a plurality of microcapsules capable of absorbing and dissipating heat in response to change in temperature.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0017]** FIG. 1 is a perspective view of one of heat storage granules according to an embodiment of the present invention;

**[0018]** FIGS. 2(a), 2(b), 2(c) and 2(d) shows the heat storage material in different manufacturing steps;

**[0019]** FIG. 3 is a graph showing the latent heat retention rates for an example and comparative examples 1 and 2 obtained as a result of alcohol resistance tests; and

**[0020]** FIG. 4 is a perspective view of a known heat storage granule.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0021]** Each of the additional features and teachings disclosed above and below may be utilized separately or in conjunction with other features and teachings to provide improved heat storage materials and methods of manufacturing the heat storage materials. Representative examples of the present invention, which examples utilize many of these additional features and teachings both separately and in conjunction with one another, will now be described in detail with reference to the attached drawings. This detailed description is merely intended to teach a person of skill in the art further details for practicing preferred aspects of the present teachings and is not intended to limit the scope of the invention. Only the claims define the scope of the claimed invention. Therefore, combinations of features and steps disclosed in the following detailed description may not be necessary to practice the invention in the broadest sense, and are instead taught merely to particularly describe representative examples of the

invention. Moreover, various features of the representative examples and the dependent claims may be combined in ways that are not specifically enumerated in order to provide additional useful embodiments of the present teachings.

**[0022]** An embodiment of the present invention will now be described with reference to FIGS. 1 to 3. Referring to FIG. 1, there is shown a heat storage granule 10. In use, a plurality of the heat storage granules 10 may be mixed with an adsorption material (not shown) and may be stored within a canister provided in a fuel vapor processing apparatus for processing fuel vapor that may be produced within a fuel tank of an automobile (not shown). A granulation process of a mixture of a plurality of microcapsules 11 and a binder may form the heat storage granules 10. As shown in FIG. 1, the heat storage granule 10 has an underlying layer 20 and a cover layer 30. The heat storage granule 10 is designed to be suitably used in connection with the operation for absorbing and desorbing fuel vapor of alcohol-containing fuel that contains a few % to a few tens % of biomass-ethanol derived from plants, such as sugarcane, molasses, corn, sugar beet, sorghum, Irish potato, sweet potato and wheat, mixed with gasoline. Of course, the heat storage granule 10 can also be suitably used for normal gasoline that does not contain biomass-ethanol. A mixing ratio of alcohol in alcohol-containing fuel that is being practically used is about 1 to 20 vol %. For example, in the United States, gasoline containing 10 vol % or less of ethanol (E10) is now being used. In Brazil, gasoline containing 20 vol % of ethanol (E20) is used as a standard. In Japan, it is considered that alcohol-containing fuel can be safely used for automobiles if a mixing ratio of ethanol is 3 vol % (E3) or less.

#### Microcapsules

**[0023]** As shown in FIG. 2(a), each microcapsule 11 includes a hollow spherical outer case 15 made of synthetic resin and a phase change material 16 sealingly contained within the outer case 15. The phase change material 16 can absorb and dissipate latent heat in response to change of temperature. Preferably, the microcapsules 11 have an average diameter of between about 0.1  $\mu\text{m}$  and 25  $\mu\text{m}$ . The microcapsules 11 may be manufactured by forming the outer cases 15 by using a coacervation method, an in-situ method (interface reaction method) or any other known methods, around the phase change materials 16 serving as core materials. If the size of the microcapsules 11 is too small, the percentage occupied by the outer case 15 in each microcapsule 11 may be too large, while the percentage of the phase change material 16 in each microcapsule 11 may be too small. Therefore, a heat storage capacity per unit volume of the microcapsule 11 may be small. On the contrary, if the size of the microcapsules 11 is too large, it would be necessary to increase a thickness of the outer case 16 for ensuring sufficient strength (in particular, sufficient strength against a pressure applied during the granulation process) of the microcapsule 11. This may also result in a small heat storage capacity per unit volume.

**[0024]** The outer case 15 may be made of a material selected from a group consisting of melamine resin, styrene resin, polyorganosiloxane, or a mixture of two or more of these materials. Among these materials, melamine resin is most preferable. The melamine resin may be produced by a condensation reaction between formaldehyde and melamine under an alkali condition to obtain methylolmelamine and by a polycondensation process of the obtained methylolmelamine. Methylolmelamine can be easily cross-linked to have a three-dimensional network structure by suitably set-

ting the temperature during the polycondensation process. By forming the outer case 15 by the melamine resin (having a three-dimensional network structure), the phase change material 16 can be reliably sealingly contained within the outer case 15.

