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**OAK
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**Life and Stability Testing of
Packaged Low-Cost Energy
Storage Materials**

Galen R. Fryinger

MASTER

**OPERATED BY
UNION CARBIDE CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY**

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LIFE AND STABILITY TESTING OF PACKAGED LOW-COST
ENERGY STORAGE MATERIALS

Galen R. Frysinger

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ABSTRACT

The Institute of Energy Conversion, in cooperation with the Du Pont Company, has developed a low-cost laminated plastic film which is used to contain a Glauber's salt-based phase change thermal energy storage material in sausage-like containers called Chubs. This report describes the results of tests performed on the Chub packages themselves and on the thermal energy storage capacity of the packaged phase change material. From the test results, a set of specifications have been drawn up for a film material which will satisfactorily contain the phase change material under anticipated operating conditions. Calorimetric testing of the phase change material with thermal cycling indicates that a design capacity of 45 - 50 Btu/lb for a ΔT of 30°F can be used for the packaged material.

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EXECUTIVE SUMMARY

The University of Delaware has developed a thermal energy storage system which uses a Chub package to contain the phase change thermal energy storage material. The Chub is fabricated from a low cost laminated plastic film which has a low rate of water vapor transmission.

This report describes the results of testing performed on a phase change thermal energy storage material contained in Chubs. The first part of the report discusses the characteristics that the laminated film must have in order to successfully contain the phase change material for long periods of time and the second part describes calorimetric testing of the phase change material.

Laminated Plastic Film and Chub Package

A set of criteria defining acceptable characteristics of the laminated film are given with a brief discussion of the reason for each criterion. A list of test methods to ensure that the laminate meets the necessary criteria is given. A detailed discussion of a test program designed to measure the moisture retention properties of the qualified laminate is given and it is concluded that a laminate consisting of several layers of polyethylene and metallized polyethylene terephthalate performs satisfactorily.

A program was performed which tested the ability of the Chub package to withstand extremes of temperature, handling and transportation. The above-mentioned laminated film was found to perform satisfactorily.

The Chub package was tested for its ability to withstand prolonged thermal cycling. Some problems were encountered with leakage at the end clips of the Chub in these tests. Several types of secondary seals of the end clips were tested and found to resolve the problem satisfactorily. Aside from this mechanical problem, which is due to shortcomings of the packaging machinery, the laminate performed satisfactorily.

Thermal Energy Storage Performance

The phase change material that was tested is a mixture of sodium sulfate, water and other salts which nominally undergoes a phase change transition at 55°F. The material was tested as a function of thermal cycling in three different, complementary calorimeters:

- 1) A differential scanning calorimeter
- 2) A laboratory scale liquid calorimeter
- 3) A large scale air calorimeter

For convenience, all calorimetric measurements were normalized to a ΔT of 30°F.

It was found that the results obtained from the differential scanning calorimeter were inconsistent and difficult to interpret. It was concluded that this method is not useful for measuring thermal energy storage capability with respect

to thermal cycling. Nonetheless, the technique may be useful for quality control purposes such as might be necessary during large scale production of the Chub packages. Differential scanning calorimetry was also used to test the effects of prolonged vibration on the Chub packaged phase change material. It was concluded that no significant change in the performance of the material due to vibration could be determined from this test.

Test results from the liquid calorimeter correlated well with results obtained from the large scale air calorimeter. The material, with one exception, showed a decline in thermal energy storage capability with cycling. For use in design considerations, a nominal capacity of 45-50 Btu/lb is recommended.

The performance of the material with cycling can be improved as can be seen from two pieces of evidence:

- 1) In all cases, the capability of the material is greater than or equal to 70 Btu/lb for the first thermal cycles.
- 2) A batch of Chubs which had been cycled more than 400 cycles stored more than 70 Btu/lb.

Specification and Test Procedures

A detailed listing of the specifications for the laminated plastic film, the Chub package and the mixing phase change material is given. In addition, a series of test procedures are given to ensure that the Chubs are fabricated properly.

INTRODUCTION

This report presents the results of the life and stability testing research performed at the Institute of Energy Conversion (IEC) during 1978-79 on a thermal energy storage phase change material. This work was performed as part of sub-contract # 7585 between Oak Ridge National Laboratory and the Institute of Energy Conversion. As part of its thermal energy storage research program, the Institute is investigating a storage assisted air conditioning system which, with the aid of a thermal energy storage unit using a phase change material, will enable the user to defer the consumption of electrical power to off-peak hours. The advantages of such load shifting or load leveling are well known and will not be discussed here.

The thermal energy storage unit consists of a bin, approximately 125 ft³ in volume, filled with a 52°-55°F Glauber's salt based phase change material packaged in sausage-type packages called Chubs. The energy storage bin is connected into the ductwork of a residence and suitable thermostatic controls are employed to allow the unit to operate in the desired manner. Workers at the IEC have tested this concept in various configurations in several different installations over the past few years and over this period of time the Chub package for the phase change material was developed.

The purpose of the project reported here was to test the capability of the Chub package to contain the phase change material under simulated operating conditions for an adequate period of time. The research was divided into two major areas: testing and qualification of the laminated plastic film and the Chub package; and testing of the thermal energy storage capability of the Chub package filled with the phase change material. In addition, a detailed list of specifications from the Chub package and laminated plastic film is given.

The report discusses these two objectives in detail; the first part deals with the development and qualification of the laminated plastic film and the Chub package which has been developed in conjunction with E. I. du Pont de Nemours Company (Du Pont) and the second describes the results of testing the phase change material under various conditions.

The successful development of a thermal energy storage package which is long lived and has a large energy storage density will have a significant impact on the solution of the energy problem facing the United States today because it makes load leveling feasible. The ability to defer power consumption to off-peak hours is desirable because it can reduce the consumption of imported petroleum and reduce future capital investments needed for power generation facilities.

1. PACKAGING MATERIAL AND THE CHUB PACKAGE

This section describes the characteristics of the thin laminated plastic film, developed with help from the Du Pont Company, which is used to package the phase change thermal energy storage material. A series of tests were performed which were designed to test the material's capability to successfully contain the phase change thermal energy storage material in Chub packages under a variety of extreme conditions. On the basis of these tests, a set of specifications for the plastic laminate have been generated. The Chubs are prepared by a machine manufactured by Kartridg-Pak of Davenport, Iowa. The machine is used extensively in the food industry for packaging sausages, cheese, etc. Therefore, the laminated film described in this section must be compatible with the operating requirements of the Chub machine.

A. Film Characteristics' Specifications

The laminated film used to package the thermal energy storage material represents about one percent by weight of the finished Chub, yet this thin film (thickness about 102 micrometers, or 0.004 inches) must possess a number of critical properties if the finished Chub is to be fully functional. These film characteristics are:

Ability to form a heat seal - To perform satisfactorily on the Chub machine, the film must be capable of forming a strong, uniform seal when first heated and then cooled on one side by a jet of hot or cold air. To do this, the inner and outer layers of the laminate must have similar melting points and

viscosities at temperatures just above the film's melting point, however, its melting point must be lower than the peak temperature attained at the film interface. These criteria limit the maximum film thickness which in turn limit production on the Chub machine.

Low density polyethylene film, made from resin with a density close to 0.92 g/ml (range 0.919 to 0.922) is preferred for the inside and outside layers of the laminate.

Proper slip - The level of slip (related to the inverse of the coefficient of friction) of the inner and outer plies of polyethylene film in the laminate must be properly controlled. If the slip is too high (coefficient of friction ≤ 0.5) difficulty will be experienced in forming and holding the film tube in position during the heat sealing operation. The presence of surface active additives in high or medium slip film will also interfere with treatment of the polyethylene film that is required to achieve adequate adhesion between the polyethylene layer and the polyester film layer using suitable adhesives.

The low density polyethylene outside layers should be treated for adhesion on one side, and should have a kinetic coefficient greater than 0.50, as measured by ASTM Test Method ASTM D1894.

Physical strength - The 48 or 50 gauge oriented polyethylene terephthalate film used as the core of the laminated film imparts the desired impact strength, puncture resistance, and stiffness to the laminate. The water vapor transmission rate of polyester film of this thickness, while good, can be further improved by adding a film of vacuum deposited aluminum to its surface. This metallized polyester film provides a composite with acceptable water vapor transmission rates.

Adhesion between layers - The overall performance of the laminate is dependent upon good adhesion between adjacent layers. In laminates of polyethylene film and biaxially oriented polyester film, the stress-strain characteristics of the two films are very different. The polyethylene film has relatively low tensile modulus, yield point, and tensile strength at break, but high elongations on the order of 100 to 600 percent. In contrast, the polyester film has a high tensile modulus, high yield point, and high tensile strength at break, but low elongations on the order of 5 to 25 percent at break. The desirable combination of good impact resistance, high tear strength and high tensile strength of the laminate depend on the level of adhesion achieved between the adjacent film layers.

In the Chub package, good adhesion is required over a temperature range of 0° to 65°C (150°F). Adhesion must not be adversely affected by exposure of the cut edge of the laminate to the contents of the Chub. The effectiveness of many common film adhesives depends on completion of a chemical curing reaction before full adhesive strength is achieved. Thus adhesives used in the film laminate, if not adequately cured, may allow penetration of salt solutions into the film-film interface, leading to destruction of the adhesive bond. Permeation of salt solutions into the metallic layer will cause disintegration of the metallic vapor barrier coating and result in an increase in the water vapor transmission rate of the laminate.

As a practical test for adequate adhesion, the film is stretched uniformly beyond the yield point in both machine and transverse directions. Visible separation of the film layers after release of the tensile stress is an

indication of inadequate adhesion. To determine the sensitivity of the adhesive joint in the laminate to chemical attack, a sample of the laminate with freshly cut edges is stored in a hot (150°F) saturated slurry of water, sodium sulfate and borax for several days. If adhesion is acceptable, there will be no visual evidence of delamination or attack of the metallic barrier coating adjacent to the cut edges of the laminate.

