(12) UK Patent Application (19) GB (11) 2 252 327 (13) A

(43) Date of A publication 05.08.1992

(21) Application No 9202032.0

(22) Date of filing 30.01.1992

(30) Priority data
(31) 03010717 (32) 31.01.1991 (33) JP

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(51) INT CL[5]
C09K 5/00, C08K 3/24 3/30

(52) UK CL (Edition K)
C3V VDJ
C3W W100 W209 W212 W215 W225 W227
U1S S1405 S1958

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(58) Field of search
UK CL (Edition K) C3L LDF, C3P PJG, C3V VBX VDJ
INT CL[5] C08K, C09K
Online databases: DERWENT WPI, WPIL

(54) Heat storage composition and process for preparing the same

(57) A heat storage composition contains (1) at least one compound which is sodium sulfate or a eutectic salt thereof, (2) water and (3) a cross linkable polymer which comprises a polyfunctional monomer and at least one monomer selected from an unsaturated carboxylic acid, an organic unsaturated sulfonic acid or a salt thereof, wherein the molar ratio of water to sodium sulfate or the eutectic salt thereof is from 13:1 to 27:1, which composition maintains its large latent heat after a number of heating cycles. The said monomer may be acrylic, methacrylic or itaconic acid or mixtures thereof, 2-acrylamide-2-methyl-propanesulfonic acid, p-styrenesulfonic acid, sulfoethyl methacrylate or (meth) allylsulfonic acid and is preferably sodium acrylate or sodium methacrylate. The polyfunctional monomer is preferably N, N'-methylene bis(meth) acrylamide. Sodium tetraborate decahydrate may be added as a supercooling-preventing agent. The composition is prepared by polymerizing the polyfunctional monomer and said at least one monomer or a salt thereof in the presence of water and sodium sulfate or a eutectic salt thereof.

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FIG. 1.