**[0025]** As the phase change material 16, any material can be used as long as it can change in phase between a solid phase and a liquid phase depending on the temperature (i.e., the temperature of the adsorption material). For example, organic compound or inorganic compound having a melting point of about 10° C. to 80° C. can be used as the phase change material 16. More specifically, the phase-change material 16 may be selected from a group consisting of linear aliphatic hydrocarbon including tetradecane, pentadecane, hexadecane, heptadecane, octadecane, nonadecane, eicosane, heneicosane and docosane; natural wax; petroleum wax; inorganic compound hydrate selected from a group consisting of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ; aliphatic acid including capric acid and lauric acid; higher alcohol having a carbon number of 12 to 15; and ester including methyl palmitate and methyl stearate. Among these compounds, one having a melting point of about 20° C. is preferable. For example, hexadecane having a melting point of 18° C. and heptadecane having a melting point of 22° C. may be preferable. In addition, one of the compounds listed above or a mixture of two or more of the listed compounds can be used as the phase change material 16.

#### Heat Storage Granule

**[0026]** A number of the microcapsules 11 are mixed with the binder and the mixture is then granulated into a number of granules having a predetermined configuration. Although various kinds of thermosetting resin can be used as the binder, phenol resin or acrylic resin may preferably be used in light of the temperature resistance and the strength required for the canister. In addition, the heat storage granule 10 may preferably have a pellet-like configuration (cylindrical configuration) with a diameter of between about 1 and 3 mm and a length of between about 2 and 5 mm. By configuring the heat storage granule 10 to have a pellet-like configuration, when the heat storage granules 10 are filled into the canister, it is possible to ensure suitable spaces or voids between the heat storage granules 10, so that fuel vapor or air can easily flow through the canister. Therefore, it is possible to minimize loss of pressure and to effectively perform adsorption and desorption operations by the adsorption material. The heat storage granule 10 may have any configuration, such as a spherical configuration, a polygonal column-like configuration or a flat configuration, other than a cylindrical configuration as long as suitable spaces or voids can be ensured between the heat storage granules when filed into the canister. The heat storage granule 10 may have a porous structure having spaces or voids formed between the microcapsules 11. Alternatively, the heat storage granule 10 may have a non-porous structure that may be achieved by a mixture of the microcapsules 11 and a sufficient amount of a liquid binder. In the case that the heat storage granule 10 is formed to have a non-porous structure, the binder may also serve as the underlying layer 20.

#### Underlying Layer

**[0027]** In the case that the heat storage granule 10 has a porous structure, the underlying layer 20 is formed before the cover layer 30 is formed. The underlying layer 20 can provide



a smooth surface, so that the cover layer **30** can be formed to have a uniform thickness. The underlying layer **20** is formed to fill spaces or voids existing within at least a surface layer of an unfinished porous heat storage granule **10a** (see FIG. 2(b)). Although the material of the underlying layer **20** can be chosen from various kinds of synthetic resins including thermosetting resins and thermoplastic resins, the underlying layer **20** may preferably be made of a synthetic resin having resistance against alcohol. A preferable thermosetting resin may be phenol resin (PF). A preferable thermoplastic resin may be polyethylene resin (PE), polypropylene resin (PP) or polyphenylene sulfide (PPS). Phenol resin may be advantageous because it is compatible with the binder and the strength is large. Polyethylene resin and polypropylene resin may be advantageous because they are inexpensive and have relatively low specific gravities. However, it is not necessary to entirely fill the voids of the surface layer of the unfinished porous heat storage granule **10a** if the unfinished porous heat storage granule **10a** has a substantially smooth surface.