Water vapor transmission rate - To obtain a reproducible measure of the moisture vapor transmission rate of the laminate, film samples of known exposed areas are used to seal demineralized water in an aluminum cup. The sealed cup is then placed in a dessicator in a thermostatically controlled oven at 100°F, so that the effective humidity difference across the film is from 100 percent to zero percent. A plot of loss in gross weight with time permits calculations of the film's water vapor transmission rate (WVTR), normally expressed in grams lost per 24 hours per 100 in² of exposed area at 100°F and 100 percent water vapor pressure differential. ASTM Test Method E-96, "Test for Water Vapor Transmission of Materials in Sheet Form," provides a detailed procedure for determining the WVTR.

The film laminate should have a WVTR below 0.10 g/24 hrs/100 in²/100°F and 100 percent RH. High quality laminates with multiple metallized layers should have WVTR values close to 0.03 g/24 hrs/100 in²/100°F and 100 percent RH.

Abrasion resistance - The abrasion resistance of the Chubs is provided by the exterior polyethylene film layer. For polyethylene films in general, abrasion resistance is improved by an increase in the resin density. However,

an increase in resin density increases the resin melting point and decreases film impact resistance. To retain the desired heat seal characteristics, a resin density of 0.920 ± 0.001 represents an acceptable compromise. The use of a thicker outer layer of polyethylene film is another method that can improve the abrasion resistance. For the present Chub film laminate, the polyethylene film thickness is 38 micrometers (0.0015 in) for both the inner and the outer layers so that the total laminate thickness is about 102 micrometers (0.004 in). With this laminated film thickness, heat seals of good uniformity and strength can be produced consistently on the Kartridg-Pak Chub machine at acceptable production rates. The inside layer of polyethylene film in the Chub package protects the polyester layer(s) from attack by the aqueous salt solution in the Chub.

Sheet flatness - Production of consistently strong and uniform heat seals on the Chub package is dependent on precise positioning of the overlapping films as the heat seal is made. If the laminate used is not flat, but is stretched along one or both edges as it is unwound from the roll, the precise positioning of film in the heat seal area becomes difficult to maintain. As a result, variations in heat seal width, puckers and transverse wrinkles in the seal area may occur. Such defects in the Chub heat seal may lead to leakage of the liquid Chub contents through narrow capillaries across the seal area. In an extreme case, openings in the seal area may lead to catastrophic leakage of the Chub contents.

A specification on sheet flatness may be necessary to ensure acceptable film tracking and sealing on the Chub machine.

Color - Chub color, achieved by pigmentation of the outside polyethylene film layer, serves as a convenient method of identifying Chub contents. A standard "Blue" color has been selected for Chubs containing the 55°F material used in cooling applications.

B. Specification - Blue Film Laminate for Thermal Energy Storage Chubs -

The laminated film structure defined by this specification shall have, in order, the following components:

- a) 38 micrometers (.0015-in) blue polyethylene film
- b) adhesive
- c) metallized 48 or 50-gauge oriented polyester film
- d) adhesive
- e) metallized 48 or 50-gauge oriented polyester film
- f) adhesive
- g) 38 micrometers (.0015-in) clear polyethylene film

Specifications

- a. The 38 micrometers (0.0015-in) thick opaque blue polyethylene film shall be produced from 0.92 g/ml density polyethylene resin, and shall be pigmented blue to provide an approximate match to the standard sample after lamination. Film color shall be uniform.
- b. The adhesive shall be effective at temperatures from -18°C to 82°C (0°F to +180°F) without delamination of any of the interfaces involved. It shall be uniformly applied at a coverage of 2.5 g/m³ (1.5 lb per ream) for each interface.

- c. The 48 or 50-gauge oriented polyester film shall be metallized uniformly to a resistivity of 2-3 ohms per unit square.
- d. The 38 micrometer (0.0015-in thick) clear polyethylene shall be produced from 0.92 density polyethylene resin.
- e. The finished laminate shall have a water vapor transmission rate of 0.03 to 0.06 grams per 100 in² per 24 hr at 38°C (100°F) and 90-100 percent relative humidity. ASTM Standard Method D-1653-72 "Moisture Vapor Permeability of Organic Coating Films", or an equivalent method, shall be used to measure the WVTR of the laminate.
- f. The finished laminate shall be capable of being soaked at 65.6°C (150°F) for seven days in a saturated water slurry of sodium sulfate and borax, with no visible evidence of delamination.
- g. The finished laminate shall be free of blocking, and shall have adequate slip to perform satisfactorily on a Kartridg-Pak "Chub" machine.
- h. The finished laminate width shall be 177.8 ± 1.6 mm ($7.00 \pm 1/16$ in).
- i. The finished laminate shall be supplied in rolls not larger than 356 mm (14.0 in) O.D. on 76 mm (3.0 in) I.D. cores with end plugs. Each roll shall be individually wrapped with kraft paper. Rolls shall be packed in boxes or on pallets so as to prevent damage during shipping.

c. Test Methods

Many of the test methods and specifications applicable to the Chub laminate and its components are standard procedures as defined by the American Society for Testing and Materials (ASTM). A list of the relevant ASTM test methods is given for reference;

- a) ASTM D2103-73 - Standard Specifications for Polyethylene Film and Sheeting
- b) ASTM D374 - Test for Thickness of Solid Electrical Insulation
- c) ASTM D1505 - Test for Density of Plastics by the Density Gradient Technique
- d) ASTM D1604 - Test for Flatness of Plastic Sheet or Collapsed Tubing
- e) ASTM D1893 - Test for Blocking of Plastic Film
- f) ASTM D1894 - Test for Static and Kinetic Coefficients of Friction of Plastic Film and Sheeting
- g) ASTM D2578 - Test for Wetting Tension of Polyethylene and Polypropylene Films
- h) ASTM D3418-75 - Standard Test Method for Transition Temperatures of Polymers by Thermal Analysis
- i) ASTM E-96 - Test for Water Vapor Transmission of Materials in Sheet Form
- j) ASTM E-252-67 - Test Method for Thickness of Thin Foil and Film by Weighing

D. Moisture Vapor Retention Tests

The ability of the Chub package to retain moisture is a critical requirement of an effective packaging system. The amount of water present in the thermal energy storage material is sufficient to form the sodium sulfate decahydrate at the transition temperature. Consequently, any loss of moisture during the life of the Chub may result in a decrease in its effective thermal storage capacity.

A development program was undertaken with Du Pont to evaluate different laminated films for the Chub package and to investigate the effect of various end closures. In the course of the six-month program, a total of 1303 Chubs, representing 24 variations, were supplied by Du Pont. Properties of these Chubs, and identification of the intended packaging variations, are summarized in Table I. Data on the average values and the standard deviations for Chub weight and length were recorded to give a measure of the process reproducibility. The results of a series of moisture vapor retention tests are also recorded.

Chubs selected at random from the lots were stored at room temperature (72°F) and in Blue M circulating ovens maintained at 120, 150 and 180°F. The Chubs were removed periodically and weighed to within ± 0.01 grams on a Mettler PL1200 automatic balance.

TABLE I
12-INCH CHUBS FROM DU PONT

CHUB Lot No.	No. of CHUBS	Weight-g		Length-cm		Wt. Loss-g/1000 hrs				Comments
		$\bar{X}$	σ	$\bar{X}$	σ	180°F	150°F	120°F	72°F	
A	31	773.4	22.2	-	-	22.0	9.0	-	0.51	Clip closure only
B	31	770.4	16.8	-	-	-	-	-	-	Clip & wax
C	35	767.7	18.0	-	-	-	-	3.1	-	Clip & ultra-sound
D	64	769.1	19.1	31.3	3.9	-	-	-	-	
E	109	856.5	26.1	-	-	-	5.5	3.0	1.2	
F	13	863.1	26.8	-	-	-	-	-	-	Poor heat seals
G	87	870.6	35.9	31.0	0.74	-	4.32	1.56	0.34	
H	10	890.6	28.2	32.4	1.0	-	18.0	6.3	1.4	Delaminated
I	20	853.4	55.4	30.8	1.7	-	12.8	3.5	1.0	
J	15	762.0	23.6	33.1	0.3	-	5.4	1.1	-	
K ₁	15	773.0	10.1	30.2	0.6	-	3.1	0.90	0.21	Plain clip
K ₂	65	862.5	36.7	32.6	1.1	-	2.7	1.0	0.33	Flamed end
L	68	865.8	29.4	31.8	0.8	-	-	-	1.1	
M	48	867.9	41.3	32.5	1.4	-	-	1.8	-	
N	8	854.0	42.7	32.1	-	-	5.2	-	0.15	Thicker clay mix
O	17	788.3	35.7	30.7	1.1	-	-	-	-	
P	118	836.0	22.1	30.6	0.8	-	-	-	-	Clip pressure 9
Q	64	869.4	39.1	32.6	1.3	-	-	-	-	Clip pressure 8
R	29	825.4	20.2	30.9	0.6	-	-	-	-	Clip pressure 8
S	89	856.2	25.2	32.3	0.9	-	-	-	-	
T	36	860.4	18.3	31.9	0.8	-	-	-	-	Clip pressure 9
U	43	860.6	25.7	31.8	0.5	-	-	-	-	Clip pressure 8
V	78	891.4	16.4	32.3	0.6	-	3.3	1.2	.47	Clip pressure 6,7,8,9
W	57	932.1	73.2	34.3	2.6	-	-	-	-	
X	153	906.7	99.1	33.9	0.6	-	-	-	-	
Y-1	578	806.7	13.1	30.3	0.48	-	2.3	0.68	0.085	Qualification
Y-2	327	790.5	9.8	29.8	0.31	-	-	-	-	Lots
Y-3	220	794.5	17.0	30.0	0.32	-	-	-	-	

The loss in weight with time of the Chubs at each of the test temperatures was recorded. The data for each of the lots were plotted for each test temperature. Figure 1 is a plot of cumulative weight loss (grams) vs. time (hours) for a representative set of Chubs held at 150°F. From this and similar graphs, values of weight loss per 1,000 hours were obtained for each of the test temperatures. These were plotted as a graph of log "weight loss per 1,000 hours" vs. the reciprocal of the absolute temperature in degrees K. Figure 2 is an example of this type of plot for lot G.