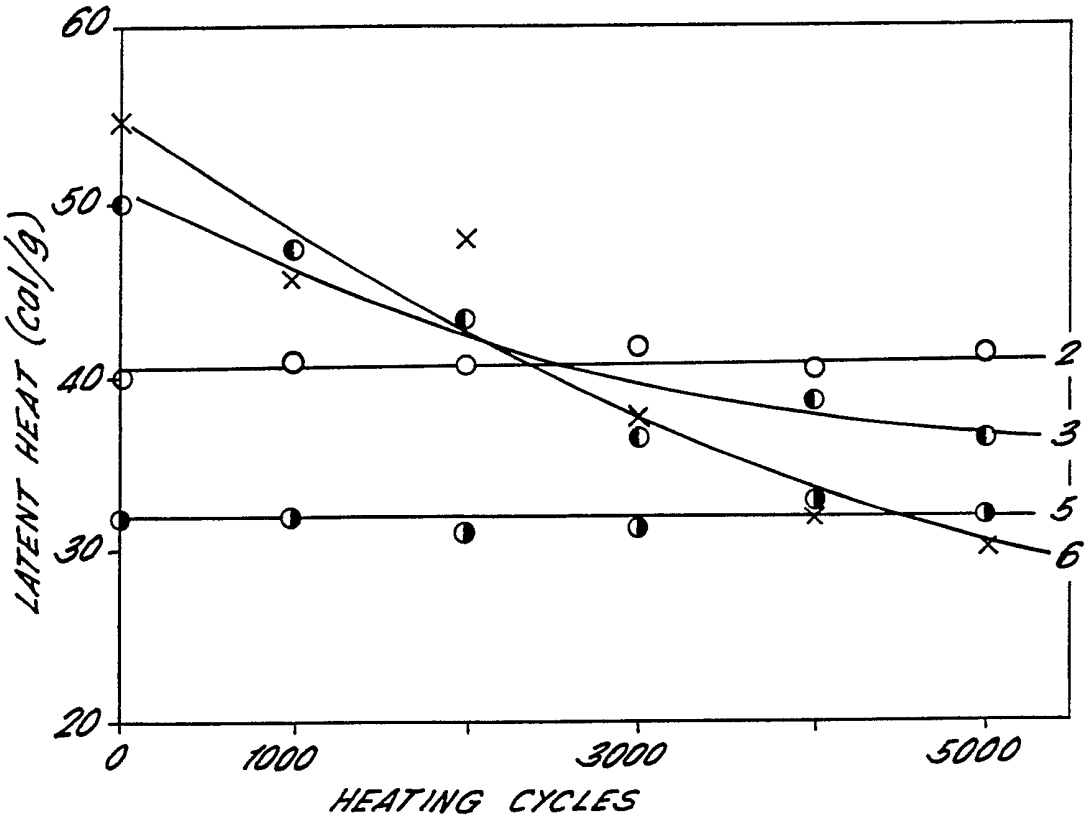
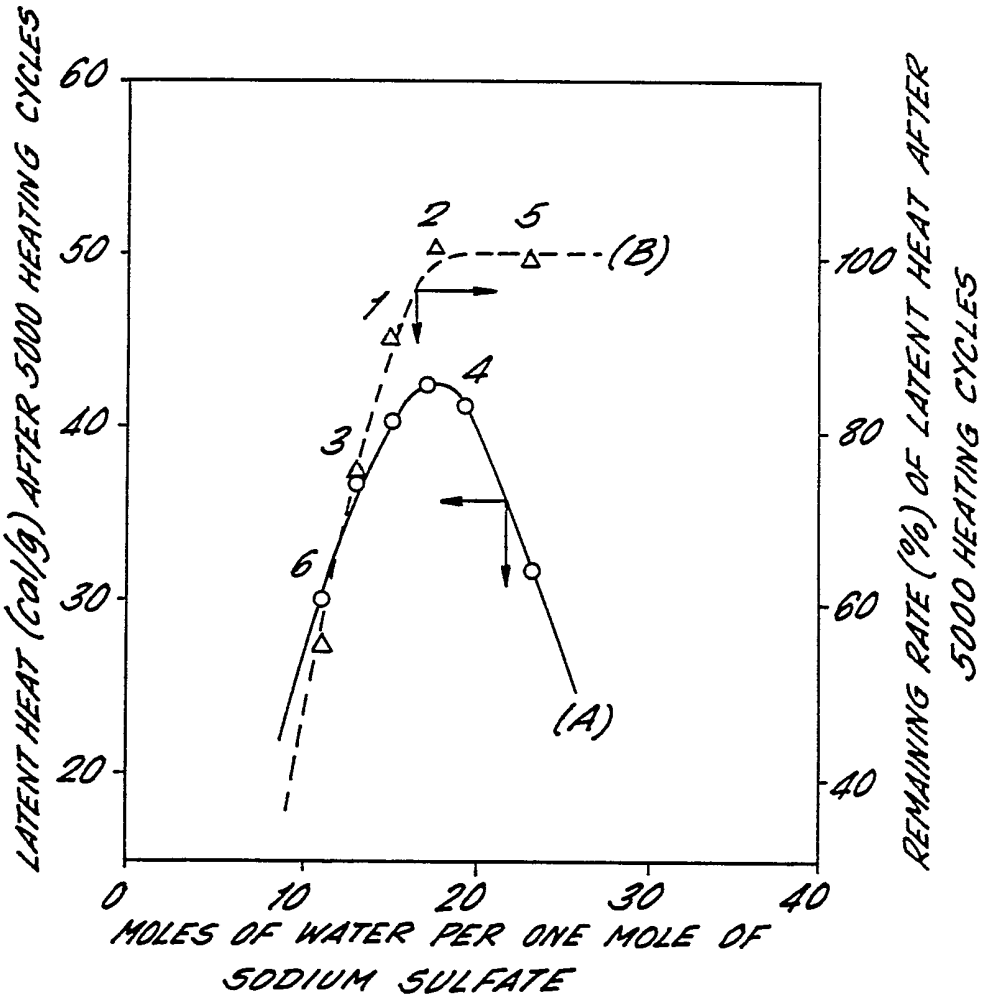

60
50
40
30
20
LATENT HEAT (cal/g)
0
1000
3000
5000
HEATING CYCLES
2
3
5
6

FIG. 2.