#### Cover Layer

[0028] The cover layer **30** gives resistance against alcohol to the heat storage granule **10** and may be made, for example, of metal or diamond-like carbon (DLC) that has higher heat conductivity than the outer case **15** and has resistance against alcohol. The thickness of the cover layer **30** may preferably be about 1 to 30  $\mu\text{m}$ . If the thickness of the cover layer **30** is less than 1  $\mu\text{m}$ , there is a possibility that a defect may be developed in the cover layer **30** and may not have good resistance against alcohol. On the contrary, if the thickness of the cover layer **30** is more than 30  $\mu\text{m}$ , unnecessarily higher resistance against alcohol may be given and the weight and the cost of the heat storage granule **10** may be increased. As the metal material for the cover layer **30**, Ni, Co, Au, Ag, Sn, Cu, Cr, Pb, Zn, Rh, Ru or Pt can be used and can be formed by deposition or plating. In the case that the cover layer **30** is plated, an electroless nickel plating process is preferable. Because the outer case **15** and the underlying layer **20** are made of synthetic resins, it may be difficult to form the cover layer **30** by an electrolytic plating process. In the case that the cover layer **30** is made of DLC that is amorphous isotope of carbon or carbon hydride, the cover layer **30** may be formed as a hard layer having Vickers hardness of 1500 to 7000 Hv. The cover layer **30** may be formed only by the DLC layer or may have an additional layer(s) made of a different material(s) from DLC and layered with the DLC layer.

#### Manufacturing Method

[0029] A representative method of manufacturing the heat storage granule **10** will now be described with reference to FIGS. 2(a), 2(b), 2(c) and 2(d) in connection with steps of forming the unfinished porous heat storage granule **10a** and steps of forming the underlying layer **20** and the cover layer **30** on the surface of the unfinished porous heat storage granule **10a**. FIG. 2(a) shows a half sectional view of the microcapsule **11**. FIG. 2(b) shows the unfinished porous heat storage granule **10a** formed by a granulation process of a mixture of the microcapsules **11** and the binder and having spaces or voids formed between the microcapsules **11**. FIG. 2(c) shows a second unfinished heat storage granule **10b** having the underlying layer **20** formed on the surface of the unfinished porous heat storage granule **10a** for filling the voids of at least the surface layer part of the underlying layer **20**. FIG. 2(d)

shows the finished heat storage granule **10** having the cover layer **30** formed on the second unfinished heat storage granule **10b**.

#### Granulating Process

[0030] The unfinished heat storage granule **10a** is obtained by mixing a number of microcapsules **11** with the binder, molding the mixture to have a predetermined shape, and thermally hardening the binder for bonding the microcapsules **11** to each other. The binder may be applied in a form of a solvent solution, a dispersion of solid resin into a solvent, or a liquid binder resin. A suitable amount of hardening agent may be added to the binder. Coating, spraying, dipping, extrusion molding or any other suitable technique may apply the binder. In order to improve the heat conductivity, the percentage of the voids or pores may be increased. However, because the underlying layer **20** is formed in this embodiment, there may be substantially no limit to the amount of application of the binder. Nevertheless, the amount of the binder may preferably be limited to be equal to or less than 10% by weight of the total weight of the microcapsules **11**, because the costs may be unnecessarily increased and the heat conductivity may be lowered if the amount of the binder is too large. In general, the unfinished heat storage granule **10a** may have a porous structure by setting the amount of the binder to be less than about 3% by weight of the total weight of the microcapsules **11**. It may be preferable that the amount of the binder is more than about 1% by weight of the total weight of the microcapsules **11**. If the amount of the binder is less than 1% by weight of the total weight of the microcapsules **11**, the stability in shape may be lowered and a possibility may exist that it is difficult to maintain the predetermined shape.

#### Underlying Layer Forming Process

[0031] After obtaining the unfinished porous heat storage granule **10a** by the above granulating process, the underlying layer **20** is formed on the surface of the unfinished heat storage granule **10a** to obtain the second unfinished heat storage granule **10b** shown in FIG. 2(c). The material of the underlying layer **20** may be applied by coating, spraying or dipping or other suitable techniques similar to the binder. Among these techniques, a spraying technique is most preferable. The spraying technique may be performed, for example, during the rotation of a number of the unfinished heat storage granules **10a** within a flow vessel rotatable about an axis. When phenol resin is used as the material of the underlying layer **20**, the spraying process may be performed under the condition that the temperature is about 50 to 100° C., the spraying time is about 0.5 to 2 h, and the rotational speed of the flow vessel is about 5 to 50 rpm. In addition, this spraying process may preferably be performed under the reduced pressure, such as 500 to 700 mmHg. By spraying the material under the reduced pressure, it may be possible to give a uniform thickness to the underlying layer **20**, and it is possible to easily control the thickness of the underlying layer **20**.

