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AN EVALUATION OF PHASE CHANGE MICROCAPSULES FOR USE IN ENHANCED HEAT TRANSFER FLUIDS

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ABSTRACT

The results of an experimental study to evaluate the properties of microencapsulated phase change materials have been presented. Two phase change materials, n-eicosane and stearic acid, have been used in the study. The microcapsules were manufactured with two different wall thicknesses, comprising of approximately 15% and 30% of the total microcapsule volume. Three different microcapsule sizes ranging from 50μ to 250μ have been considered. The microcapsules with thinner walls are unable to withstand repeated thermal cycling past the melting point. However, the microcapsules with thicker walls were found to be both structurally as well as thermally stable.

Introduction

Heat transfer augmentation is an extremely important problem in engineering. As a result, numerous techniques to increase heat transfer rates have been developed over the years. Recent studies [e.g. 1,2] have suggested that heat transfer can be greatly enhanced by adding microcapsules of phase change materials to a pure fluid. This enhancement is due to a combination of four factors: the often higher thermal conductivity of the added particles, the increased microconvection due to the particles, a higher effective specific heat during the phase change process and finally the greater temperature difference that is maintained as the phase change material melts/solidifies.

In order to develop phase change material suspensions for use as heat transfer fluids, it is necessary to investigate the feasibility of manufacturing microcapsules which can be used for such applications. The microcapsules must be manufactured such that their thermal properties remain constant, and they withstand the mechanical stresses caused by repeated thermal cycling about the melting point. In addition to these structural and

thermal stability requirements, it may also be necessary that these microcapsules be manufactured to certain tolerances as required for a particular applications. Some investigations in these directions have been done prior to this study [3-6]. Unfortunately, these were extremely limited in scope and their results are also not available widely. Results of a study to evaluate the stability of microcapsules which may be used for heat transfer fluids are presented in this paper.

The Microcapsules

There are a numerous techniques, both chemical and physical, for manufacturing different types of microcapsules. After consulting with a number of manufacturers throughout the U.S. and studying their capabilities, Ronald T. Dodge Co., Dayton, Ohio, was chosen to supply the microcapsules. The manufacturing technique was based on U.S. Patent No. 3,726,803 entitled "Capsule Wall Treating Process Utilizing Condensation Polymerization and Capsule Product," assigned to Robert G. Bayless and Donald D. Emrick of the National Cash Register Company, Dayton, Ohio.

The phase change materials in the microcapsules must have characteristics similar to those used in thermal energy storage applications. Based on previous work [7-8], n-eicosane and stearic acid were selected. In practice, for a specific heat transfer application, the phase change material must be selected so that the melting point lies in the operating temperature range. The coating material, cross-linked polyvinyl alcohol was specified by the manufacturer. Six different samples of microcapsules were finally made to the following specifications:

TABLE I
Microcapsule Specifications

No.	Core material	Encapsulating material	Diameter(μm)	Wall thickness % by volume
1.	n-eicosane	Cross-linked PVA	50	30
2.	n-eicosane	----- " " ------	100	30
3.	n-eicosane	----- " " ------	250	30
4.	Stearic acid	----- " " ------	50	15
5.	Stearic acid	----- " " ------	100	15
6.	Stearic acid	----- " " ------	250	15

Description of Tests

In order to evaluate the stability of the microcapsules, two tests were done:

Thermal Cycling Tests: The microcapsules were repeatedly cycled through the melting point of the phase change material. These were done in a Delta Design Environmental Test Chamber Model 800. Each cycle consisted of a 30 minute soaking period at room temperature (23°C $\pm$2°C) followed by an identical 30 minute soaking period at 90°C ($\pm$2°C). Each sample was tested through 10, 50 and 100 cycles, both in a dry condition as received, as well as in a suspension in water.

Radiation Tests: Radiation tests have been done on a single sample of microcapsules (n-eicosane 100μ) in order to study any effects of radiation on the microcapsules. This test is useful for possible future applications in avionics cooling for military aircraft. It consisted of a 10^6 rad 1MeV gamma radiation from a cobalt-60 source.

Methods of Evaluation Before and After Tests

Samples of microcapsules as received, and after each of the tests above, were carefully evaluated to study the feasibility of their use in heat transfer fluids. The following investigations were done:

Visual and Photographic Studies: In addition to qualitative visual inspection of the samples, the microcapsules were photographed using an Unitron Series-N optical microscope before and after the tests. A scanning electron microscope (Model ISI-DS-130) was also used to evaluate the thickness of the microcapsule coating as received. In addition, sections of microcapsules were also studied under transmission electron microscope (Model Philips 300).