LATENT HEAT (Cal/g) AFTER 5000 HEATING CYCLES
REMAINING RATE (%) OF LATENT HEAT AFTER 5000 HEATING CYCLES
MOLES OF WATER PER ONE MOLE OF SODIUM SULFATE
60
50
40
30
20
100
80
60
40
0
10
20
30
40
1
2
3
4
5
6
(A)
(B)

HEAT STORAGE COMPOSITION AND PROCESS FOR PREPARING THE SAME

The present invention relates to a heat storage composition which is used in an air conditioning system for a building or the like and a process for preparing the same.

A heat storage material should have various properties such as a large amount of stored heat, functioning at a predetermined temperature level, long term stability, a low cost, non-toxicity and non-corrosiveness. As a material which satisfies these properties, a phase changeable hydrated salt has been most extensively studied, an one typical example is sodium sulfate decahydrate.

Since sodium sulfate decahydrate has a melting point of 32°C and a latent heat of 60 cal/g, many attempts for utilizing this salt as a heat storage material have been made since sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$) was found to be an effective supercooling-prevention agent which was used in combination with sodium sulfate decahydrate in 1952. One of the problems which arises in the practical application of such a combination is that

sodium sulfate decahydrate exhibits an incongruent melting behavior. That is, upon melting, anhydrous sodium sulfate forms and precipitates at the bottom of a liquid system. When such a system is cooled, a surface layer of the anhydrous salt is rehydrated which an inner part of the precipitated salt remains in a dehydrated form. Since the remaining anhydrous sodium sulfate does not contribute to the phase change, the amount of the stored heat decreases. To solve this problem, many methods have been studied for preventing the precipitation of the anhydrous salt and dispersing and maintaining it in the liquid. Most of them comprise the addition of an organic or inorganic additive to increase viscosity and prevent precipitation.

For example, the use of an inorganic compound has been proposed (cf. Japanese Patent Kohyo Publication No. 501180/1980 and Japanese Patent Kokai Publication No. 34687/1978). However, a sufficient effect on the prevention of precipitation has not been achieved.

As the organic additive, organic polymers such as a water-soluble polymer (e.g. polysodium acrylate) and a crosslinkable polymer have been proposed (cf. Japanese Patent Publication Nos. 30873/1982 and 48027/1982 and Japanese Patent Kokai Publication Nos. 132075/1983 and 102977/1984). However, they are not necessarily satisfactory in view of their long term stability.

In a Glauber's salt base heat storage composition, it is known to suppress the decrease in the amount of stored heat by the addition of water containing a silicone defoaming agent and a chelating agent to the Glauber's salt (cf. Japanese Patent Kokai Publication No. 203687/1985). In this method, the silicone defoaming agent and the chelating agent are essential. In the absence of these two agents, the amount of stored heat decreases after 500 heating cycles.

We have now developed a heat storage composition which can solve the above problems and which comprises sodium sulfate and water and does not suffer from a decrease in the amount of stored heat for a long time after repeated melting and freezing (heating cycle), and a process for preparing such a composition.

According to a first aspect of the present invention, there is provided a heat storage composition comprising (1) at least one compound which is sodium sulfate or a eutectic salt thereof, (2) water and (3) a crosslinkable polymer which comprises a polyfunctional monomer and at least one monomer selected from an unsaturated carboxylic acid, an organic unsaturated sulfonic acid or a salt thereof, wherein the molar ratio of water to sodium sulfate or the eutectic salt thereof is from 13:1 to 27:1.

According to a second aspect of the present invention, there is provided a process for preparing a heat storage

composition, which comprises polymerizing a polyfunctional monomer and at least one monomer selected from an unsaturated carboxylic acid, an organic unsaturated sulfonic acid or a salt thereof in the presence of water and at least one compound which is sodium sulfate or a eutectic salt thereof in a molar ratio of 13:1 to 27:1.