[0032] The underlying layer **20** is provided for giving a smooth surface to the unfinished heat storage granule **10a** by filling the voids of at least the surface layer part of the unfinished heat storage granule **10a**. Therefore, it is not necessary to fill the voids of the entire unfinished heat storage granule **10a** and it is preferable that the thickness of the underlying layer **20** is as small as possible. More specifically, the thick-

ness of the underlying layer **20** may preferably be set to about 0.1 to 10  $\mu\text{m}$  (measured from a maximum diameter of the porous heat storage granule **10a**). If the thickness of the underlying layer **20** is less than 0.1  $\mu\text{m}$ , it may be possible that the smoothness of the surface of the second heat storage granule **10b** is not sufficient and it may be difficult to form the underlying layer **20** to have a uniform thickness. On the other hand, if the thickness of the underlying layer **20** is more than 10  $\mu\text{m}$  (measured from the maximum diameter of the heat storage granule **10a**), the weight and the costs may be unnecessarily increased.

#### Cover Layer Forming Process

[0033] The surface of the second heat storage granule **10b** obtained by the above underlying layer forming process may then be covered by the cover layer **30**. In the case that metal or DLC is used as the material of the cover layer **30**, the cover layer **30** may be formed by a chemical vacuum deposition method using plasma (plasma CVD method) or a physical vacuum deposition method (PVD method). The plasma CVD method may be performed by using radio-frequency wave, microwave or direct current. The PVD method may include a vacuum evaporation method, an ion plating method, a sputtering method, a laser ablation method, an ion beam deposition method and an ion implantation method. For example, in order to form the cover layer **30** by DLC by the plasma CVD method, hydrocarbon gas, such as acetylene gas, may be used as a raw material gas. According to this method, the raw material gas is converted into plasma within a chamber to produce a gas-phase synthesized hydrocarbon gas that is deposited on a surface of a target (i.e., the surface of the second heat storage granule **10b**). This method is advantageous in that the temperature of the second heat storage granule **10b** may be kept low and that the time required for processing may be relatively short. In order to form the cover layer **30** by DLC by using the PVD method, graphite may be used as a raw material. According to this method, graphite is exposed to an ion beam, arc discharge or glow discharge under a vacuum condition, so that carbon atoms scatter to be deposited on a surface of a target (i.e., the surface of the second heat storage granule **10b**). This method enables to form the DLC cover layer **30** by only carbon.

[0034] In the case that the cover layer **30** is made of metal, in particular nickel-based material, an electric plating method for discharging electrons by applying electric current may not be used, but instead, an electroless plating method may be used. According to the electroless plating method, electrons may be discharged by oxidization of reducing agent contained in a plating liquid, so that nickel layer is deposited on a target (i.e., the surface of the second heat storage granule **10b**). Because no electric current is necessary to be applied in the case of the electroless plating method, it is possible to plate nickel on electrically non-conductive materials, such as plastics and ceramics. The nickel-based cover layer **30** may be a Ni—P layer formed by a reduction action of hypophosphorous acid, an Ni—B layer formed by a reduction action of dimethylamin borane (DMAB), or an Ni layer formed by a reduction action of hydrazine ( $\text{H}_2\text{NNH}_2$ ) using hydrazine hydrochlorid or hydrazine sulfate. If desired, it is possible to mix powder of the other metal (than nickel), such as Cr, Mo, W and Ti, into the plating bath, so that the other metal can be deposited simultaneously with the deposition of nickel. Therefore, a composite metal layer that may have improved resistance against corrosion can be formed.

[0035] As a first step of the electroless plating method, the second unfinished heat storage granules **10b** are degreased by using surfactant. For example, the second unfinished heat storage granules **10b** may be dipped into a solution containing surfactant in concentration of about 100 to 1000 ml/l and may then be ultrasonically washed for about 2 to 30 minutes under a condition heated to about 50 to 90° C. Next, metal catalyst, such as that of iron group and platinum group element, may be added in concentration of about 10 to 50 ml/l to a plating bath containing a plating liquid, such as a water solution of hypophosphorous acid. The iron group catalyst may be palladium, iron, or cobalt. The temperature of the plating bath may be a room temperature. In general, three moles of hypophosphorous acid may be necessary for one mol of the plating nickel. Thereafter, nickel is added in concentration of about 100 to 200 ml/l to the plating bath and the plating bath is heated to about 70 to 100° C., so that nickel may be electrolessly deposited on the second unfinished heat storage granules **10b**. As a result, the finished heat storage granules **10** can be obtained. Preferably, the second unfinished heat storage granules **10b** are washed by water after each of the grease removing and washing process, the catalyst adding process and the plating process.

