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MACRO— ENCAPSULATION OF PCM

**QUARTERLY REPORT
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MACRO-ENCAPSULATION OF HEAT STORAGE
PHASE-CHANGE MATERIALS
for Use in Residential Buildings

Second Quarterly Progress Report

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by

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16. Abstracts Objectives are to assess the feasibility of macro-encapsulated PCM's for residential solar systems, to develop and evaluate such materials. Encapsulant materials under consideration are multilayer flexible plastic films, steel cans, and plastic bottles. PCM's under study are $Mg(NO_3)_2 \cdot 6H_2O$, naphthalene-benzoic acid eutectic, stearic acid, $Mg(NO_3)_2 \cdot 6H_2O - NH_4NO_3$ eutectic, and $CaCl_2 \cdot 6H_2O$. Compatibility studies between the PCM's and encapsulant materials are underway. A test device has been designed and is under construction.			
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FOREWORD

The work described in this report is an extension of a basic effort already performed under contract NSF-C906. The general objectives are: 1) to assess the technical and economic feasibility of encapsulated phase change materials (PCM's) for storing heat in residential solar energy systems, and 2) to develop and evaluate such encapsulated phase change materials.

The project involves three tasks:

Task 1 - Materials selection, including a limited literature search, selection of candidate phase change materials, and selection and characterization of encapsulating materials.

Task 2 - Procurement of phase-change and encapsulating materials, encapsulation studies, and testing of the encapsulated material.

Task 3 - Preliminary design and economic evaluation of a residence-sized heat storage sub-system.

Task 1 has been completed, and Task 2 efforts are in progress.

I. COMPATIBILITY OF PHASE CHANGE MATERIALS AND
ENCAPSULATING MATERIALS

The PCM's under study are listed in Table I.

TABLE I
PHASE CHANGE MATERIALS
SELECTED FOR STUDY

Materials	m.p., °C	ΔH , cal./g	Cost, ¢/lb.
$Mg(NO_3)_2 \cdot 6H_2O$	89	38	15
Naphthalene + Benzoic Acid	67	35 (est.)	15
Stearic Acid Mix	60	48	25
$Mg(NO_3)_2 \cdot 6H_2O + NH_4NO_3$	52	40 (est.)	10
$CaCl_2 \cdot 6H_2O$	27	46	5

The following packaging materials are being evaluated as encapsulants for these PCM's:

R-2 Retort Film, a laminate of 3 mil polyethylene,
.35 mil Al foil, and .5 mil polyester.

Alure MD Film, a laminate of 2 mil medium density
polyethylene and .5 mil aluminized polyester.

Alure LD Film, a laminate of 3 mil low density
polyethylene and .5 mil aluminized polyester.

Plastic Bottle, 16 oz. high density polyethylene.

Aerosol Can, 2.5 x 6.5 seamed steel.

Aerosol Can, 2.5 x 6.5 drawn steel.

A. Film Evaluation

The compatibility of PCM's with laminated plastic films was tested by fabricating 3 1/4" x 5 3/4" pillows filled with the molten PCM's, and storing them at a temperature 5-15°C above the melting point of the PCM. As shown in Table II, the lower-melting inorganic materials proved compatible, while the higher-melting materials attacked the heat sealed areas at the seams.

TABLE II
EVALUATION OF PLASTIC FILMS WITH PCM's

Materials	R-2 Retort Film	Alure MD	Alure LD
Mg(NO ₃) ₂ ·6H ₂ O, 100°C.	Seams Leak in 7 days	—	Seam Failed, 1-3 days
Naphthalene + Benzoic Acid, 90°C.	PCM migrates thru seam, 1 day	—	—
Stearic Acid mix, 75°C	Leaked out, 13 days	Seam rupture, 1 day	—
Mg(NO ₃) ₂ ·6H ₂ O + NH ₄ NO ₃ , 70°C	OK, 32 days	—	OK, 32 days
CaCl ₂ ·6H ₂ O, 45°C	OK, 32 days		OK, 32 days

Attempts to test the strength of the seams, before and after exposure, were unsuccessful. Films either broke at the seam, tore, or delaminated.

B. Plastic Bottle Evaluation

The compatibility of PCM's with high density polyethylene was studied by cutting 4" long "dog bone" test bars 1/8" wide in the test area. These specimens were formed from the sides of

the plastic bottles and selected to be similar in thickness. Tensile strength was measured before exposure, after dry exposure to the test temperature, and after immersion 4 weeks at the test temperature in the liquid PCM. Test temperatures were the same as used for the plastic films. As outlined in Table III, only the lower-melting storage materials are completely satisfactory. The two lower-melting PCM's are compatible with the bottle material.

TABLE III
EVALUATION OF PLASTIC BOTTLES WITH PCM's

Materials	Storage Temp., °C	Tensile Strength, Psi
None	20	2660
None	100	Failed: brittle
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	100	3200; brittle
None	90	2860
Naphthalene + Benzoic Acid	90	2200; 8-13% wt. gain
None	75	2820
Stearic Acid Mix	75	2800; 5% wt. gain
None	70	2860
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$	70	2940
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	45	2870

The two next higher-melting materials will not weaken the bottles, but dissolve into the plastic. No conclusion can be drawn about the highest-melting PCM, since the bottle itself fails at this temperature.