The present invention is further described hereinbelow with reference to the accompanying drawings, in which:

Figure 1 is a graph showing the change of latent heat of the heat storage composition of the present invention during up to 5000 heating cycles in a temperature history test comprising melting and freezing; and

Figure 2 is a graph showing the relationship between the amount of water contained (moles per one mole of sodium sulfate) and the latent heat of a unit weight of the heat storage composition after 5000 heating cycles (A) and the relationship between the amount of water contained and the remaining latent heat after 5000 heating cycles (B).

In the heat storage composition of the present invention, sodium sulfate may be used in an anhydrous form or in eutectic salt form. In addition, sodium sulfate decahydrate may be used. Examples of compounds which form eutectic salts with sodium sulfate are sodium chloride,

potassium chloride, sodium nitrate, potassium nitrate, magnesium sulfate and urea. This compound is used in an amount of from 0.2 to 1.0 mole per one mole of sodium sulfate. The eutectic salt has a lower melting point than sodium sulfate as such and can be used to adjust the melting point.

One of the important characteristics of the composition of the present invention is the molar ratio of water to sodium sulfate in the heat storage composition. Water is used in an amount of from 13 to 27 moles, preferably 15 to 25 moles, more preferably 16 to 24 moles per one mole of sodium sulfate (in anhydrous form). By the use of water in this molar ratio range, the latent heat of the composition does not substantially decrease after heating cycles for a long time. Therefore, the calculation of the heat load is easy, and excessive loading of the heat storage composition to compensate for the decrease of latent heat is not necessary. When the heat storage composition of the present invention is used in a floor heating system, the floor can be made thin and the floor weight is thus decreased.

When the amount of water is less than 13 moles per one mole of sodium sulfate, the initial latent heat is large but the latent heat is decreased significantly by the repeated heating cycles. Then contrary to the composition of the present invention, the composition is not

practically acceptable in view of the equipment and the control.

When the amount of water exceeds 27 moles per one mole of sodium sulfate, the change of latent heat can be suppressed after the repeated heating cycles, but the composition has a small latent heat and a large amount of the composition should be used. Therefore, the equipment has some drawbacks such as an increase of floor thickness and inability to withstand load.

When the amount of water is from 16 moles to 24 moles per one mole of sodium sulfate, the remaining latent heat is 95% or higher after 5000 heating cycles and its absolute value is sufficient for practical use.

The critical meaning of the amount of water in the composition of the present invention will be explained quantitatively in the Examples and Comparative Examples given below.

The crosslinkable polymer and its component monomers will be explained.

As the unsaturated carboxylic acid, a water-soluble unsaturated carboxylic acid is preferred. Specific examples of the unsaturated carboxylic acid are acrylic acid, methacrylic acid and itaconic acid. Among them, acrylic acid is preferred. A mixture of acrylic acid with methacrylic acid, itaconic acid or hydroxyethyl acrylate may be used.

Specific examples of the organic unsaturated sulfonic acid are 2-acrylamide-2-methylpropanesulfonic acid, p-styrenesulfonic acid, sulfoethyl methacrylate, allylsulfonic acid and methallylsulfonic acid.

As the salt of the unsaturated carboxylic acid or the organic unsaturated sulfonic acid, a water-soluble salt such as an alkali metal salt or an ammonium salt is used. Among them, a sodium salt is preferred. In particular, sodium acrylate and sodium methacrylate are most preferred.

It may be possible to use an unsaturated amide together with the above monomers. Examples of the unsaturated amide are acrylamide and methacrylamide.

The amount of the monomers, namely the polymer in the composition is 1 to 10 % by weight, preferably 2 to 5 % by weight based on the total weight of the heat storage composition. When this amount is less than 1 % by weight, the composition has a poor effect on preventing the precipitation of anhydrous sodium sulfate caused by the phase change. When it exceeds 10 % by weight, the amount of stored heat decreases.