#### EXAMPLES

[0036] Alcohol resistance properties were evaluated for the porous unfinished heat storage granules **10a** as Comparative Example 1, the second unfinished heat storage granules **10b** having only the underlying layers **20** as Comparative Example 2, and the finished heat storage granules **10** having the underlying layers **20** and the cover layer **30** as Example of Present Invention. The evaluation was made as follows:

##### Comparative Example 1

[0037] First, an initial melamine-formaldehyde condensation product solution was prepared by adding 6.5 g of 37% formaldehyde water solution and 10 g of water to 5 g of melamine resin powder, adjusting pH of the mixture to 8, and thereafter heating the mixture to about 70° C. A mixed liquid was prepared by dissolving 80 g of hexadecane as the phase change material into 100 g of a sodium salt water solution of styrene anhydride copolymer adjusted to have a pH of 4.5. The mixed liquid was then added to the initial melamine-formaldehyde condensation product solution and was mixed therewith for emulsification while being strongly agitated. The pH of the emulsified mixture was adjusted to 9, so that an encapsulation process was completed. The emulsified mixture was then dried to remove unnecessary solutions to obtain a number of microcapsules having an average diameter of 7  $\mu\text{m}$  and each having hexadecane covered by an outer case made of melamine resin. As a binder, 3% by weight of phenol resin was added to the microcapsules and mixed therewith. The mixture was then extruded in a continuous cylindrical shape and was thereafter cut and dried to obtain porous pellet-like heat storage granules (unfinished porous heat storage granules) each having a cylindrical configuration with a diameter of about 2 mm and a length of about 3 mm.

##### Comparative Example 2

[0038] Unfinished porous heat storage granules were obtained by the same process as in Comparative Example 1, and thereafter, 3% by weight of phenol resin is applied to the porous heat storage granules by way of a rotary spray (appli-

cation condition: about 100° C. in temperature, 1 h of spraying period, and 30 rpm of rotational speed of rotary spray). With this process, phenol resin cover layers serving as the underlying layers 20 covered the porous heat storage granules, so that second unfinished heat storage granules can be obtained. In this example, the thickness of the cover layers was set to be about 6 μm. The voids of each of the unfinished porous heat storage granules, including the voids positioned centrally of the unfinished heat storage granule, were filled with the underlying layer.

#### Example

**[0039]** Second unfinished heat storage granules covered by underlying layers were obtained by the same process as in Comparative Example 2, and the second unfinished heat storage granules were then immersed into a water solution of surfactant in the concentration of 500 ml/l, and were ultrasonically washed for five minutes at 75° C. The heat storage granules were then again washed by water, immersed into a plating bath containing nickel in the concentration of 155 ml/l, and electrolessly plated for 25 minutes at 90° C. As a result, cover layers having a thickness of 5 μm were formed on the second heat storage granules.

#### (Immersion Tests)

**[0040]** Immersion tests were conducted to the heat storage granules of Example and Comparative Examples 1 and 2 by immersing the heat storage materials into ethanol-containing gasoline filled within pressure resistant bottles. During the immersion tests, the pressure resistant bottles were sealingly closed and were immersed into an oil vessel that contains oil having a temperature of 65° C., so that the temperature within each pressure resistant bottle was maintained to be constant. The amount of latent heat produced by the heat storage granules of each of Example and Comparative Examples 1 and 2 was measured every hour after immersion by using a differential scanning calorimeter (Model SSC/5200 DSC220C manufactured by Seiko Instruments Inc.). Thereafter, based on the measured amount of the latent heat, a latent heat retention rate was calculated for every hour after immersion by the expression of "Latent Heat Retention Rate (%) = (Amount of Latent Heat after Immersion/Amount of Latent Heat before Immersion)\*100." The result of calculation of the latent heat retention rate for each of Example and Comparative Examples 1 and 2 is shown in FIG. 3. For the immersion test, degraded gasoline (E30) containing 30% of ethanol and a small amount of impurities (organic acid and peroxide) was used as ethanol-containing gasoline.

**[0041]** As shown in FIG. 3, in the case of the heat storage granules having no underlying layer and no cover layer of Comparative Example 1, the latent heat retention rate was rapidly dropped during a short period of time. This may mean that the cross-linking degree of the melamine resin forming the outer case was lowered by the action of the alcohol-containing fuel to cause outflow of the phase change material because the microcapsules are directly exposed to the outside. In the case of the heat storage granules having the underlying layers of Comparative Example 2, the latent heat retention rate was largely increased in comparison with Comparative Example 1. This may mean that potential corrosion of the outer cases by alcohol was inhibited because the microcapsules are not exposed to the outside. Thus, the underlying layers cover the surfaces of the porous heat storage granules

to prevent the microcapsules from being exposed to the outside. However, FIG. 3 shows that increase in the latent heat retention rate is still limited when only the underlying layers are provided. On the other hand, in the case of the heat storage granules having metal cover layers in addition to underlying layers according to Example, the test result indicated that the latent heat retention rate was not substantially changed with time and was improved remarkably in comparison with Comparative Example 1 and largely in comparison with Comparative Example 2. Therefore, it could be found that providing metal cover layers having good resistance against alcohol can reliably prevent potential corrosion of the outer cases.