As a reference point, weight loss per 1,000 hours was measured at 72°F (room temperature). Initial data obtained during the first six-ten weeks of testing of samples selected from the Du Pont Chubs indicated a weight loss range of 0.35 - 0.55 g/1,000 hrs for the standard 12" x 2" (length x diameter) research Chub. This represents a percentage weight loss of from 0.04 - 0.07 percent in the 1,000-hour period at room temperature.

An accumulated weight loss of from 0.35 - 0.55 g/1,000 hrs at 72°F extrapolates to a 10-year weight loss of from 3.5 - 6 percent. This is estimated to be equivalent to a reduction of 10 - 15 percent of the phase change material's energy storage capacity assuming that all of the weight loss is water needed for the formation of the sodium sulfate decahydrate.

Figures 3 and 4 show equivalent data for other Chub lots obtained from Du Pont as part of the qualification program.

IEC79127

FIGURE 1

Effect of Temperature on Weight Loss Rate

IEC79128

FIGURE 2

FIGURE 3
Effect of Temperature on
Weight Loss Rate - 12" CHUBS
IEC79129

FIGURE 4 IEC79130
Effect of Temperature on
Weight Loss Rate - 12" CHUBs

In a number of cases, weight loss tests were continued beyond 1,000 hours. The plots at 120°F remained linear out to times in excess of 5,000 hours. Higher test temperatures have induced changes in the laminate thus obscuring long-term data.

In the extended tests of weight loss at room temperature, the observed rate of weight loss frequently decreased with time. The mechanism for this behavior is not understood. One possibility is that, since the Chubs at room temperature are under relatively low internal pressure, the capillaries, which may have existed in the end closure, filled with crystallized salt and effectively sealed themselves.

From the data, it is clear that Chubs, which are normally used at room temperature (72°F) or lower, should lose weight less rapidly than predicted from the tests at high temperatures.

Long term test data (to 5,000 hrs) are shown for lot G in Figures 5, 6 and 7 for test temperatures of 150°F, 120°F and 72°F.

After the qualification program was completed, three qualification lots, designated as Y-1, Y-2 and Y-3, were produced at the University of Delaware as the standard 12-inch long, 2-inch diameter research Chubs.

IEC79124

FIGURE 5

FIGURE 6

IEC79125

FIGURE 7

IEC79126

Data on weight loss vs. time were obtained for these qualification Chubs using the standard procedure. The weight loss rates vs. temperature are plotted in Figure 8. To allow for convenience, the data have been normalized to a constant weight (1,000 g) of phase change material. The qualification Chubs, (lot Y-1) exhibited lower weight loss rates than most of the Du Pont lots. This was probably due to the following factors:

- a) Uniformly high quality laminate.
- b) Strong uniform heat seals, as a result of careful adjustment of the heat sealing mechanism during extended production runs.
- c) Well-formed end closures produced under optimized machine conditions.

The weight loss rate data on the qualification lot extrapolate to a room temperature moisture weight loss of about 0.92 percent in ten years, corresponding to a theoretical efficiency reduction due to water loss of 2.0 percent (see Table II).

For comparison, weight loss data are plotted on thermal energy storage material packaged in a 1-1/2 inch diameter black polyethylene tube with a 0.040 inch wall thickness. The data are normalized to a fixed weight of 1,000 grams of thermal energy storage material. The weight loss data for the best Chub package, at a wall thickness of 0.004 inches, are comparable to those for the polyethylene tube.

Effect of Temperature on Weight Loss Rate

IEC79131

FIGURE 8

TABLE II

CHUB WEIGHT LOSS

12-Inch CHUBs

	Lot G Early Du Pont <u>Prototype</u>	Lot Y-1 First <u>Qualification Lot</u>
Wt. Loss - G/1000 Hrs.		
150°F	4.30	2.30
120°F	1.55	0.68
72°F	0.34	0.085
Wt. Loss - 1000 Hrs.		
72°F	.042%	.0105%
Wt. Loss - 10 years		
% of initial weight	3.72	.92
% Efficiency lost Assuming all weight loss is water	8.6	2.0

The water vapor permeability of several plastic films were experimentally measured using the permeability cup method, ASTM D-1653-72.

<u>Film</u>	<u>Nominal Thickness</u> (micrometers)	<u>Water Vapor Permeability*</u>
Chub Laminate	102	0.08
Cast Polypropylene	89	0.55
Oriented Polyethylene	102	0.40

* (grams of water transport/24 hrs across 100 in² at 38°C and 100% relative humidity difference)

It is clear from these data that the laminate film has significantly better water vapor permeation properties than the single-ply materials.

E. Package Integrity Testing

Since the object of these tests was to examine the integrity of the Chub package, no attempts were made to correlate these tests with the thermal energy storage capability of the package. Consequently, no calorimetric testing was performed in conjunction with the tests described in this section.

1. Temperature Stability

The Chub package is made from a polyethylene/polyethylene terephthalate (PET) film laminate. The adhesive used to form the laminate is of a type used in the preparation of retortable food packages. After adequate curing, the adhesive/PET structure will withstand oven temperatures up to 205°C (400°F). The oriented PET film will retain its integrity at still higher temperatures. The polyethylene films, which constitute the inner and outer surfaces of the Chub package, are heat sealable at temperatures above their crystalline melting points of 112 to 130°C (234 to 266°F). The outer polyethylene layer will undergo some softening at 100°C (212°F), but pouches with well-formed heat seals in polyethylene/PET laminates are used to contain frozen foods in "heat-in-the-pouch" packages during storage and during cooking in boiling water. Thus, the components of the present Chub package can hold the Chub contents at temperatures well above those encountered in actual use. The Chub package has been used to contain thermal energy storage materials in accelerated weight loss tests at 150°F (65.6°C) for more than 6,000 hours without any evidence of package deterioration as determined by visual inspection.

The Chub package components also have excellent low temperature characteristics, as illustrated by their extensive commercial use for packaging frozen foods. The brittleness temperatures of polyethylene films, oriented PET films and the cured adhesive are well below -40°C (-40°F). Filled Chub packages have been stored in a refrigerator at temperatures below 14°F (-10°C) for more than 7,000 hours without adverse effects on the film packages as determined by visual inspection.

The laminate used in the Chub package is thus capable of withstanding the stresses encountered over normal temperature ranges. When the Chub contents are fluid, localized stresses from rough handling or dropping will be distributed over the Chub surface, and absorbed by reversible stretching of the flexible film. However, when the Chub contents are solid, the film is effectively locked in place so that it will not be free to stretch to absorb the stress. A localized impact may then cause breaks and pinholes in the film. For example, Chubs which have undergone temperature cycling may contain large crystals with sharp edges. If the Chub is undisturbed, the crystal edges will not puncture the film because of the high tensile strength of the oriented PET layers and the tear resistance of the polyethylene layers. If the frozen Chub is squeezed or dropped, however, the sharp crystal edges may be forced through the film, causing pinholes.

In the case of the blue Chubs with a 55°F transition temperature for cooling applications, the Chubs will normally be handled while in the fluid condition at ambient temperatures, thus precluding the above type of handling problems.

2. Stability During Field Handling

a. Drop Tests

The mechanical tests as outlined in Section 2a of the Statement of Work consist of a series of drop tests with a filled 12-inch (30.5 cm) Chub. A total of 20 Chubs as prepared by Du Pont were dropped from a height of one meter successively in each of four orientations. The orientations for the drop test consisted of a horizontal drop with the heat seal up and alternately with the heat seal down and a vertical drop on each of the package's ends. A successful drop test meant the package retained its contents without leakage. None of the qualified Chubs which were tested showed any leakage for the first ten successive drops. The number ten was chosen to represent extremes in rough handling that might be encountered during unloading or assembly of the Chubs into the Chub thermal energy storage bin. Extension of the tests beyond the qualification point for mechanical testing to a sequential set of 20 drops indicated that of the 20 Chubs tested, 12 of them were capable of sustaining 20 drops without any leakage. The type of failures noted on the non-surviving Chubs were splits along the heat seal and puncture of the laminate by the end clip.

Eight of the Chubs in the test sample were taken from a lot in which difficulties were encountered in making a satisfactory heat seal. These had been rejected by the normal quality assurance procedures. On testing,

however, it was found that four of the eight survived the total 20 drops, two failed after drops 17 and 18, and two failed on the fourth drop. The heat seal, which is critical in making the Chub, cannot be directly related to loss of mechanical integrity.

b. Vibration

The Chub should be capable of absorbing mechanical energy in the form of vibration during transportation or use while maintaining its integrity. Likewise, the gelled contents should be capable of maintaining their performance and function after exposure to vibration.

Transportation - A laboratory apparatus called the Du Pont Travelometer was used to simulate the effects of vibration on the Chubs. The travelometer was developed by the Fabrics and Finishes Department of E. I. du Pont de Nemours and Company. It has been used by them to test (Du Pont TM-228-A) the settling of pigments and other particulates in paints and enamels since 1948. The travelometer used in the present work is located in the Annex of the Marshall Laboratory of E. I. du Pont de Nemours and Company, 3500 Grays Ferry Avenue, Philadelphia, PA. The travelometer provides horizontal elliptical vibrations with an amplitude of about 0.3 mm and a frequency of 12 cycles per second. Vibration of particulate-containing paints on the travelometer for 24 hours is thought by Du Pont personnel to be comparable to transportation for five to seven days in a railway car, followed by a year in storage on a store shelf; thus allowing for rail shipment to, and storage at, any warehouse in the continental United States.