The polyfunctional monomer is used to crosslink the polymer. Preferably, a water soluble polyfunctional monomer is used. Specific examples are N,N'-methylenebisacrylamide, N,N'-methylenebismethacrylamide, N,N'-dimethylenebisacrylamide and N,N'-dimethylenebismethacrylamide. Among them, N,N'-methylenebisacrylamide and N,N'-

methylenebismethacrylamide are preferred. The amount of the polyfunctional monomer is from 0.01 to 1 % by weight, preferably from 0.05 to 0.5 % by weight based on the total weight of the heat storage composition. When this amount is less than 0.01 % by weight, the polymer has poor crosslinkability. Even when it exceeds 1 % by weight, the effect is not improved in comparison to the increased amount.

When the above monomer and the polyfunctional monomer are polymerized in the manner explained below, a crosslinkable polymer is obtained. The amount of the crosslinkable polymer in the heat storage composition is the same as the total amount of the monomers and usually from 1 to 11 % by weight, preferably from 2 to 5.5 % by weight.

As the polymerization initiator, any conventional radical polymerization initiators can be used. Examples are diacyl peroxides such as acetyl peroxide, lauroyl peroxide and benzoyl peroxide; hydroxyperoxides such as cumene-hydroxyperoxide; alkyl peroxides such as di-tert.-butyl-peroxide; ammonium or potassium peroxydisulfate; hydrogen peroxide; and 2,2-azobisisobutyronitrile. Among them, a redox type polymerization initiator is preferred since it is active at a comparatively low temperature.

A preferred redox type polymerization initiator is water-soluble. As an oxidant, ammonium or potassium peroxydisulfate and hydrogen peroxide are exemplified. As a reducing agent, sodium thiosulfate, sodium sulfite and ferrous sulfate are exemplified.

The crosslinking temperature is the same as or higher than the melting point of sodium sulfate decahydrate or its eutectic salt. Usually, it is from 20 to 50°C.

The redox type polymerization initiator exhibits polymerization activity in a comparatively short time when the oxidant and the reducing agent are mixed. After the start of the polymerization activity, the contact with air will deactivate the active species. Therefore, the mixture of the oxidant and the reducing agent should be charged in a polymerization reactor as quickly as possible without exposing to the air.

The process of the present invention can be carried out in various ways. For example, the polymerization may be carried out in a comparatively large volume reactor and the produced heat storage composition portioned and filled in a container which constitutes the heat storage part of a heating equipment. In this case, an internal atmosphere of the large volume reactor is replaced with nitrogen gas and the raw materials are charged and reacted.

In the present invention, since the monomers are used as the raw material in place of the polymer, mixing is easy.

Alternatively, the polymerization can be carried out in a heat storage container of a heating unit. In particular, the characteristics of the present invention can be realized in this mode of polymerization.

Since the monomers are used as the raw materials in place of the polymer, the mixture before the polymerization is a liquid composition having a low viscosity. Therefore, the raw material composition can be easily poured in a container having a complicated shape. By polymerization in the container, the heat storage material in a gel or solid state can be contained in the container having the complicated shape. When the raw material mixture is filled in the container and then polymerized, the interior of the container is not necessarily replaced with the nitrogen gas.

When the liquid mixture before polymerization is poured in the container for the heat storage material and the redox type polymerization initiator is used, it is preferred that the oxidant and the reducing agent are continuously mixed in a flow system of the composition and poured in the container.

For example, the oxidant and the reducing agent are separately added whilst pouring a liquid mixture of anhydrous sodium sulfate or its eutectic salt, water and the monomers into the container. One of the oxidant and the reducing agent are dissolved in the liquid mixture and the other is added to the mixture whilst pouring the mixture in the container. The liquid mixture is divided into two portions and the oxidant is added to one of them and the reducing agent is added to the other. Then, two portions are mixed in a pouring conduit and poured in the container. It

is possible to provide an in-line mixer in the pouring conduit to more sufficiently mix the components.

In the process of the present invention, it may be preferred to add a thickener to the mixture in order to prevent the precipitation of anhydrous sodium sulfate or other additive after pouring the raw materials into the container and before the increase of the viscosity achieved by the polymerization of the monomers. As the thickener, any conventional ones may be used. Specific examples of the thickener are inorganic materials such as fumed silica, fine silica produced by a wet process and various clays, water-soluble polymers such as polysodium acrylate and hydrogel. The amount of the thickener is from 0.1 to 7 % by weight of the composition. In case of the monomer, the thickener is added in such an amount that the mixture has a viscosity to prevent the sedimentation of anhydrous sodium sulfate in the short time in which the crosslinking reaction proceeds and the viscosity of the composition increases.

