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ORGANIC COMPOUNDS AS CANDIDATE PHASE CHANGE MATERIALS IN THERMAL ENERGY STORAGE

P.E. ARNDT, J.G. DUNN * and R.L.S. WILLIX *

School of Applied Chemistry, W.A. Institute of Technology, Kent Street, Bentley 6102 (Australia)

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ABSTRACT

Organic compounds have been screened as potential phase change materials for thermal energy storage in the temperature range 60–90 °C. Differential scanning calorimetry (DSC) was used to assess the melting range, enthalpy of fusion and thermal stability of the compounds. The Cleveland open cup method was used to determine flash points. Of the materials studied, Neofat 18S, a local Slackwax and the Hoechst F wax were considered suitable for further study.

INTRODUCTION

A large number of inorganic and organic materials have been investigated for their ability to act as phase change materials (PCMs) in the low temperature storage of solar thermal energy [1–10]. Most of the inorganic materials of interest are salt hydrate solutions, but these have disadvantages because of a tendency to segregate during heating–cooling cycles, resulting in loss of storage efficiency and incongruent melting; and in many cases the solutions are corrosive causing containment problems.

An alternative group of phase change materials which appear worthy of consideration, especially for applications in the 60–90 °C temperature range, is commercially available organic compounds. As part of an on-going project, a number of these organic compounds have been assessed. In the first instance, melting characteristics and enthalpies of fusion were determined, and these values used to select a sub-set for the investigation of long term thermal stability, and flash point measurement. Differential scanning calorimetry (DSC) was affirmed as a rapid and accurate assessment technique [11].

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* To whom correspondence should be addressed.

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EXPERIMENTAL

Materials

Materials were obtained from the following sources: Freeman waxes (K.H. Freeman Pty Ltd.); Interstab Waxes (Akzochemie, G.D.R.); Hoechst F Waxes (Hoechst Australia Ltd.); Mobil waxes (Mobil Oil Australia Ltd.); Golden Fleece waxes (Golden Fleece Petroleum Ltd., Australia); Slackwax (BP Refinery, Western Australia); tristearin, stearax, hydrogenated castor oil and stearic acid (Neofat 18S; Armour Hess Chemicals Ltd., U.S.A.); Laboratory reagent grade chemicals stearic acid, palmitic acid, diphenyl, acetamide, naphthalene and acenaphthene and AR grade stearic acid (Ajax Chemicals, Australia); 12-hydroxy stearic acid (ICI); Carnauba waxes (Ramprie Laboratories, Western Australia); Crodacid (Croda Chemicals Pty Ltd.); and general purpose reagent grade stearic acid (B.D.H.)

Apparatus

A DuPont 990 Thermal Analyser equipped with a standard DSC cell and interfaced to a DEC PDP 11-10 computer was used for the measurement of thermal properties [12].

For recycling tests, a specially constructed cooling jacket was required to provide controlled cooling rates [13].

Flash points were determined by the Cleveland Open Cup Method [14].

Procedure

For DSC experiments, samples of approximately 10 mg were sealed in aluminium pans, and heated or cooled under programmed conditions of 10 K min^{-1}. All experiments were carried out in a flowing nitrogen or air atmosphere (flow rate 100 ml min^{-1}). The extrapolated onset temperature (T_0) of melting was taken as the intersection of the baseline and the slope of the peak, and a similar construction on the high temperature side gave the extrapolated offset temperature, T_f. For the cooling cycle, the extrapolated onset of solidification was designated T_0. The enthalpy of fusion was calculated from the computed area of the melting endotherm. The calibration constant was determined from a standard sapphire sample.

It should be noted that special care is needed in hermetically sealed pans containing volatile compounds such as naphthalene, especially when samples are subjected to hundreds of heating–cooling cycles.