To evaluate the effects of vibration on the Chubs and their contents, corrugated cardboard trays containing eight Chubs each 12" x 2" (length x diameter) were placed horizontally on the travelometer tray, with the Chubs parallel to the short side of the tray. After being vibrated for specified times at room temperature, the bottom sides of the Chubs were checked for evidence of abrasion and leakage. The physical integrity of the packages was checked at intervals. After predetermined vibration times, the individual Chubs were frozen quickly in dry ice in their original orientation in order to retain the position and physical structure of the Chub contents. These frozen Chubs were cross-sectioned into 5-6 mm thick slices, and examined visually and microscopically. The sections were then allowed to thaw at room temperature, with visual observations continuing during the thawing process. Selected portions of the Chub cross-section were analyzed by differential scanning calorimetry (see Section II-A-(3)).

There was no evidence of leakage or abrasion damage in the individual Chubs tested on the travelometer over a period of five months (254 million cycles). Packaging materials and techniques, therefore, are deemed adequate to pass transportability test considerations.

To exaggerate the effects of vibration on the Chub contents, a sample Chub was vibrated on the travelometer for 166 hours (7 million cycles). The cross-section of the frozen Chub was then compared visually with that of a control Chub frozen without prior vibration. The frozen vibrated Chub

had a band of loosely consolidated crystals across the top, comprising about 10-15% of the cross-sectional area. The balance of the cross-sectional area was uniform in appearance, with clear crystals of about 1 mm diameter imbedded in a gray matrix. The control Chub had a thin band of loose crystals across the top, comprising about 1% of the cross sectional area. A similar Chub, which had been thermally cycled in the cooling system at Solar One, the University of Delaware's model solar house, also had a thin band of loose crystals across the top. This evidence suggests that the effects of vibration on the Chub contents during normal shipping, which usually involves only a few days of vibration-like motion, are minimal.

It is conceivable that in practical field installations, vibration from the motors and fans of air handling equipment could be transmitted to stacks of the thermal energy storage materials, thereby subjecting them to long-term vibration. Our limited practical experience with field applications indicates that this vibration transmission, if any, would be slight. It is expected that the results would be no different than those obtained in the limited transportability test, and that the only cumulative results may be a slight stratification because of density differences. Since this would probably be an effect less pronounced than the same type of effects due to thermal cycling, it was decided to concentrate upon an analysis of thermal cycling effects instead of undertaking a long-term study of the effects due to vibration.

c. Transportation by Common Carrier to Field Sites

A box of 24 Chubs was prepared and shipped to the Oak Ridge National Laboratory for two reasons: first as an example of the preparation of the materials based on the specifications of the qualified Chub laminate, and second as a demonstration of the transportability of the materials. The box was sent by a common carrier trucking company without any additional protection. A report of the receipt of these materials and their condition is given in the following pages.

Similarly, 5,400 pounds of Chubs were sent in boxes placed upon pallets to the Pacific Gas & Electric Company test location in California. Also included is their letter detailing the condition of the shipped thermal energy storage material as it was received in California.

OAK RIDGE NATIONAL LABORATORY

OPERATED BY

UNION CARBIDE CORPORATION
NUCLEAR DIVISION POST OFFICE BOX Y
OAK RIDGE, TENNESSEE 37830

September 5, 1979

Mr. Galen P. Frysinger
University of Delaware
Institute of Energy Conversion
One Pike Creek Center
Wilmington, DE 19808

Dear Galen:

On August 24 we received the box of 24 CHUBs you sent to us by common carrier. They arrived on an Interstate truck. The outside of the box was fairly heavily worn. The tape on the bottom was worn through in several places, apparently as a result of extensive sliding. Virtually all the edges and corners of the box were rounded. Attached are several photographs taken before the box was opened. On the inside we found all the CHUBs to be intact, although one CHUB leaked. The leak was very small and located in one of the creases formed by the end closure. This particular CHUB was located at the edge of the box, thus the leak may have resulted from stresses associated with the rounded edges of the box. It was noted on several of the CHUBs that the outside layer of blue film had worn away, exposing the aluminum at the tip of the end closure creases. We were unable to determine if the aluminum was penetrated. Finally, we weighed all the CHUBs (to the nearest gram), and these are tabulated on the attached data sheets.

Sincerely yours,

[Handwritten signature]
Robert J. Kedl
Low-Temperature Thermal Energy
Storage Program

RJK:nr
Attachment
cc: D. M. Eissenberg
H. W. Hoffman

<u>Group</u>	<u>Item No.</u>	<u>Weight (Grams)</u>	<u>Weight (Pounds)</u>
29177	1	1487	3.28
	2	1453	3.20
	3	1465	3.23
	4	1455	3.21
2.907	1	1443	3.18
	2	1477	3.26
	3	1452	3.20
	4	1464	3.23
	5	1438	3.17
	6	1462	3.22
	7	1458	3.21
	8	1463	3.23
	9	1462	3.22
	10	1460	3.22
29170	1	1524	3.36
	2	1473	3.25
	3	1463	3.23
	4	1450	3.20
2.908	1	1449	3.19
29171	1	1477	3.26
	2	1479	3.26
	3	1480	3.26
2916(?)	1	1366	3.01
No Number	<u>1</u>	<u>1444</u>	<u>3.18</u>
TOTAL	24	35044G 35.044KG	77.26 lbs

FIGURE 9

Photo of Package of 24 CHUBs as Received
by ORNL After Common Carrier Shipment

PACIFIC GAS AND ELECTRIC COMPANY

PG&E

DEPARTMENT OF ENGINEERING RESEARCH • 3400 CROW CANYON ROAD • SAN RAMON, CALIF. 94583 • (415) 820-2000

September 10, 1979

Mr. Galen R. Frysinger
Manager, Energy Systems
Institute of Energy Conversion
University of Delaware
One Pike Creek Center
Wilmington, Delaware 19808

Dear Mr. Frysinger:

In response to our recent telephone conversation, I am writing to confirm our receipt of the CHUB thermal energy storage materials. We have received 78 boxes of the CHUB materials, each containing approximately 23 individual CHUB packages. The materials were received in good condition, and have since been unpacked and installed in the storage bin. The stacking hardware was received several days prior to the CHUB materials, and while the boxes were in poor condition, the contents were not damaged.

As I have indicated above, the CHUB materials have been installed and the system is now in operation. Data are now being collected for determination of system performance, and I will keep you informed on our findings as operation continues.

Sincerely,

E. G. D'Albora

F. Performance Cycle Testing

1. Preliminary 100-Cycle Test

From April 12 to May 22, 1979, an array of 228 12" long Chubs were cycled in an experimental bin (Figure 10). The bin was 12 Chubs deep by 19 Chubs high. The Chubs selected for this initial accelerated cycle test were from the lots prepared by Du Pont and received by the Institute of Energy Conversion as part of the qualification program. Those on the left in Figure 10 had a black polyethylene outer layer and those on the right had a clear outer polyethylene layer, which gave them a metallic appearance due to the inner metallized layer.

A fan was mounted (Figure 11) to exhaust air through the experimental test bin at the rate of approximately 1,000 CFM. The temperature of the room air drawn through the test bin was tempered by the use of the inside coil of a heat pump (shown in Figure 11 in the upper left). A York Model CHP030 heat pump was used which had a cooling capacity of 29,500 Btu's per hour at an EER of 8.1, and a heating capacity of 30,500 Btu's per hour at a COP of 3.0 for a rating point of 47°F outside air temperature. For convenience in use, the compressor portion of the heat pump was placed in the laboratory (Figure 12).

The bin containing 228 Chubs had a total of approximately 400 pounds of phase change salts, with a rated capacity of approximately 20,000 Btu's. A thermistor placed on the air trailing side of a Chub in the bin was used to monitor the Chub's skin temperature during the freeze and thaw cycle. To be certain that the Chub's skin temperature was monitored instead of the air

FIGURE 10
Preliminary 100-Cycle Test Bin

FIGURE 11

Test Apparatus for Preliminary 100-Cycle Test

FIGURE 12
Compressor Section of York Heat Pump

temperature within the bin, the thermistor probe was taped to the Chub and a 1/2-inch thick layer of urethane pipe insulation was placed over the thermistor.

The cycling was initiated by drawing cooled room air across the Chubs in the experimental bin (Figure 11). This was continued until the temperature of the reference Chub was reduced to less than 50°F as measured by the thermistor. At this point the cooling was stopped and room temperature air was drawn through the bin until the Chubs were thawed. When the temperature of the reference Chub was at room temperature, the cooling cycle was again initiated. This cycling was continued for 100 cycles, with a number of interruptions due to other activities in the laboratory. The average cycle time was less than four hours. In later cycles, the heating operation of the heat pump was used to increase the temperature of the air being drawn through the Chub bin. This decreased the time required for thawing the Chubs, and also subjected them to higher air temperatures during the thawing operation.

Since the Chubs tested included over one dozen variations in the type of film, adhesive, and manufacturing conditions, no attempt was made to correlate package integrity with the particular Chub characteristics. As would be expected, these unqualified Chubs produced the normal type of deficiencies that were noted from the general work in the qualification program. These were:

- a) One of the Chubs, out of the 228 tested, showed separation of the film-to-film heat seal in a section about 1/8-inch long where the heat seal was visibly non-uniform.

- b) Two out of the 228 Chubs showed large salt deposits at the end closure after 100 cycles. The leakage was judged to be due to inadequate pressure when the clip was applied.
- c) 29 out of the 228 Chubs tested exhibited white salt deposits around the end closure due to the small amount of Glauber's salt mixture which was compressed in the area around the end clip during its manufacture. The amount of salt was weighed and found to be insignificant in relation to the total contents and probably has little effect on the performance of the material.