To the heat storage composition, a supercooling-preventing agent is usually added. In the process of the present invention, the supercooling-preventing agent may be added to the liquid mixture before polymerization. When the polymerization of the raw material mixture is carried out in the container in which the heat storage composition is finally contained, the supercooling-preventing agent should be added to the mixture before polymerization.

In general, it is known that sodium tetraborate decahydrate is effective as the supercooling-preventing agent. The amount of supercooling-preventing agent is usually from 2 to 5 % by weight based on the total weight of the heat storage composition. Since the pH range in which sodium tetraborate decahydrate is stably present in an aqueous medium is neutral to basic, the mixture is preferably neutralized when the mixture is acidified by the monomer and/or the polymer.

The present invention will be illustrated by the following Examples.

Example 1

To a 10 wt. % aqueous solution of sodium acrylate (150 g) which had been prepared by neutralizing acrylic acid with an aqueous solution of sodium hydroxide to pH of 7.5, water (135 g) was further added. To the solution, N,N'-methylenebisacrylamide (0.75 g), anhydrous sodium sulfate (142 g) and sodium tetraborate decahydrate (20 g) were added while stirring at 30°C to obtain a homogeneous mixture containing no precipitate. In this mixture, a molar ratio of water to sodium sulfate (in the anhydrous form) is shown in the Table.

This mixture was divided into two portions. To one of them, ammonium peroxydisulfate (0.5 g) was added, and to the other, sodium thiosulfate pentahydrate (0.5 g) was

added. They were flowed through respective flow conduits and collided with each other to mix them and then poured in a polyethylene bag having a width of 40 mm and a length of 600 mm.

The bag was hung in an air oven at 40°C. After one hour, the crosslinking proceeded and the contents of the bag formed a homogeneous gel form elastic composition. This composition phase changed at about 32°C.

The obtained composition (50 g) was charged in a cylindrical glass container having a diameter of 30 mm and a height of 100 mm and subjected to the heating cycle test comprising repeating heating and cooling between 40°C and 10°C. After 5000 heating cycles, the composition was stable and no phase separation was observed. Before the heating cycle, the latent heat was 44.5 cal/g. With this value being "100", a relative latent heat after 5000 heating cycles was 91 (an absolute latent heat being 40.5 cal/g), which means that the composition maintained the high latent heat for a long time.

Examples 2 to 5 and Comparative Example

In the same manner as in Example 1 but using the components shown in the Table, a heat storage composition was prepared. In Example 5, sodium chloride formed an eutectic salt with sodium sulfate.

The results of the heating cycle test are shown in the Table.

The results are also plotted in the graphs of Figs. 1 and 2, in which the numerals 1 to 5 and 6 stand for "Examples 1 to 5" and "Comparative Example".

Table

Example No.	Molar ratio to Na_2SO_4		Heating cycle test: Latent heat (cal/g) and its remaining rate (%) in brackets After heating cycles of					
	Water	NaCl	0	1000	2000	3000	4000	5000
1	15.0	--	44.5 (100)	40.6 (91)	41.8 (94)	39.6 (89)	40.5 (91)	40.5 (91)
2	17.0	--	40.6 (100)	40.2 (99)	41.4 (102)	42.2 (104)	40.6 (100)	42.2 (104)
3	13.0	--	49.8 (100)	47.8 (96)	43.8 (88)	36.4 (73)	38.8 (78)	36.9 (74)
4	19.0	--	36.3 (100)	37.3 (103)	40.0 (110)	39.9 (110)	40.6 (112)	40.6 (112)
5	23.0	0.5	32.3 (100)	32.0 (99)	31.0 (96)	31.3 (97)	32.6 (101)	32.3 (100)
Comp. Ex.	11.0	--	55.2 (100)	45.8 (83)	48.0 (87)	37.5 (68)	32.0 (58)	30.4 (55)

CLAIMS:

1. A heat storage composition comprising (1) at least one compound which is sodium sulfate or a eutectic salt thereof, (2) water and (3) a cross-linkable polymer which comprises a polyfunctional monomer and at least one monomer selected from an unsaturated carboxylic acid, an organic unsaturated sulfonic acid or a salt thereof, wherein the molar ratio of water to sodium sulfate or the eutectic salt thereof is from 13:1 to 27:1.