TABLE 1

Effect of heating rate on determined values of T_0 and T_f (stearic acid, 6.3 mg; wax, 6.3 mg)

Heating rate ($K\ min^{-1}$)	Stearic Acid (Neofat 18 S)		Golden Fleece Ceretal 165 Wax	
	T_0(°C)	T_f(°C)	T_0(°C)	T_f(°C)
1	62	68	30	78
2	61.5	69		
5	62	72	30	80
10	62	75		
20	63	80	31	85

RESULTS AND DISCUSSION

Melting properties and enthalpies of fusion

DSC tests were performed on a wide range of commercially available organic compounds as a rapid screening procedure. Only those materials which had melting values within the desired 60–90 °C range, and acceptable enthalpy of fusion values (i.e., > 150 kJ kg^{-1}) were then investigated further. The extrapolated onset temperature of melting (T_0) and the extrapolated offset temperature (T_f), were used as an indication of the melting range of the compounds. Results obtained on these values at different heating rates (see Table 1) indicated that T_0 was relatively constant, and could be used as a good guide to the melting point of the material. The T_f value, which is not the temperature at which the melting process has finished, increased as the heating rate increased. Nevertheless, if all T_f values are determined under similar experimental conditions the difference between T_0 and T_f gives a comparative indication of the melting ranges of different materials.

TABLE 2

DSC data for paraffin waxes

Material	Heating		Cooling		Enthalpy of fusion (kJ kg^{-1})
	T_0(°C)	T_f(°C)	T_0(°C)	T_f(°C)	
Golden Fleece Ceretal 165	30	80	70	25	210
Freeman 155/160 Paraffin	45	70	65	45	135
Mobil Paraffin Wax 150-155 F	40	65	60	40	155
Deoiled Slack-Wax	64	78	73	60	160

Paraffin waxes

The enthalpies of fusion and T_0 and T_f values for some commercially available paraffin waxes are given in Table 2. The enthalpy values are acceptable for heat storage purposes, and indeed the value of 210 kJ kg^{-1} for the Golden Fleece Ceretal 165 wax is high for this class of compounds. Since waxes tend to consist of a range of compounds of similar chain length rather than a discrete compound, their melting range tends to be large. This is demonstrated for the Freeman paraffin wax (Fig. 1), where the difference between T_0 and T_f is 25 °C on the heating cycle and 20 °C on the cooling cycle. This wide melting range might mitigate against the application of these waxes to solar energy storage if the application requires the energy to be stored in a narrow temperature range.

Of particular interest were the results obtained for the slackwax, which is a by-product from a local oil refinery. The wax extracted contained significant quantities of entrained oil, which produced a broad and indistinct DSC trace (see Fig. 2A). After deoiling the wax by rinsing the crude material with a toluene/dimethyl ketone mixture (40/60%, v/v), the DSC trace (Fig. 2B) had a distinct melting endotherm and freezing exotherm with a much narrower range between T_0 and T_f. The major advantage of this material was its relative cheapness compared to other paraffin waxes.

Microcrystalline waxes

The enthalpies of fusion and T_0 and T_f values for some commercially available microcrystalline waxes are shown in Table 3. The enthalpy of

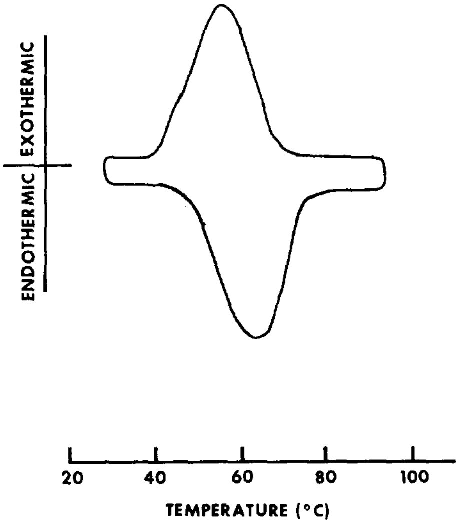

Fig. 1. DSC trace of a Freeman paraffin wax.