One of the interesting observations on the basis of this limited 100-cycle test was the appearance of a different consistency in about 1/3 of the Chubs contained in the bin which was noticed when the bin was disassembled. Table III indicates the placement of the Chubs within the 19 x 12 test matrix. Those Chubs indicated by an "X" exhibited a "crunchy" consistency. Examination of the contents of one of the "crunchy" Chubs indicated that large crystals were formed over the two-month cycling test, which gave the Chub a "crunchy" feel. As is seen from Table III, the Chubs with this crystal growth were located along the exit of the array and in the lower front corner.

While disassembling the experimental test bin, it was noted that under severe handling conditions the crystals penetrated the film and caused the Chub contents to leak. When the Chubs were removed and examined, four of them were found to be perforated. Note that this did not happen during the freeze-thaw cycling, but occurred when the Chubs were handled after cycling.

TABLE III

CONSISTENCY VS. BIN POSITION FOR PRELIMINARY 100-CYCLE TEST

	1	2	3	4	5	6	7	8	9	10	11	12
1	-	-	-	-	-	-	-	-	-	X	X	X
2	-	-	-	-	-	-	-	-	-	X	X	X
3	-	-	-	-	-	-	-	-	X	X	X	X
4	-	-	-	-	-	-	-	-	-	-	X	X
5	-	-	-	-	-	-	-	-	X	X	X	X
6	-	-	-	-	-	-	-	-	X	X	X	X
7	-	-	-	-	-	-	-	-	-	X	X	X
8	-	-	-	X	-	-	-	-	X	-	X	X
9	-	-	-	-	-	-	-	-	X	-	X	X
10	-	-	-	-	-	-	-	-	X	X	X	X
11	-	-	-	-	-	-	-	-	X	X	X	X
12	-	-	X	-	-	-	-	-	X	-	-	-
13	-	X	X	X	-	-	-	-	X	X	X	-
14	-	X	X	X	-	-	-	-	X	X	X	-
15	X	X	-	-	-	-	-	-	-	X	-	-
16	-	X	X	X	-	-	-	-	-	-	X	X
17	-	X	X	X	-	-	-	-	-	X	X	X
18	-	X	X	X	-	-	-	-	X	-	X	X
19	-	X	X	X	-	-	-	-	-	-	X	-

X is the symbol for "Crunchy" CHUBs

In later tests using qualified Chubs (71 cycles for daily test schedule and 405 cycles for the accelerated test schedule) the "crunchy" consistency was not common. Only 2 out of 456 Chubs exhibited this behavior. This phenomenon is tentatively attributed to poor mixing of the materials (stirrer in a barrel) used in filling the Du Pont research sample Chubs. The mixing and dispersion of material components at the University of Delaware's prototype fabrication facility was done in an Agi-Mixer (Figure 22) whose high speed head was used to form the thixotropic gel. The tentative conclusion is that proper mixing of the phase change material can mitigate the appearance of the "crunchy" consistency.

Air calorimetry was not performed on these Chubs because the instrument was not yet operational when these tests were performed.

2. Diurnal Cycle Tests

A thermal energy storage bin containing 456 Chubs was constructed adjacent to the Institute of Energy Conversion's 1/4-House test facility (Figure 13). This bin, containing approximately 800 pounds of salt hydrate material having a nominal capacity of 40,000 Btu's of thermal energy storage with a phase transition of 55°F, was operated on a daily cycle. During the "on-peak" portion, the heaters were turned on in the interior space of the 1/4-House facility for a fixed time to simulate the daytime heat gain of the living space. During this period, and for an hour after the heaters were turned off, the fan, under thermostatic control, removed air from the room, pulled it across the precooled Chub thermal energy storage bin and returned it to the room. At the end of the "on-peak" period, the 1/4-House temperature was at its initial control temperature. At the onset of the "off-peak" period, the air conditioner was run continuously for a set period with the circulation fan on. After this period the fan was run continuously for two hours and the air conditioner compressor was cycled off and on as required under thermostatic control to maintain the set 1/4-House chamber temperature. The system was then ready for a new "on-peak" cycle.

Because of the results from the initial 100-cycle tests, it was considered important in the one season procedure (100 days of diurnal cycling) to incorporate not only full freeze-thaw cycles, but also a significant amount of shallow cycling where the Chubs are only partially thawed before being refrozen.

1/4 House

Therefore, a regimen was devised whereby an amount of heat equivalent to 60-80% of the bin storage capacity was injected into the test chamber. This was accomplished by using one of the heaters with a three-hour on-time over a six-hour period to simulate the daily heat gain. This was later extended to eight hours at the suggestion of the ORNL representative. During the corresponding refreeze period, the air conditioner was run for a two-hour fixed period, and then on demand, to maintain the test chamber temperature.

The initial cool down of the diurnal test cycle Chubs was accomplished on June 10, 1979. After stabilization and check-out of the system, the first cycle was initiated on June 16, 1979. After completion of 37 cycles (July 24, 1979), the heat load was reduced from approximately 80% to approximately 60% (25,000 Btu's). Forty-five cycles had been accumulated by the first of August with completion of the cycle scheduled for September 25, 1979.

The testing was discontinued on August 27, after 71 cycles so that the Chubs could be tested in the air calorimeter. These data are included in Section II-C. The air calorimeter only became available for testing towards the end of June 1979. When the above testing program was being set up, a decision had to be made as to whether or not to delay the start of the cycling program until the air calorimeter was ready. Due to uncertainties in the amount of time that would be required to have the air calorimeter operational, it was decided not to delay the test program. As a consequence, calorimetric data was obtained for Chubs that were cycled in the 1/4-House test facility and

in the later accelerated test program (see below). When the air calorimeter became available it was realized that a measurement in the calorimeter takes at least one work week. Thus it became clear that the test program would be thrown even further off schedule if calorimetric measurements were made every 25 cycles as stated in the work statement. Therefore, measurements every 25 cycles were not made.

3. Accelerated Life Testing

Using the same test fixture employed in the preliminary 100-cycle test, accelerated life testing was initiated in June 1979 using qualified Chubs fabricated at the University of Delaware. This was the same series of Chubs prepared for testing in the diurnal cycle sequence. 228 Chubs containing approximately 400 pounds of salts were loaded into the experimental test bin for the accelerated life test. Initially, five rows of Chubs (19 Chubs high) were involved in the test (Figure 14). These Chubs were identical except for six different variations in secondary end closures. This secondary end seal may be required since small amounts of the salt mixture are compressed in the area around the end clip during manufacture and this is slowly released. The standard procedure adopted for this preparation of the Chubs uses an epoxy-type sealant first placed in a small plastic end cap which is then pressed against the clip and extended material of the Chub end seal to form an effective bond. The variations of secondary end closures involved in this accelerated life test include: several materials into which

FIGURE 14

Initial Configuration for Accelerated Life Test

the end clip was dipped and coated, a secondary mechanical clip and the use of different elastomers or epoxies with a plastic cap. Several control Chubs were also placed in the array for comparison evaluation. When the cycling was started, it was thought that additional trial secondary end closures would be added to the test chamber. After approximately 150 cycles, however, most of the above-described end seal procedures appeared satisfactory and therefore the bin was completely loaded with additional control Chubs and the cycling resumed.

The test procedure was based on a time schedule of three hours cooling and one hour heating (105°F from the heat pump) using a timeclock controlled by the laboratory computer. In this manner, six freeze-thaw cycles were completed in a 24-hour day.

The cycling was stopped on September 6 at 405 cycles so that performance data could be obtained in the air calorimeter. These data are presented in Section II-C. The calorimetry was not performed as outlined in the work statement for the reasons described above.

4. Analysis of Laminate After Being Exposed to Cycle Testing

From results on the cycle testing, the laminated film, prepared in accordance with the specification for the qualified Chub, performed as desired. The film was fully functional in the Chub cooling storage application using 55°F phase change material. The cut edges of the laminate which were exposed to the hydrated salts showed no visible evidence of attack or

delamination. There was no evidence of degradation of flexibility or damage from normal abrasion. The critical parameters in producing a qualified film package are the package machinery and its ability to create the proper heat seal and end closure using the metallic clip. Punctures of the laminated film are possible, but the 0.004-inch thick laminate is judged to be a good choice for cooling applications where normal handling can be accommodated by the laminate's abrasion resistance. Increased thickness not only increases cost, but also creates machinery problems and appears not to be warranted for the cooling applications. Where the Chubs are normally handled in a frozen condition (e.g., mixtures which have a transition point above room temperature), increased polyethylene film thickness for abrasion purposes may be desirable.

II. THERMAL STORAGE PERFORMANCE EVALUATION

A. Test Methods

In the final analysis, the property that is of most interest in a thermal energy storage material is its energy storage capacity. The most direct measure of that capability is calorimetry. Three different complementary calorimeters have been used to characterize the thermal energy storage materials.

(1) The air flow calorimeter measures the thermal performance of the material on a scale approaching that of the anticipated end use. Thus it measures the material as packaged into the Chub under conditions approximating the full scale end use. As its name suggests, conditioned air is blown over the sample and the energy is transferred to or from the Chubs depending on whether the Chubs are being cooled or thawed. However, a half cycle can take as long as 24 to 48 hours to be completed and thus testing with this calorimeter is a slow process.

(2) The laboratory calorimeter yields information under conditions which give a quantitative measure of the amount of energy stored in the material of interest. The sample size (150 g) eliminates the problem of representative sampling since the sample is tested in its entirety. However, due to heat loss considerations, it is feasible to perform measurements on the heat storage (i.e., melting) half cycle only since the freezing process takes too long to be measured by this method.

(3) The differential scanning calorimeter allows samples to be tested rapidly (in a matter of minutes to hours) because of the small size of the samples. It is a useful technique for screening a large number of samples and for attaining complete thermal cycling data in short times. However, because of the small sample sizes one must be careful to choose a representative sample.