2. A heat storage composition as claimed in claim 1, wherein the amount of the crosslinkable polymer is from 1 to 11% by weight based on the total weight of the composition.

3. A process for preparing a heat storage composition, which comprises polymerizing a polyfunctional monomer and at least one monomer selected from an unsaturated carboxylic acid, an organic unsaturated sulfonic acid or a salt thereof in the presence of water and at least one compound which is sodium sulfate or a eutectic salt thereof in a molar ratio of 13:1 to 27:1.

4. A process as claimed in claim 3, wherein the total weight of the polyfunctional monomer and the monomer is

from 1 to 11% by weight based on the total weight of the composition.

5. A process as claimed in claim 3 or claim 4, wherein the monomer is a water-soluble monomer.

6. A process as claimed in any one of claims 3 to 5 wherein the monomer is acrylate or sodium methacrylate.

7. A process as claimed in any one of the claims 3 to 6 wherein the polyfunctional monomer is a water-soluble polyfunctional monomer.

8. A process as claimed in any one of claims 3 to 7 wherein the polyfunctional monomer is N,N'-methylenebisacrylaminde or N,N'-methylenebismethy-acrylamide.

9. A heat storage composition as claimed in claim 1 substantially as hereinbefore described with reference to any one of the Examples.

10. A process as claimed in claim 3 substantially as hereinbefore described with reference to any one of the Examples.

Patents Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

Application number

9202032.0

Relevant Technical fields

(i) UK Cl (Edition K) C3V (VDJ,VBX); C3L (LDF); C3P (PJG)

(ii) Int Cl (Edition 5) C08K; C09K

Search Examiner

B J BALDOCK

Databases (see over)

(i) UK Patent Office

(ii) ON-LINE DATABASES:- DERWENT WPI, WPIL

Date of Search

2 MARCH 1992

Documents considered relevant following a search in respect of claims 1 TO 10

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2151249 A IC GAS See Claims 1, 6 to 9, 14, page 1 lines 110, 111, page 1 line 128 - page 2 line 23	1
X	GB 2110708 A THE CALOR GROUP See Claims 3, 8, Examples, Comparative Examples, page 1 line 50 to page 2 line 63	1, 2
X	GB 1584559 THE CALOR GROUP See Claims 1, 3-6, Example 1, page 1 line 62 - page 2 line 50	1, 2
X	EP 0273779 A SUMITOMO See the whole specification	At least 1, 3
X	EP 0133803 A2 ALLIED COLLOIDS See Claims 1, 2, 5, 6, 9, 10 Example 1	1
X	EP 0087859 A1 ALLIED COLLOIDS See Example 1	1, 3, 7, 8
X	EP 0011411 A1 THE CALOR GROUP See whole specification	1, 2
X	EP 0000099 A1 THE CALOR GROUP See Claims 1, 3, 4, page 3 line 25 - page 4 line 21, page 5 lines 8-20, Examples 1, 2	1; 2

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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Patents Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

Application number

9202032.0

Relevant Technical fields

(i) UK Cl (Edition) Contd. from page 1

(ii) Int Cl (Edition)

Search Examiner

B J BALDOCK

Databases (see over)

(i) UK Patent Office

(ii)

Date of Search

2 MARCH 1992

Documents considered relevant following a search in respect of claims

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	JP 062025188 A SUMITOMO See WPI Accession No:- 87-070307/10	1, 3, 5 to 8
X	JP 061111389 A AGENCY OF IND See WPI Accession No:- 86-178928/28	1
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