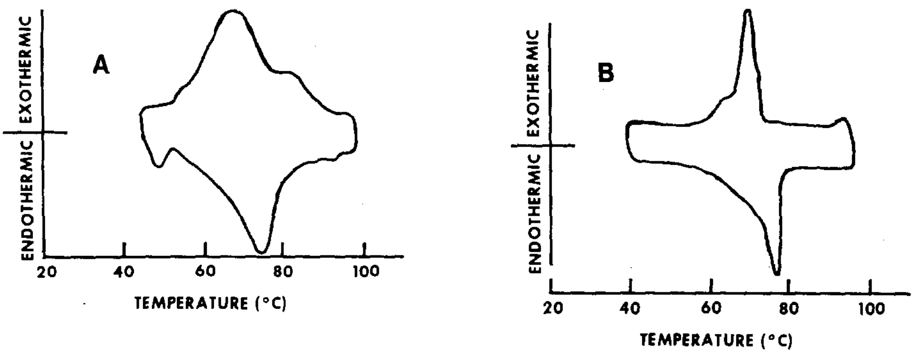

Fig. 2. DSC trace of slackwax: (A) as received; (B) after removal of entrained oil.

fusion obtained for these materials is generally higher than that obtained for the paraffin type waxes, being of the order of 190–220 kJ kg^{-1}. The melting and freezing ranges occurred, however, over a very broad range (see Fig. 3, a DSC scan for the Golden Fleece Ceretal microcrystalline wax). This behaviour could be expected due to the much more variable composition of these waxes and, additionally, the tendency for this type of wax to retain entrained oil. An exception to this is the Interstab 8208 microcrystalline wax (Fig. 4), which is basically an aliphatic hydrocarbon, and which demonstrated a fairly narrow melting and freezing range and possessed a heat of fusion of 195 kJ kg^{-1}.

Natural waxes

Values of enthalpies of fusion and T_0 and T_f for natural waxes are included in Table 4. While some of these materials showed promise, such as the Carnauba waxes (see Fig. 5), there are significantly more problems in quality control, depending on the source of the wax. The cost of the wax is often high and supplies limited.

TABLE 3

DSC data for microcrystalline waxes

Material	Heating		Cooling		Enthalpy of fusion ($kJ\ kg^{-1}$)
	T_0(°C)	T_f(°C)	T_0(°C)	T_f(°C)	
Golden Fleece Ceretal 180-185	35	90	80	30	210
Freeman 180AM	45	90	85	40	220
Interstab 8206	35	65	60	30	190
Interstab 8208	50	70	65	48	195
Mobil NY 190	45	95	95	45	215

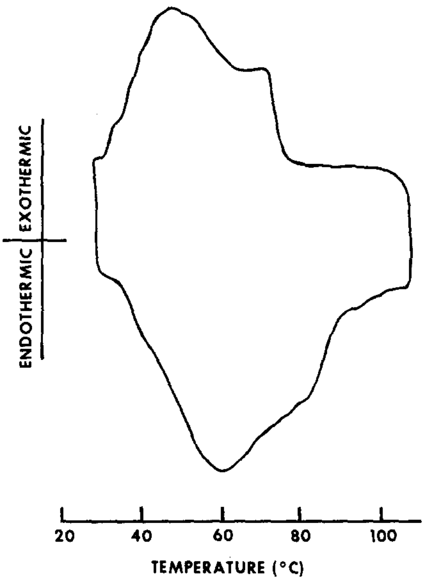

Fig. 3. DSC trace of Golden Fleece Ceretal microcrystalline wax.