Differential Scanning Calorimetry: Differential calorimetry tests are required in order to investigate the variation of effective specific heat with temperature. These tests have been done on dry samples with n-eicosane as the core material using a Netzsch STA at Netzsch, Inc., Pennsylvania. These dry samples consisted both uncycled and cycled microcapsules obtained from the thermal cycling tests. The following were the specifications of the differential calorimetry tests:

One cycle for given sample: Low temp → High temp → Low temp
Lower temperature: Room temperature (Below 30°C)
Upper temperature: 75°C
Temperature variation: 5.0°C/minute during the heating phase
Cooled in ambient air during the cooling phase

Sizing of Microcapsules: Sizing of the microcapsules, as received, was done using a Coulter Multisizer in order to find the typical tolerances of the manufacturing process. Sizing of the samples which had completed the thermal cycling tests in water were also done at a later stage. Statistical results including the mean and median diameters of the particles, the variance, standard deviation and skewness of the samples were obtained for all cases.

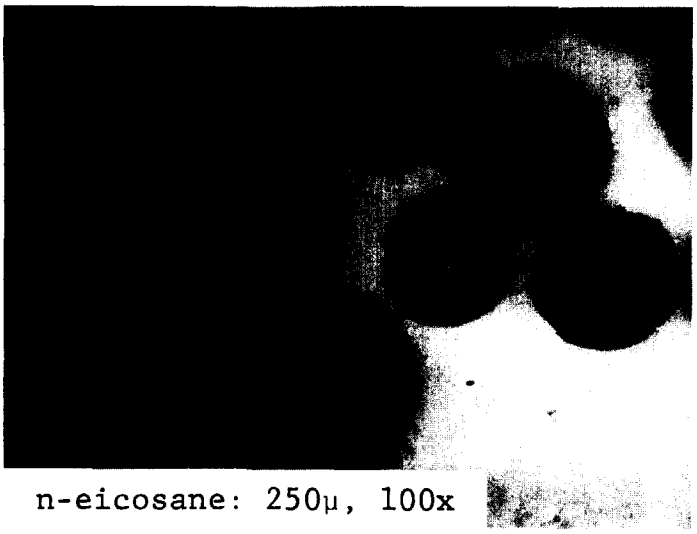
Results and Discussion

Results of Visual and Photographic Inspection: The microcapsules come as a free-flowing light brown powder. After the thermal cycling tests, the dry samples were found to coagulate in all cases. However, the suspension of microcapsules in water behaved in a different fashion. For the case of n-eicosane microcapsules where the wall thickness was 30%, a small portion of the capsules (~ 10%) were found to fail, and the broken shells would settle to the bottom. The remainder of the microcapsules remained in suspension as before, and being lighter than water, would rise to the surface after a period of time. In contrast, a large fraction of the stearic acid microcapsules was found to have failed the thermal cycling tests and relatively large pieces of stearic could be seen floating in the water. Furthermore, unlike the n-eicosane microcapsules, the water would no longer be clear, but would have a cloudy appearance.

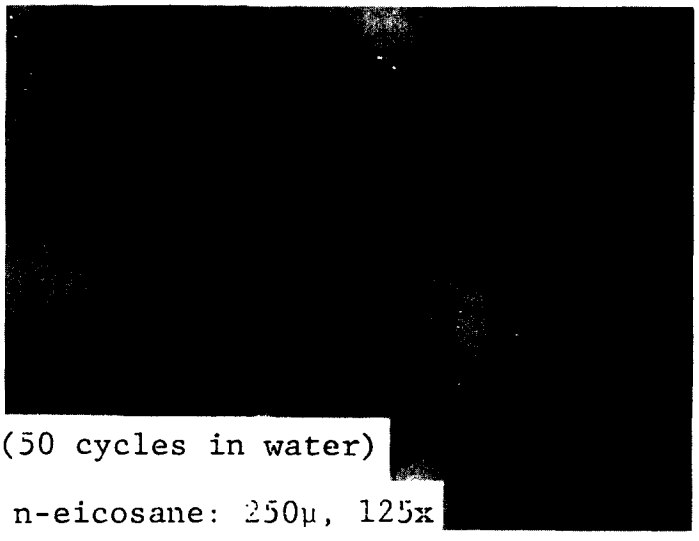
Photographs of the microcapsules before and after the thermal cycling tests taken using an optical microscope are shown in Fig. 1. These also tend to confirm that n-eicosane microcapsules survived the thermal cycling tests, but the stearic acid microcapsules were structurally not sufficiently strong. The probable reason for this is the reduced wall thickness for the stearic acid microcapsules, since in both cases, the change is specific volume during melting is of the same order (~10%).