B. Air Calorimeter

A calorimeter using air as the heat transfer fluid was constructed to allow testing of 100 to 200 lbs of phase change materials under well characterized conditions. The unit's design is based on ASHRAE Standard 94-77.

Description of Apparatus

The calorimeter (shown in Figure 15) consists of: (1) a test chamber containing the material to be tested; (2) a duct system to convey the air in a closed loop; (3) a heater and cooler to condition the air; (4) a blower; (5) a damper; (6) a flow measuring device; (7) a controller for the air conditioning system (not shown); (8) a differential thermopile to measure the temperature change of the air passing through the test chamber (not shown) and thermocouples to measure the temperatures of the storage material and air. The system design was based on ASHRAE Standard 94-77 (ANSI B199.1-1977), "Methods of Testing Thermal Storage Devices Based on Thermal Performance." The

EXISTING IEC AIR CALORIMETER

FIGURE 15

only major deviations from this standard were in the use of a MonitAire multiple pitot tube device to measure air flow and R-19 insulation on the test chamber and duct between the hot and cold junctions of the thermopile. The MonitAire was chosen as an accurate air-flow-measuring device in the range of expected flows; it is comparable to a flow nozzle in accuracy and is readily available from its manufacturer, the Air Monitor Corp. R-19 insulation was deemed more than adequate since temperature transients are controlled with this thickness of insulation.

The test chamber has been designed to hold as much as 250 lbs of thermal energy storage material. Any container which will fit into the available 5-3/8" x 24-1/2" x 76" test chamber can readily be accommodated. The operating specifications for the air calorimeter are given in Table IV.

Test Procedures (Air Calorimeter)

A weighed amount (between 100-250 lbs) of storage material is placed in the test chamber and the air is turned on. The air flow rate and temperature are adjusted to the desired level. When the storage material has reached a constant temperature, the temperature controller is set at a new level either above the former level if the storage material is to be heated, or below if the storage material is to be cooled. The air flow rate, air temperature, temperature difference across the test chamber and storage temperature are recorded as a function of time while the storage temperature approaches the newly set

air temperature. Because of the closed-loop design, significant humidity changes are not expected to be observed. Methods for monitoring the sample's temperature have been provided.

The data are then digitized and reduced by means of a computer program which has been specially written for this purpose. A listing of the program is given in Table V. From the data, the amount of energy transferred by the air to or from the storage material is calculated with appropriate corrections for heat losses to the atmosphere and the calorimeter itself. As a check on the accuracy and precision of the data, frequent calibration runs are made with an identical test configuration in which water has been substituted for the storage material. We estimate the precision to be $\pm 5\%$ and the accuracy $\pm 10\%$.

Sample Calculation

The equation of interest for the air calorimeter involves a heat balance between the material being tested and the circulating air with appropriate corrections for losses to the surroundings and the calorimeter itself.

$$Q_{\text{sample}} = Q_{\text{air}} + Q_{\text{heat loss}} - Q_{\text{calorimeter}} \quad (1)$$

The value for Q_{air} is given as:

$$Q_{\text{air}} = \int_t \dot{M} c_{\text{air}} (T_i - T_o) dt$$

TABLE IV
AIR CALORIMETER

System Specifications

	<u>Min.</u>	<u>Max.</u>	<u>Variations</u>
Air Flow	200 cfm	440 cfm	<u>±</u> 5%
Cold Side Temperature	35 ⁰ F	150 ⁰ F	<u>±</u> 1%
Hot Side Temperature	35 ⁰ F	150 ⁰ F	<u>±</u> 1%
Test Chamber Capacity	Up to 10 ⁴ cubic inches of material		Not applicable

	<u>Accuracy</u>	<u>Precision</u>
Air Flow Measurement	<u>±</u> 15 cfm	<u>±</u> 5 cfm
Differential Temperature Measurement	<u>±</u> 5%	<u>±</u> 1%

TABLE V

PROGRAM LISTING FOR AIR CALORIMETER

```

P CALC1
#FILE (13530)CALC1 ON PACK
9000 FILE 1(KIND=DISKPACK,TITLE=DATA,MAXRECSIZE=14,BLOCKSIZE=470)
9500 FILE 6(KIND=REMOTE,MYUSE=IO,MAXRECSIZE=22)
10000     DIMENSION MV(999),CF(999),CFM(999),TC15UC(999),TC15(999)
11000     DIMENSION CFAVE(999),M(999),SIMRUL(999),BTU(999)
12000     DIMENSION SECTOT(20),TBTULB(20),BARA(999)
13000     DIMENSION DT(999),QT(999),QPHOE(999),SALRTU(999)
14000     DIMENSION TC14UC(999)
15000     INTEGER TM,TM2,TMM2
16000     REAL MV,M1,M2,M3,M
16050     WRITE(6,104)
16060     READ(1,/)PAGE,NB,DATE
16070     WRITE(6,*/ )PAGE,NB,DATE
17000     READ(1,/) SECTS,AIRTMP,AMSAL,CFPHOE
17010     102 FORMAT(F14.3,F14.3)
18000     WRITE(6,*/ ) SECTS,AIRTMP,AMSAL,CFPHOE
19000     DO 75 K=1,SECTS
20000     READ(1,/) TOTMIN,BAR,TROOM,DX
20010     103 FORMAT(F14.3,F14.3,F14.3,F14.3)
21000     WRITE(6,*/ ) TOTMIN,BAR,TROOM,DX
22000     TM=TOTMIN/DX+1
23000     WRITE(6,*/ ) TM
23010     WRITE(6,207)
23011     207 FORMAT(//20X,'EXPERIMENTAL DATA',///)
24000     DO 4 I=1,TM
25000     READ(1,/) BARA(I),MV(I),TC15UC(I),TC14UC(I)
25005     CFM(I)=20.55*SQRT(BARA(I))
25010     WRITE(6,208)CFM(I),MV(I),TC15UC(I),TC14UC(I),BARA(I)
25011     206 FORMAT(4(5X,F14.3))
25015     208 FORMAT(5(5X,F14.3))
26000     4    CONTINUE

```

```

27000      CP=0.24
28000      ALPHA=(0.07498)*(1.3283)*(BAR)
29000      DO 30 I=1,TM
29010      TC15(I)=0.0
30000      TC15UC(I)=(TC15UC(I)+TC14UC(I))/2
32000      IF (TC15UC(I).LT.17.5) TC15(I)=2*TC15UC(I)+2.3
33000      IF (TC15(I).GT.0.0) GO TO 30
34000      IF (TC15UC(I).LT.19.0) TC15(I)=2*TC15UC(I)+2.8
35000      IF (TC15(I).GT.0.0) GO TO 30
36000      IF (TC15UC(I).LT.22.5) TC15(I)=2*TC15UC(I)+3.2
37000      IF (TC15(I).GT.0.0) GO TO 30
38000      IF (TC15UC(I).LT.25.0) TC15(I)=2*TC15UC(I)+3.7
39000      IF (TC15(I).GT.0.0) GO TO 30
40000      IF (TC15UC(I).LT.27.5) TC15(I)=2*TC15UC(I)+4.2
41000      IF (TC15(I).GT.0.0) GO TO 30
42000      IF (TC15UC(I).LT.30.0) TC15(I)=2*TC15UC(I)+4.6
43000      IF (TC15(I).GT.0.0) GO TO 30
44000      IF (TC15UC(I).LT.32.5) TC15(I)=2*TC15UC(I)+5.0
45000      IF (TC15(I).GT.0.0) GO TO 30
46000      IF (TC15UC(I).LT.35.0) TC15(I)=2*TC15UC(I)+5.4
47000      IF (TC15(I).GT.0.0) GO TO 30
48000      IF (TC15UC(I).LT.37.5) TC15(I)=2*TC15UC(I)+5.6
49000      IF (TC15(I).GT.0.0) GO TO 30
50000      IF (TC15UC(I).LT.40.0) TC15(I)=2*TC15UC(I)+5.7
51000      IF (TC15(I).GT.0.0) GO TO 30
52000      IF (TC15UC(I).LT.42.5) TC15(I)=2*TC15UC(I)+5.8
53000      IF (TC15(I).GT.0.0) GO TO 30
54000      IF (TC15UC(I).LT.45.0) TC15(I)=2*TC15UC(I)+5.7
55000      IF (TC15(I).GT.0.0) GO TO 30
56000      IF (TC15UC(I).LT.47.5) TC15(I)=2*TC15UC(I)+5.6
57000      IF (TC15(I).GT.0.0) GO TO 30
58000      IF (TC15UC(I).LT.50.0) TC15(I)=2*TC15UC(I)+5.5
59000      IF (TC15(I).GT.0.0) GO TO 30
60000      IF (TC15UC(I).LT.52.5) TC15(I)=2*TC15UC(I)+5.4
61000      30 CONTINUE