Manufactured organic compounds

A listing of the heats of fusion and T_0 and T_f values of some manufactured organic compounds is given in Table 4. Many of these compounds showed

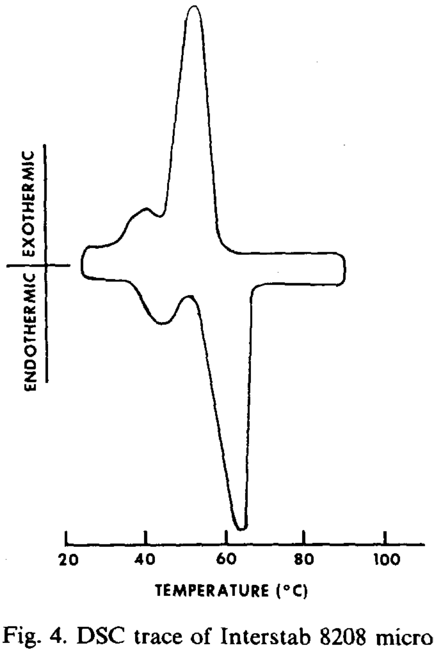

Fig. 4. DSC trace of Interstab 8208 microcrystalline wax.

TABLE 4

DSC Data on other organic materials and waxes

Material	Heating		Cooling		Enthalpy of fusion (kJ kg^{-1})
	T_0(°C)	T_f(°C)	T_0(°C)	T_f(°C)	
Hoechst Wax KPS	55	90	85	50	190
Hoechst Wax KP	60	90	82	55	180
Hoechst Wax KSS	55	75	70	45	180
Hoechst Wax F	63	80	78	55	210
12-Hydroxy Stearic Acid	70	85	57	52	150
Tristearin	56	60	75	67	
	70	80	57	50	190
Stearax	50	70	60	45	175
Stearic Acid	50	70	65	48	200
Neofat 18S	67	75	70	65	200
Palmitic Acid	56	66	60	52	165
Carnauba (brown) Wax	55	85	80	45	185
Carnauba (yellow) Wax	70	90	85	60	190
Carnauba/10% Paraffin B.	55	80	75	50	180
Diphenyl	67	74	70	66	140
Hydrogenated Castor Oil	75	95	65	45	185
Acetamide	70	82	40	35	225
Naphthalene	84	91	74	67	150
Acenaphthene	87	98	95	85	220

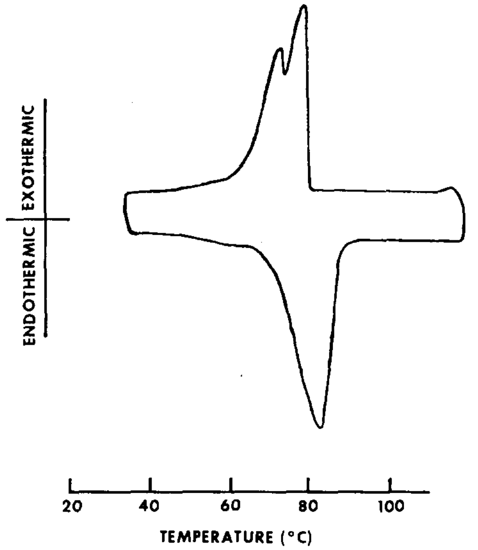

Fig. 5. DSC trace of Carnauba wax.

significantly sharper melting/freezing ranges than for the paraffin and microcrystalline waxes, no doubt due to the higher purity of these compounds.

The peculiar behaviour of many of the materials when undergoing a phase change is highlighted by the DSC technique. For example, acetamide appeared promising as a PCM, due to its relatively high heat of fusion (225 kJ kg^{-1}) and narrow melting range. The DSC profile for this material however, revealed a number of unusual properties (Fig. 6). The melting and freezing peaks were clearly offset from one another, with the value of ΔT, the difference between the T_0 value on the heating cycle and the T_0 value on the cooling cycle, being 28 °C. The backward "skew" of the crystallisation peak is typical of supercooled liquids, as the liquid/solid system is heated back towards the expected crystallization temperature by the release of energy on solidification. The very sharp onset of solidification, as demonstrated by the very rapid movement away from the baseline at T_f, is also typical, as once the thermodynamic barriers have been overcome crystal growth occurs at a rapid rate. While supercooling is inversely related to the mass of the sample [15], and one would therefore not expect the degree of supercooling to be nearly as significant in a full-scale storage device, it is evident that the DSC technique provides a very sensitive means of probing supercooling phenomena.