The single radiation test of the 100μ n-eicosane sample showed no obvious visible change in the microcapsules, either under the microscope or to the naked eye. Thus, the microcapsules seem to be structurally stable under radiation.

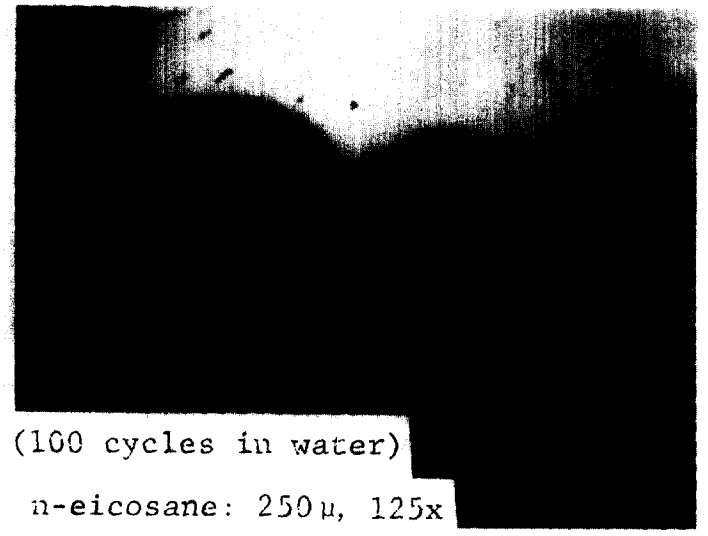
In order to further investigate structure of the microcapsules, samples of microcapsules were carefully investigated under scanning and transmission electron microscopes. Photographs are shown in Fig. 2. Typical thicknesses of the microcapsule walls are seen to be about 5μm, or about 5% of the microcapsule diameter.