```

```

62000      DO 40 I=1,IM
62010      CF(I)=0.0
63000      IF (TC15(I).LT.40.0) CF(I)=7.85
64000      IF (CF(I).GT.0.0) GO TO 40
65000      IF (TC15(I).LT.45.0) CF(I)=7.70
66000      IF (CF(I).GT.0.0) GO TO 40
67000      IF (TC15(I).LT.50.0) CF(I)=7.63
68000      IF (CF(I).GT.0.0) GO TO 40
69000      IF (TC15(I).LT.55.0) CF(I)=7.58
70000      IF (CF(I).GT.0.0) GO TO 40
71000      IF (TC15(I).LT.60.0) CF(I)=7.56
72000      IF (CF(I).GT.0.0) GO TO 40
73000      IF (TC15(I).LT.65.0) CF(I)=7.53
74000      IF (CF(I).GT.0.0) GO TO 40
75000      IF (TC15(I).LT.70.0) CF(I)=7.52
76000      IF (CF(I).GT.0.0) GO TO 40
77000      IF (TC15(I).LT.75.0) CF(I)=7.51
78000      IF (CF(I).GT.0.0) GO TO 40
79000      IF (TC15(I).LT.80.0) CF(I)=7.50
80000      IF (CF(I).GT.0.0) GO TO 40
81000      IF (TC15(I).LT.85.0) CF(I)=7.47
82000      IF (CF(I).GT.0.0) GO TO 40
83000      IF (TC15(I).LT.90.0) CF(I)=7.40
84000      IF (CF(I).GT.0.0) GO TO 40
85000      IF (TC15(I).LT.95.0) CF(I)=7.32
86000      IF (CF(I).GT.0.0) GO TO 40
87000      IF (TC15(I).LT.100.0) CF(I)=7.23
88000      IF (CF(I).GT.0.0) GO TO 40
89000      IF (TC15(I).LT.105.0) CF(I)=7.15
90000      IF (CF(I).GT.0.0) GO TO 40
91000      IF (TC15(I).LT.110.0) CF(I)=7.12
92000      IF (CF(I).GT.0.0) GO TO 40
93000      IF (TC15(I).LT.115.0) CF(I)=7.10
94000      IF (CF(I).GT.0.0) GO TO 40
95000      IF (TC15(I).LT.120.0) CF(I)=7.07
96000      IF (CF(I).GT.0.0) GO TO 40
97000      IF (TC15(I).LT.125.0) CF(I)=7.03
98000      IF (CF(I).GT.0.0) GO TO 40
99000      IF (TC15(I).LT.130.0) CF(I)=6.98
100000     IF (CF(I).GT.0.0) GO TO 40
101000     IF (TC15(I).LT.135.0) CF(I)=6.98
102000     IF (CF(I).GT.0.0) GO TO 40
103000     IF (TC15(I).LT.140.0) CF(I)=6.96
104000     IF (CF(I).GT.0.0) GO TO 40
105000     IF (TC15(I).LT.145.0) CF(I)=6.91
106000     IF (CF(I).GT.0.0) GO TO 40
107000     IF (TC15(I).LT.150.0) CF(I)=6.80
108000     40 CONTINUE

```



```

108001      WRITE(6,201)
108002      201 FORMAT(/,10X,'AVG BIN TEMP',30X,'CORRN FACTOR',///)
108010      DO 20 L=1, TM
108020      WRITE(6,202) TC15(L), CF(L)
108021      202 FORMAT(6X,F14.3,22X,F14.3)
108030      20 CONTINUE
108031      IF(K.GT.0) GO TO 25
108035      TBIN=(TC15(TM)+TC15(TM-1)+TC15(TM-2)+TC15(TM-3)+TC15(TM-4)
108036      *+TC15(TM-5))/6.0
108040      TAVE=TRROOM-TBIN
108042      CFNEW=(CF(TM)+CF(TM-1)+CF(TM-2)+CF(TM-3)+CF(TM-4)+CF(TM-5)
108043      */6.0
108045      AMDOT=(CFM(TM)+CFM(TM-1)+CFM(TM-2)+CFM(TM-3)+CFM(TM-4)
108046      *+CFM(TM-5))/6.0
108050      AFLO=AMDOT*60.0*SQRT(ALPHA/(TBIN+460))
108052      DELT=(MV(TM)+MV(TM-1)+MV(TM-2)+MV(TM-3)+MV(TM-4)+MV(TM-5))
108053      */6.0
108055      AHA=ABS((CF*AFLO*DELT*CFNEW)/(TAVE))
109000      25 CONTINUE
109010      AHA=3.0
109030      J=0
109090      TMM2=TM-2
110000      DO 50 I=1, TMM2, 2
111000      J=J+1
112000      SIMRUL(J)=(DX/3)*(MV(I)+(4*MV(I+1))+MV(I+2))
113000      CFAVE(J)=(CF(I)+CF(I+1)+CF(I+2))/3
114000      M1=CFM(I)*SQRT(ALPHA/(TC15(I)+460))
115000      M2=CFM(I+1)*SQRT(ALPHA/(TC15(I+1)+460))
116000      M3=CFM(I+2)*SQRT(ALPHA/(TC15(I+2)+460))
117000      M(J)=(M1+M2+M3)/3
118000      BTU(J)=SIMRUL(J)*CFAVE(J)*M(J)*CF
118050      DT(I)=TRROOM-TC15(I)
119000      DT(I+1)=TRROOM-TC15(I+1)
119010      DT(I+2)=TRROOM-TC15(I+2)
127000      QT(J)=(DX/3)*(DT(I)+4*DT(I+1)+DT(I+2))*AHA/60.0
127010      IF((AIRTMP-TC15(TMM2)).GT.0.0) QT(J)=-QT(J)
127030      SALBTU(J)=BTU(J)+QT(J)
127050      101 FORMAT(5X,F14.3,5X,F14.3,5X,F14.3,5X,F14.3)
128000      50 CONTINUE

```

```

128010      WRITE(6,104)
128020      104 FORMAT(///)
128030      WRITE(6,203)
128051      203 FORMAT(10X,'RATE',12X,'HEAT LOSS',8X,'RATE-HI 01 LOSS',6X,'TIME(MF
128052      *UTES)',//)
129000      IM2=(TM-1)/2
129001      DO 10 N=1,IM2
129005      TIME=DX*N*2.0
129010      WRITE(6,101)BTU(N),RT(N),SALBTU(N),TIME
129020      10 CONTINUE
129030      WRITE(6,104)
129040      TOTBTU=0.0
129050      RTT=0.0
129060      FINBTU=0.0
129070      WRITE(6,204)
129080      204 FORMAT(///,25X,'SUM OF ABOVE PARAMETERS',//)
130000      DO 60 J=1,IM2
130010      TIMES=DX*N*2.0
131000      ADDBTU=BTU(J)
132000      TOTBTU=TOTBTU+ADDBTU
132010      RTT=RTT+RT(J)
132030      FINBTU=FINBTU+SALBTU(J)
132040      WRITE(6,101)TOTBTU,RTT,FINBTU,TIMES
132050      71 FORMAT(5X,F14.3,5X,F14.3,5X,F14.3,5X,F14.3,5X)
133000      60 CONTINUE
144000      WRITE(6,80)RTT,APHOF,CIPHOF
145000      86 FORMAT(//13X,'RTT=',F14.3,5X,'HEAT LOSS COEFF',F14.3,5X,'CIPHOF=
145001      *',F14.3)
149000      AFINOF=APS(CIPHOF*(TC15(1)-TC15(TM)))
150000      TOTBTU=TOTBTU+RTT*AFINOF
150010      BTULR=TOTBTU/AMSAI
151000      SECTOT(R)=TOTBTU
151010      BTULR(R)=BTULR
152000      85 FORMAT(//13X,'OLD TOTBTU=',F14.3)
153000      WRITE(6,80)TOTBTU,APHOF,BTULR
154000      80 FORMAT(//13X,'TOTBTU=',F14.3,13X,'APHOF=',F14.3,13X,'BTULR
154001      *',F14.3//)
155000      75 CONTINUE
155080      FBTU=0.0
155090      FBTULR=0.0
156000      DO 5 MM=1,SFCTS
156010      FBTU=FBTU+SECTOT(MM)
156020      FBTULR=FBTULR+BTULR(MM)
156030      WRITE(6,205)FBTU,FBTULR
157000      5 CONTINUE
157010      205 FORMAT(2X,'TOTAL Q FOR SALTS=',F14.3,5X,'TOTAL Q/LR FOR SALTS=',F
157011      *14.3,///)
158000      END
#

```

where $\dot{M}$ is the mass flow rate of the air, C_{air} is its heat capacity, T_i is the inlet temperature, T_o is the outlet temperature of the air and t is time.

$Q_{heat\ loss}$ is calculated as follows:

$$Q_{heat\ loss} = \int_t K_1 (T_r - T_b) dt \quad (2)$$

where K_1 is a constant, T_r is the average room temperature and T_b is the average air temperature in the sample chamber during the time dt . Values of K_1 are computed from the data for each run by assuming that after a sufficiently long time the sample has come to equilibrium with the air flowing in the calorimeter; then $Q_{air} = Q_{heat\ loss}$.

$Q_{calorimeter}$ is calculated from calibration data. Included in $Q_{calorimeter}$ are the effects of the packaging material and the hardware used to support the test sample in the calorimeter. The data are obtained by performing a series of calorimeter runs in which all experimental conditions are the same as in a test run, except that the phase change material has been replaced by water. In this way an effective product of heat capacity and mass for the calorimeter, packaging material and supporting hardware is calculated:

$$Q_{calorimeter} = K_2 (T_f - T_i) \quad (3)$$

where K_2 is the above-mentioned product, and T_f and T_i are the final and initial temperatures of the air in the sample chamber of the calorimeter.

The data are reduced by means of a computer; a sample output is shown in Table VI. The program performs the integration in equations (1) and (2) at convenient time intervals to achieve optimum precision. The data are presented as a table of values in which Q_{air} and $Q_{\text{heat loss}}$ are tabulated for each integration interval. Then the summation is performed and tabulated. Finally, the correction for $Q_{\text{calorimeter}}$ is applied, the values for each integration segment are summed and represented in a convenient form. QAIR is Q_{air} , HEAT LOSS is $Q_{\text{heat loss}}$, and the right two columns are self-explanatory. In the table headed SUM OF ABOVE PARAMETERS, the corresponding quantities are summed. At the end the summed values of TOTAL Q FOR SALTS and TOTAL Q/LB FOR SALTS are listed for each section that was integrated. QPHOE is $Q_{\text{calorimeter}}$, HEAT LOSS COEFF is K_1 , CPPHOE is K_2 , TOTBTU is Q_{sample} for the given integrated section, BTU/LB is Q_{sample} divided by the mass of the sample and QTT is the summed value of $Q_{\text{heat loss}}$ for the given integrated section. The last values of TOTAL Q FOR SALTS and TOTAL Q/LB FOR SALTS in Table VI is the sum total for that particular run. For increased precision, the data were digitized in two parts, the first four hours of the run were digitized every four minutes and the remainder of the data were digitized every hour. This is because the graph of temperature differential vs time changed very rapidly during the first four hours and then changed very slowly. The first part of Table VI gives the results for data digitized every hour and the second half shows the results of the data digitized every four minutes.