Another material to display unusual behaviour when undergoing a phase change was the tristearin (glycerol tristearate). The DSC for this compound is illustrated in Fig. 7. Tristearin actually undergoes two phase changes, melting initially at a temperature of 56–60 °C then resolidifying at around

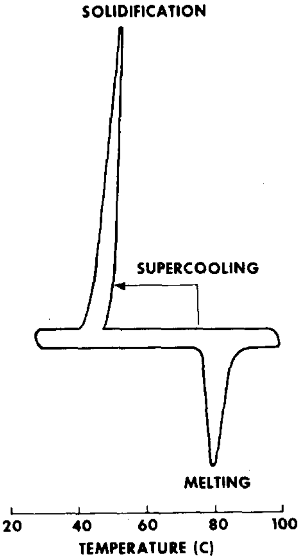

Fig. 6. DSC trace of acetamide.

65 °C before undergoing another phase change at 70–80 °C. This behaviour has been noted previously [16].

Significant variations in the behaviour of a material may be obtained when examining different grades and suppliers. This is illustrated by the various DSCs obtained for stearic acid obtained from different sources (Fig. 8). Both the location of the melting endotherm and its width varied significantly. It is interesting to note that the analytical reagent grade compound melted at a temperature lower than many of the commercial grade materials. This indicates that in determining the melting point and range the mode of manufacture and nature of the impurities is often of more importance than the absolute purity of the material. The Neofat 18S stearic acid (Fig. 8A) appeared quite promising as a PCM, having an overall enthalpy of fusion of 200 kJ kg^{-1} and a melting point in a very useful temperature region of 70 °C.

Long term thermal stability testing

From the preliminary DSC screening procedure a number of PCMs which melted in the 60–90 °C range and had acceptable enthalpies of fusion were identified for further testing, namely stearic acid (Neofat 18S), naphthalene, acenaphthene, 12-hydroxy stearic acid, diphenyl, Hoechst F wax and slack-wax.

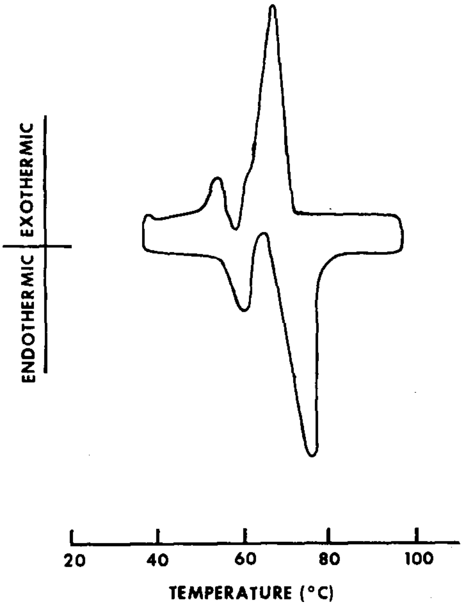

Fig. 7. DSC trace of tristearin.

The principal test used for assessing these materials was an examination of their long-term cycling stability. To assess the chemical stability of the organic materials samples were subjected to continuous melting/freezing cycles on the DSC. By monitoring the areas of the endothermic peak, any degradation of the material could be detected. The value of this screening procedure is that materials which degrade are unlikely to be suitable for solar storage applications. The system outlined allowed the thermal stability of a candidate PCM to be assessed, with one week of laboratory testing being roughly equivalent to one year's cycling in a solar storage system.