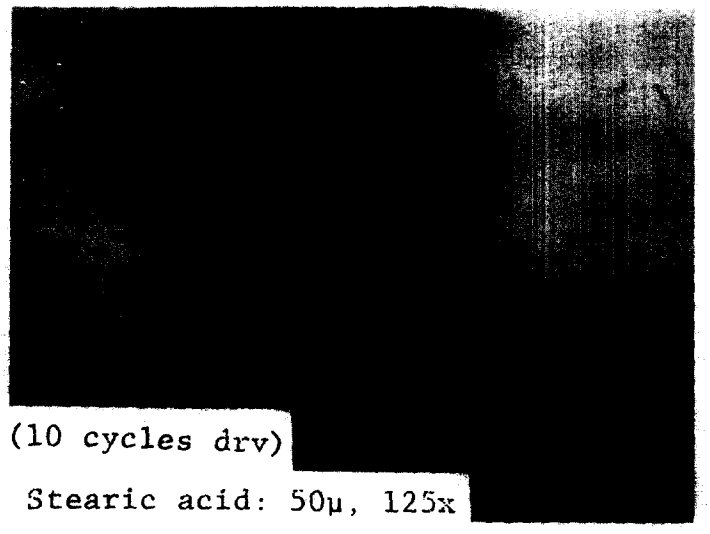
a) Before thermal cycling



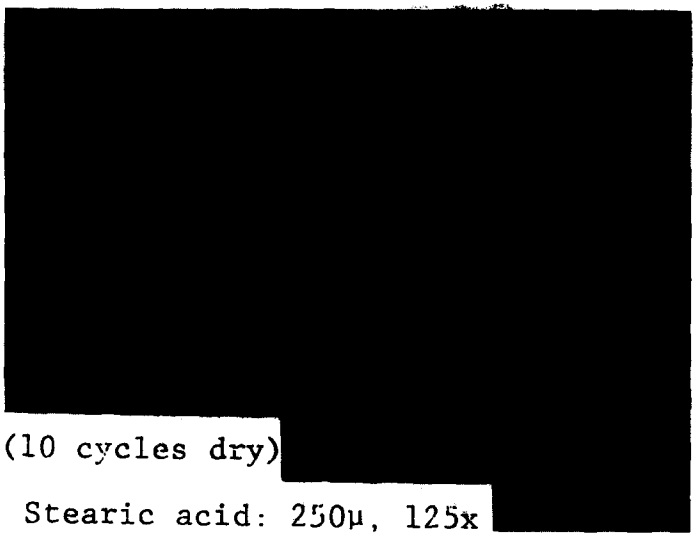
b) After 50 cycles



c) After 100 cycles



d) Broken/agglomerated stearic acid microcapsules



e) Broken stearic acid microcapsules

FIG 1

Photographs of microcapsules before and after thermal cycling

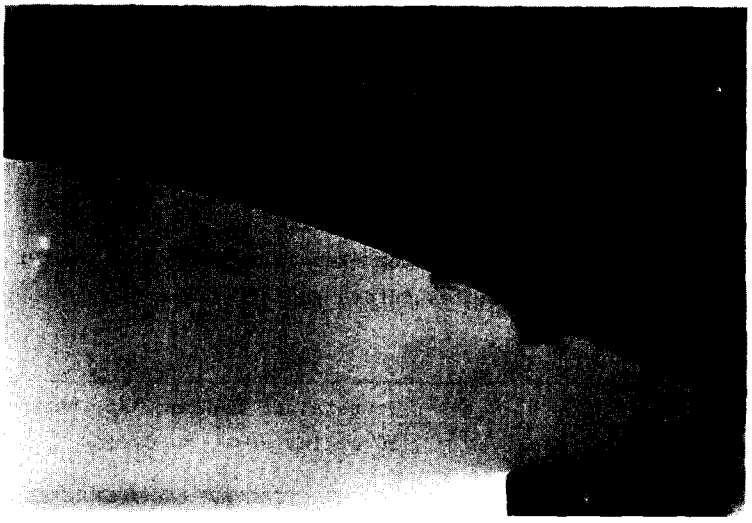


FIG. 2a

TEM micrograph of microcapsule section

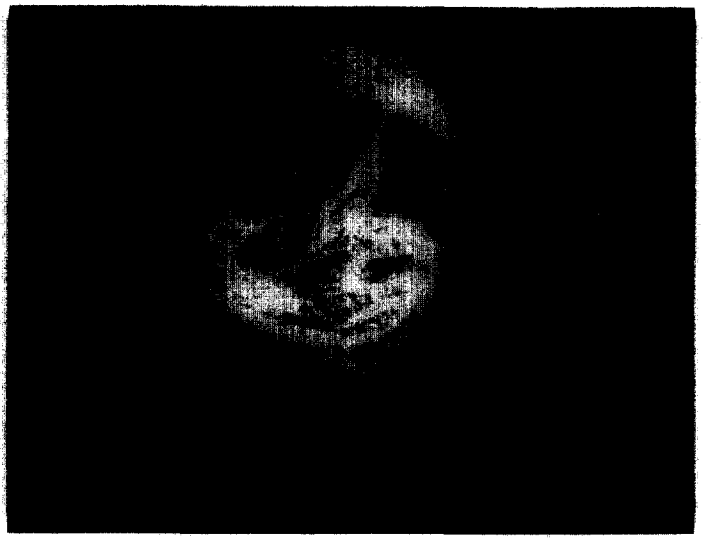


FIG. 2b

SEM micrograph: Broken microcapsule (n-Eicosane 50μsample (192x))

Results of Differential Calorimetry Tests: A typical case is shown in Fig. 3. Table II summarizes final data on the heat of transition of the different samples. The variation in the heat of transition before and after cycling is less than 10% in all cases, with the temperature for the maximum effective specific heat lying within $\pm$1.5K. Some discrepancy in the heat of transition is, of course, inevitable since a sharp transition point is not seen in any case, and it is therefore necessary to estimate the transition region.

TABLE IIA

Temperature for Maximum (Effective) Specific Heat for n-Eicosane Samples Before and After Thermal Cycling

n-Eicosane Sample	Temperature for max. sp. heat (°C)			
	As Received	10 cycles	50 Cycles	100 Cycles
50μ	43.4	42	40.8	41.9
100μ	42.5	42.9	42.7	42.8
250μ	43.7	44.8	44.3	44.0

TABLE IIB
Heat of Transition for Different Samples of n-Eicosane
Before and After Thermal Cycling

n-Eicosane Sample	Heat of Transition ($x10^3$ kJ/kg)[1]			
	As Received	10 cycles	50 Cycles	100 Cycles
50μ	218.7	N/A	209.6	192.4
100μ	240.4	255.9	260.6	265.5
250μ	275.6	269.6	267.0	285.1

[1] Initial and final points of the transition region are approximated since sharp transition points are not seen for any of the samples.