This invention claims:

1. A heat storage material comprising:  
a heat storage granule having a plurality of microcapsules mixed with a binder and granulated into the heat storage granule; wherein:  
each of the microcapsules has an outer case and a phase change material contained therein,  
the outer case is made of synthetic resin,  
the phase change material can absorb and dissipate latent heat in response change in temperature; and  
the heat storage granule has a cover layer covering a surface of the heat storage granule, the cover layer having heat conductivity and resistance against alcohol, both of which are higher than those of at least one of a thermosetting resin and a thermoplastic resin.
2. The heat storage material as in claim 1, wherein the cover layer comprises a metal layer.
3. The heat storage material as in claim 1, wherein the cover layer comprises a diamond-like carbon layer.
4. The heat storage material as in claim 1, wherein the cover layer comprises an electrolessly deposited nickel layer.
5. The heat storage material as in claim 1, wherein:  
the heat storage granule has voids formed between the microcapsules;  
an underlying layer is provided between the cover layer and a surface of the heat storage granule, so that the voids within at least a surface layer part of the heat storage granule are filled with the underlying layer.
6. The heat storage material as in claim 1, wherein the underlying layer is made of a resin having resistance against alcohol.
7. The heat storage material as in claim 1, wherein the heat storage material comprises a plurality of the heat storage granules, the heat storage material is used in combination with an adsorption material for a canister, and the adsorption material can adsorb and desorb a fuel vapor.
8. A method of manufacturing a heat storage material comprising the steps of:  
granulating a mixture of a plurality of microcapsules and a binder into a plurality of porous heat storage granules each having voids between the microcapsules; wherein:  
each of the microcapsules has an outer case and a phase change material contained therein,  
the outer case is made of synthetic resin; and  
the phase change material can absorb and dissipate latent heat in response change in temperature; and  
providing an underlying layer on each of the porous heat storage granules, so that the voids within at least a surface layer part of each of the porous heat storage granules are filled with the underlying layer; and  
providing a cover layer on a surface of each of the porous heat storage granules having the underlying layer, the

cover layer having heat conductivity and resistance against alcohol, both of which are higher than those of at least one of a thermosetting resin and a thermoplastic resin.

9. A method of manufacturing a heat storage material comprising the steps of:

granulating a mixture of a plurality of microcapsules and a liquid binder into a plurality of non-porous heat storage granules; wherein:

each of the microcapsules has an outer case and a phase change material contained therein,

the outer case is made of synthetic resin; and

the phase change material can absorb and dissipate latent heat in response change in temperature; and

providing a cover layer on a surface of each of the non-porous heat storage granules, the cover layer having heat conductivity and resistance against alcohol, both of which are higher than those of at least one of a thermosetting resin and a thermoplastic resin.

10. The method as in claim 8, wherein the step of providing the cover layer comprises electrolessly depositing nickel.

11. The method as in claim 9, wherein the step of providing the cover layer comprises electrolessly depositing nickel.

12. A heat storage granule comprising:

a granule body including a plurality of microcapsules each capable of absorbing and dissipating heat in response to change in temperature; and

a metal cover layer formed on a surface of the granule body, so that the microcapsules are prevented from being exposed to the outside of the granule body.

13. The heat storage granule as in claim 12, wherein the metal cover layer is made of nickel.

14. The heat storage granule as in claim 12, further comprising an intermediate layer formed between the granule body and the cover layer, wherein the intermediate layer is made of resin.

15. A heat storage granule comprising:

a granule body including a plurality of microcapsules capable of absorbing and dissipating heat in response to change in temperature; and

a carbon cover layer formed on a surface of the granule body, so that the microcapsules are prevented from being exposed to the outside of the granule body.

16. The heat storage granule as in claim 15, wherein the carbon cover layer is made of diamond-like carbon.

17. The heat storage granule as in claim 15, further comprising an intermediate layer formed between the granule body and the cover layer, wherein the intermediate layer is made of resin.

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