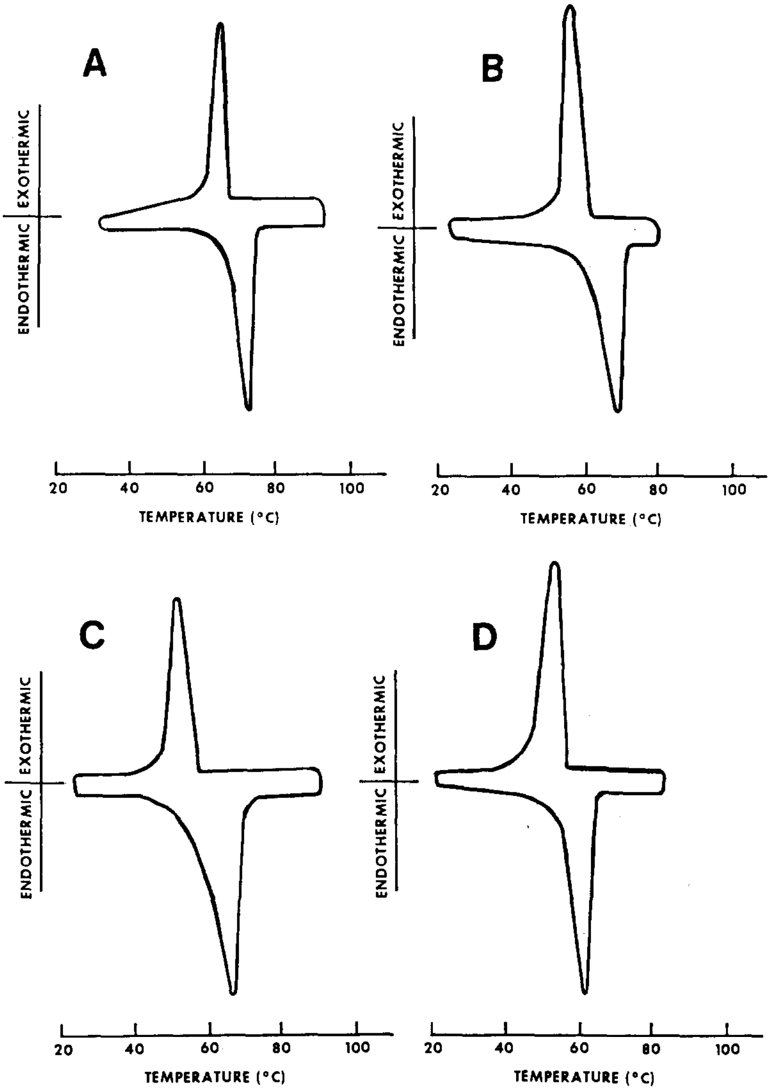

Fig. 8. DSC trace of stearic acid obtained from different sources: (A) Neofat 18S; (B) Crodacid; (C) A.R. grade ex Ajax, Australia; (D) B.D.H. general purpose reagent.

TABLE 5

Thermal stability cycling studies on candidate PCMs

Material	Number of cycles	Constancy of enthalpy of fusion
Carnauba Wax	240	15% Loss
12-Hydroxy Stearic Acid	230	30% Loss
Acenaphthene	230	Constant
Stearic Acid (Neofat 18S)	230	Constant
Hoechst F Wax	200	Constant
Naphthalene	220	Constant
Diphenyl	100	Constant
Deoiled Slackwax	100	Constant

A list of candidate PCMs examined by this technique is given in Table 5. Evidently there is no significant decrease in the heat of fusion for stearic acid (200 kJ kg^{-1} averaged over 220 cycles compared to a literature value of 198 kJ kg^{-1} [17]). This was verified by a plot of the raw data obtained for the enthalpy of melting against cycle number for stearic acid (Fig. 9). No significant downward trend was observed, and this was found to hold for 1000 heating/cooling cycles. Other materials which demonstrated a stable heat of fusion after intensive cycling included naphthalene, although this was dependent upon the quality of the hermetic seal on the sample pan, and the Hoechst F wax. Additionally the slackwax, acenaphthene and diphenyl demonstrated good stability when subjected to thermal cycling.