Based on the above results, it can be concluded that the microcapsules are thermally stable even after repeated thermal cycling. However, one additional point must be noted from Fig. 4. This shows two continuous DSC cycles of a n-eicosane sample (50μ, after 10 cycles). Supercooling can be clearly seen to occur during the freezing process, a factor that may have detrimental effects on the heat transfer under certain circumstances.

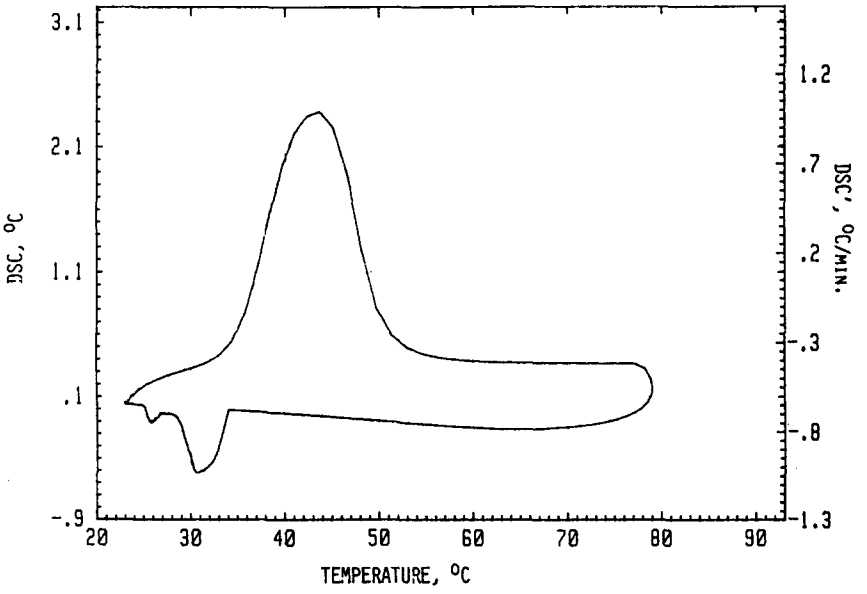


FIG. 3

DSC Plot: n-Eicosane, 250μ (As received)

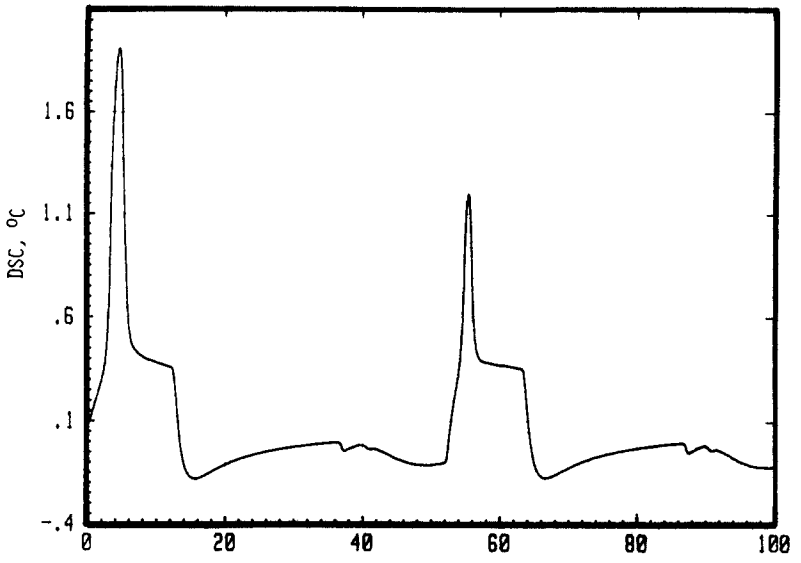


FIG. 4

DSC Plot: n-Eicosane, 50μ (After 10 cycles)

TABLE III

Comparison of Results Before and After Radiation Tests
(10^6 rad 1MeV gamma radiation from a cobalt-60 source)
(100μ n-Eicosane Sample)

n-Eicosane (100μm)	Heat of Transition (x10^3 kJ/kg)[1]	Temp. for max. sp. heat (°C)
As received	240.4	42.5
After 10 cycles	255.9	42.9
After 50 cycles	260.6	42.7
After 100 cycles	265.5	42.8
AFTER RADIATION TEST (Without thermal cycling)	166.5	39.7

[1] These values are approximate since a sharp transition point is not seen for any of the samples. The initial and final points of the transition region are therefore approximated.