C. Steel Can Evaluation

To determine the compatibility of PCM's with metal cans, 1" x 3" coupons were cut from the sides of seamed and drawn aerosol cans. No surface treatment, other than washing with acetone, was used. The coupons were immersed in molten PCM's for 31 days and the corrosion rate determined by weight loss. Tests have been completed for the two lower-melting materials, and are in progress for the other PCM's. Table IV shows the results. The corrosion rates obtained are quite satisfactory for the intended application.

TABLE IV
EVALUATION OF STEEL CANS WITH PCM's

Materials	Temp. °C	Corrosion Rate, lbs./ft. ² /day	
		Seamed Cans	Drawn Cans
Mg(NO ₃) ₂ ·6H ₂ O + NH ₄ NO ₃	70	1.9 x 10 ⁻⁶	2.6 x 10 ⁻⁶
CaCl ₂ ·6H ₂ O	50	4.9 x 10 ⁻⁷	4.0 x 10 ⁻⁷
CaCl ₂ ·6H ₂ O*	50	4.5 x 10 ⁻⁷	3.3 x 10 ⁻⁷

*0.2% Corrosion inhibitor added

Qualitatively, the samples immersed in stearic acid and in naphthalene-benzoic acid eutectic appear not to be corroding. Samples in magnesium nitrate hexahydrate began to corrode visibly shortly after the test began. The pH of the reagent grade material was measured and found to be 6.4. A sample of Mg(NO₃)₂·6H₂O was prepared by Dow's Michigan Division laboratories, intended to be representative of commercial grade material,

containing a nucleation additive. The pH of this material was 10.0. Compatibility tests have been started with this material. Qualitatively, much less corrosion is evident, however, some discoloration has occurred.

D. Status of Material Selection

Table V summarizes the present status of the materials compatibility work. For $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} - \text{NH}_4\text{NO}_3$ eutectic, all the encapsulating materials appear satisfactory. For the other PCM's no satisfactory encapsulant is now available, but it is presumed that steel cans will pass the tests with stearic acid and naphthalene-benzoic acid eutectic. For commercial grade $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, steel cans may be suitable, but the issue is not yet resolved.

TABLE V
SUMMARY OF MATERIAL COMPATIBILITY WITH PCM's

Encapsulant Material	PCM MATERIAL				
	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$	Stearic Acid	Naphthalene + Benzoic Acid	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
Polyethylene Bottle	OK	OK	Weight Gain	Weight Gain	Embrittles
R-2 Retort Film	OK	OK	Seam Leaks	Seam Migration	Seam Leaks
Alure LD Film	OK	OK	—	—	Seam Leaks
Alure MD Film	—	—	Seam Rupture	—	—
Drawn Steel Can	OK	OK	OK*	OK*	?*
Seamed Steel Can	OK	OK	OK*	OK*	?*

*Tests incomplete

We have made a tentative pairing of PCM's with encapsulant materials for purposes of future studies on encapsulated PCM's and sub-scale heat storage unit tests. Choices were made such that work will continue on each type of encapsulant. Pairings are given in Table VI.

Stearic acid and naphthalene-benzoic acid eutectic freeze in the same temperature range. Originally, both were selected for compatibility studies, with plans to drop the less promising material. Both have similar compatibility properties. The eutectic supercools slightly, but this is not serious. Since stearic acid's price is nearly twice that of naphthalene-benzoic acid, we will de-emphasis work on the fatty acid mixtures and precede with the aromatic eutectic.

TABLE VI
TENTATIVE SELECTION OF PCM-ENCAPSULANT PAIRS

Phase Change Material	Encapsulating Medium
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	High Density Polyethylene Bottle
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$ Eutectic	R-2 Retort Film
(a)(b) Stearic Acid Mix	Seamed Steel Aerosol Can
(a) Naphthalene/Benzoic Acid Eutectic	Seamed Steel Aerosol Can
(c) $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Drawn Steel Aerosol Can

(a) Assumes success of tests now in progress.

(b) This PCM changed to back-up status.

(c) Assumes success of tests now in progress, otherwise glass bottles will be used.

II. ENCAPSULATED PCM HEAT STORAGE TEST DEVICE

A sub-scale energy storage device is under construction. It is designed such that heat storage data can be collected in accord with NBS and ASHRAE recommended procedures. Figure 1 is a drawing of this test apparatus. Construction should be completed by about July 1.

III. PLANS

The following work is planned for the next quarter:

1. Materials compatibility tests will be completed.
2. Further tests will be run on potential hazards of nitrate materials.
3. Long-range melt-freeze cycling tests will continue.
4. Sufficient quantities of encapsulated $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ will be prepared for the storage test device.
5. Construction of the storage test device will be completed.

IV. CONCLUSIONS

Compatible encapsulating materials are believed available for the PCM's being studied, except perhaps for $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Containment becomes more difficult as the melting point increases. Organic PCM's are difficult to encapsulate in plastic film or plastic bottles, because of exudation.

Figure 1

Test Apparatus for Encapsulated
Phase Change Materials.

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