A material that did degrade was the 12-hydroxy stearic acid. While the cause of failure was not investigated thoroughly, the development of a second peak in the DSC trace (see Fig. 10), suggested a decomposition product. The heating/cooling cycling may have caused the elimination of water forming an olefinic carboxylic acid. Whatever the precise mechanism, there has been a significant change in the performance of the 12-hydroxy stearic acid and this would preclude its use in a practical application.

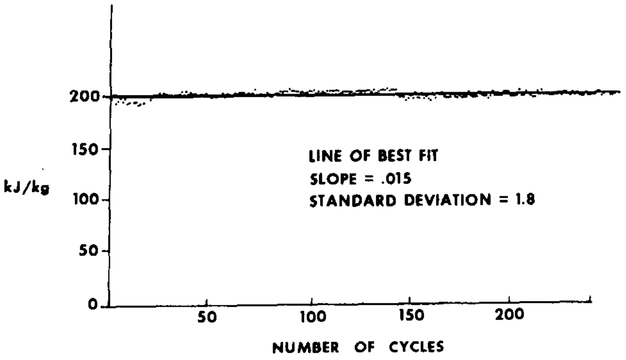

Fig. 9. Variation of enthalpy of fusion of stearic acid over 230 heating–cooling cycles.

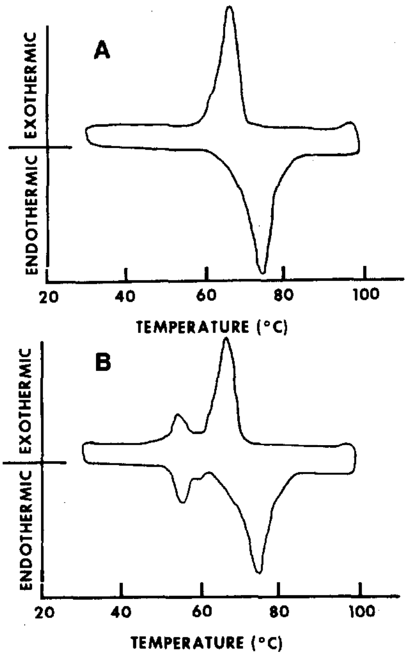

Fig. 10. DSC traces of 12-hydroxy stearic acid: (A) first heating/cooling cycle; (B) after 220 heating/cooling cycles.

Flash point determination

One of the factors that may preclude an otherwise suitable organic PCM from commercial application is that it possesses a high fire hazard. The US Department of Housing and Urban Development [18] states that "temperatures attained by fluids in solar systems under operating systems and no flow conditions shall not exceed a temperature which is 100 °F (42.5 °C) below the flash point of the fluid".

Hence, a knowledge of flash points is critical to the study of practical PCMs. Flash point determinations were carried out as part of the detailed screening process on PCMs that showed good long term thermal stability, the results obtained are given in Table 6. It can be seen that waxes generally

TABLE 6

Flashpoint data on candidate PCMs

Material	Flash point (°C)
Hoechst F Wax	250
Stearic Acid (Neofat 18S)	196
Naphthalene	106
Acenaphthene	120
Diphenyl	124
Deoiled Slackwax	200

exhibited favourable flash points in relation to melting point, the Hoechst F wax having a flash point of some 170 °C above its melting range, and the result for stearic acid was also favourable. However, naphthalene and acenaphthene have difference values of 15 and 22 °C, respectively, and were hence not permissible. Diphenyl had a difference value of 50 °C and could be used, although the margin of safety is not great.

CONCLUSIONS

From the laboratory testing programme three candidate PCMs, stearic acid (Neofat 18S), slackwax and Hoechst F wax, were selected for further testing on a small-scale test rig.

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