Results of the radiation test, summarized in Table III, are not as positive. It can be seen that the sample deteriorated during the thermal cycling with a reduction in the heat of transition of more than 25%. Further work may therefore be needed in this area to ensure insensitivity to radiation.

Microcapsule Sizing Tests: Sizing of all the microcapsules as received and after thermal cyling in water were done using a Coulter Multisizer. A comparison of these parameters before and after cycling are summarized in Table IV. This data can be used to quantify the percentage of failure of the microcapsules as a result of thermal cycling. It can also be seen that the manufacturing technique used by Ronald T. Dodge Co. results in relatively poor tolerances. Fortunately, a theoretical analysis of the phase change suspensions suggest that the microcapsule size is not a critical parameter in forced convection heat transfer [2].

Recommendations for Future Work: A number of additional tests would be useful before phase change microcapsules can be used in practice. Unlike natural convection systems, fluid shear and possible impact by the impeller in a pump may cause significant stresses in forced convection systems. Tests to evaluate the resistance to such shear and impact forces will be required. Limited testing under actual pumping conditions have been done before [3-6], but it may be more useful to investigate the effects of the shear and impact forces separately. The effects of thermal cycling on another extremely important parameter, the thermal conductivity, may also be needed. However, since the specific heat has been found to remain more or less unchanged, it appears that the microcapsule wall does not react with the phase change material during the cycling process. Thus, it is probable that the thermal conductivity will also remain approximately constant after repeated thermal cycling.

It must also be noted that similar tests will be needed to investigate the compatibility of the microcapsules with different suspending fluids. The manufacturer, Ronald T. Dodge Co. has also pointed out a limitation of these microcapsules: the suspending fluids must be selected such that the phase change material does not dissolve in it. In addition, tests must also be done for microcapsules manufactured using other techniques. Finally, tests may need to be done over a much larger number of cycles.

Table IV
Comparison of Microcapsule Sizing Results
Before and After Thermal Cycling

Sample		Median (μm)				Mean (μm)				Std Dev (μm)			
No. of cycles		0	10	50	100	0	10	50	100	0	10	50	100
n-eicosane (50μ)	a	37	41	37	37	37	43	37	38	1.0	.21	.16	.17
	b	25	26	24	24	24	26	21	22	1.0	.17	.24	.23
n-eicosane (100μ)	a	124	107	95	99	114	109	88	94	1.0	.13	.17	.17
	b	12	78	11	11	16	62	17	14	1.1	.27	.30	.34
n-eicosane (250μ)	a	215	217	215	210	195	213	210	205	1.0	.11	.12	.12
	b	68	57	45	29	57	63	55	43	1.2	.43	.43	.42
Stearic acid (50μ)	a	58	88	64	64	55	103	63	63	1.1	.33	.19	.19
	b	9.2	33	35	33	12	34	35	33	1.1	.21	.20	.20
Stearic acid (100μ)	a	117	116	114	114	110	111	110	109	1.0	.13	.14	.13
	b	14	49	37	47	23	48	42	46	1.2	.32	.32	.32
Stearic acid (250μ)	a	147	173	155	165	135	161	135	153	1.0	.18	.22	.18
	b	73	27	30	28	69	33	34	35	1.1	.32	.28	.32

Notes:

1. Results "a" and "b" are calculated using a volume weighted and an unweighted (number) distribution of diameters respectively.

2. Large pieces (~ 1-10mm) of agglomerated broken/unbroken microcapsules found in the cycled stearic acid samples (Samples 4-6) are not included in the analysis since the range of sizes would then be excessive.

Conclusions

Results from an experimental study to investigate the properties of phase change microcapsules have been presented in this paper. Microcapsules with thicker walls (30% of total volume) were found to be structurally and thermally stable for at least 100 cycles through the melting point of the phase change material. However, microcapsules with walls of 15% of the total volume were found to fail these cycling tests. Results of a radiation test (10^6 rad 1MeV gamma radiation from a cobalt-60 source) showed that radiation causes some deterioration of the thermal properties of the microcapsules.

Based on these results, it can be concluded that phase change microcapsules can be used in practical heat transfer applications.

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