TABLE VI

QAIR	HEAT LOSS	GAIR-HEAT LOSS	TIME(MI NUTES)
2585.288	71.653	2656.941	120.000
1807.735	44.057	1851.793	240.000
1251.987	-5.324	1246.661	360.000
560.969	-14.040	546.929	480.000
190.127	-8.230	181.896	600.000
147.106	-24.691	122.414	720.000
-23.727	-17.429	-41.156	840.000
75.907	-28.565	47.342	960.000

SUM OF ABOVE PARAMETERS

2585.288	71.653	2656.941	120.000
4393.023	115.711	4508.734	240.000
5645.010	110.385	5755.395	360.000
6205.980	96.345	6302.324	480.000
6396.106	88.114	6484.221	600.000
6543.212	63.423	6606.635	720.000
6519.486	45.994	6565.479	840.000
6595.392	17.429	6612.822	960.000

QTT= 17.429 HEAT LOSS COEFF = 14.524 CFFHOE= 64.000

TOTBTU= 6392.422 QPHOE= 230.400 BTU/LB = 29.27

QAIR	HEAT LOSS	QAIR-HEAT LOSS	TIME(MI NUTES)
531.071	43.315	574.386	8.000
600.280	23.626	623.906	16.000
547.099	19.334	566.432	24.000
504.121	16.493	520.614	32.000
475.892	14.524	490.417	40.000
446.258	13.588	459.846	48.000
421.554	12.523	434.077	56.000
404.607	12.104	416.711	64.000
388.725	11.716	400.441	72.000
374.783	11.329	386.112	80.000
366.328	10.942	377.270	88.000
351.117	10.587	361.704	96.000
343.336	10.361	353.697	104.000
332.636	9.973	342.609	112.000
325.801	9.586	335.387	120.000
318.960	9.231	328.191	128.000
310.253	9.037	319.291	136.000
302.665	8.844	311.509	144.000
295.539	8.650	304.189	152.000
290.027	8.456	298.483	160.000
282.868	7.940	290.808	168.000
276.201	7.682	283.883	176.000
269.693	7.488	277.181	184.000
265.792	7.294	273.087	192.000
261.570	7.101	268.670	200.000
254.764	6.907	261.672	208.000
251.835	6.713	258.548	216.000
247.953	6.681	254.634	224.000
241.158	6.520	247.678	232.000
237.157	6.326	243.483	240.000
229.904	6.294	236.198	248.000
226.377	6.132	232.510	256.000
221.887	5.939	227.825	264.000
213.586	6.036	219.621	272.000
212.296	5.874	218.170	280.000
210.361	5.681	216.041	288.000
205.622	5.487	211.108	296.000

SUM OF ABOVE PARAMETERS

531.071	43.315	574.386	8.000
1131.351	66.941	1199.292	16.000
1678.450	96.275	1764.724	24.000
2182.570	102.749	2285.338	32.000
2659.463	117.292	2775.755	40.000
3104.721	130.980	3235.601	48.000
3526.275	143.404	3669.679	56.000
3930.983	155.507	4086.390	64.000
4319.607	167.224	4486.831	72.000
4694.390	178.553	4872.942	80.000
5060.718	189.494	5250.212	88.000
5411.836	200.091	5611.916	96.000
5755.172	210.442	5965.614	104.000
6087.908	220.415	6308.223	112.000
6413.609	230.001	6643.609	120.000
6732.569	239.232	6971.801	128.000
7042.822	248.269	7291.092	136.000
7345.487	257.113	7602.601	144.000
7641.024	265.763	7906.789	152.000
7931.053	274.220	8205.273	160.000
8213.921	282.159	8496.080	168.000
8490.122	289.841	8779.964	176.000
8759.816	297.329	9057.145	184.000
9025.608	304.624	9330.232	192.000
9287.178	311.725	9598.902	200.000
9541.942	318.632	9860.574	208.000
9793.777	325.345	10119.122	216.000
10041.730	332.026	10373.756	224.000
10282.987	338.546	10621.434	232.000
10520.044	344.872	10864.917	240.000
10749.948	351.166	11101.114	248.000
10976.326	357.299	11333.624	256.000
11198.212	363.239	11561.450	264.000
11411.798	369.273	11781.071	272.000
11624.094	375.149	11999.241	280.000
11834.454	380.928	12215.282	288.000
12040.076	386.315	12426.391	296.000

QTT=	386.315	HEAT LOSS COEFF =	14.524	CFPHOE=	64.000
TOTBTU=	9981.591	QPHOF=	2444.800		
TOTAL Q FOR SALTS=	6332.422	TOTAL 2/LB FOR SALTS=		BTU/LB	= 45.77
TOTAL Q FOR SALTS=	16364.012	TOTAL 0/LB FOR SALTS=			

C. Laboratory Calorimeter

The calorimetric measurements have been obtained with a calorimeter which was assembled and tested in the Institute's laboratories. It consists of a two-liter silvered Dewar flask which is filled with about 1200 g of water. In addition, there is a slow speed stirrer, an ASTM approved precision thermometer which can be read to 0.01°C and a bayonet-type 100-Watt DC heater. The heater is powered by a Sorenson DCR 150-6B voltage regulator and the current and voltage are monitored by appropriate meters to a precision of 0.1%. The Dewar flask and associated equipment are covered with a styrofoam cap with appropriate holes for the various accessories and a port for introducing the sample.

An experimental run consists of charging the Dewar flask with a known mass of water and heating it to a known initial temperature of ca 32°C with the stirrer operating throughout the run. At this point, the sample (ca 150 g of material whose temperature is accurately known, contained in a closed plastic container) is dropped into the water in the Dewar flask and the temperature is recorded as a function of time. When the decrease in temperature with time has reached a predetermined rate, the system is considered to be at thermal equilibrium. The electric heater is then switched on and the voltage and current are recorded during the heating of both the sample and the water in the flask. When the temperature of the flask's contents are close to the temperature of the water in the Dewar flask at the beginning of the experiment the heater is switched off and the temperature is recorded as a function of time for about twenty more minutes. From these data, the heat content of the sample can be calculated in two ways:

1. By a balance between the heat lost by the water and that gained by the sample with appropriate corrections for heat losses to the surroundings, etc.
2. From the amount of electrical heat required to raise the temperature of the flask's contents back to the initial temperature an enthalpic balance is made, again corrected for heat losses to the surroundings, etc.

To determine the extent of thermal losses such as heat absorbed by the walls of the calorimeter, sample container, etc., several calibration runs were made with water as the sample. On the basis of the calibration, we estimate our results to be accurate to within 5.0% with a precision of $\pm 7.5\%$. The data are reduced by means of a computer program which was specially written for this purpose. A listing of the program is given in Table VII.

Laboratory Calorimeter - Sample Calculations

The basic equation is a heat balance between the heat lost by the sample and its container and that gained by the water in the calorimeter and the Dewar flask plus a correction for losses to the surroundings.

$$Q_{\text{sample}} = Q_{\text{water}} + Q_{\text{Dewar}} + Q_{\text{heat loss}} - Q_{\text{container}} \quad (1)$$

TABLE VII

Program (FORTRAN) for Analysis of Data from
the Laboratory Calorimeter

```

#
DROPCAL2
#VERB EXPECTED. SCANNING DROPCAL
PRINT DROPCAL2
#FILE (13530)DROPCAL2 ON PACK
1000 $RESET FREE
1010 FILE 5(KIND=REMOTE,MAXRECSIZE=22)
1020 FILE 6(KIND=PACK,TITLE="CALDATA1",FILETYPE=7)
1030 C PROGRAM DROPCAL1
1040 C THIS PROGRAM COMPUTES THE HEATS, ENTHALPIES, AND PERCENTAGE
1050 C OF THEORETICAL VALUES FOR PHASE CHANGE SALTS OF
1060 C SODIUM SULFATE DECAHYDRATE, 90 DEG.F MELTING POINT.
1070 C IF PROBLEMS SHOULD ARISE, CONTACT BOB WEBER AT 658-6565
1080 INTEGER MON, DAY, YR
1090 REAL MH2O, MCAL, MSAMP, K1HL, K2HL, K3HL
1100 DIMENSION EE(50), AMP(50)
1110 DIMENSION THETA1(500), TAMB1(500), TCAL1(500), THETA2(500)
1120 1, TAMB2(500), TCAL2(500)
1130 C
1140 C DATA INPUT FOR DROPCAL1 MUST BE DONE BY CREATING A DATA FILE.
1150 C THIS IS DONE BY MAKING THE DATAFILE CALDATA1.
1160 C THE PROCEDURE IS AS FOLLOWS:
1170 C TYPE "MAKE CALDATA1"
1180 C TYPE "SEQ1000"
1190 C COMPUTER WILL COME BACK WITH 1000 AND WILL ANTICIPATE
1200 C THE INPUT OF DATA AS DESCRIBED BELOW.
1210 C
1220 C
1230 C DATA AS READ IS SPECIFIED WITH 1 AS SUFFIX FOR THE COOLING
1240 C RUN, AND WITH 2 AS SUFFIX FOR THE CALIBRATION RUN.
1250 C E.G. TCAL1(40) REFERS TO THE TEMPERATURE OF THE CALORIMETER
1260 C AT TIME 40 MINUTES, TAMB2(0) REFERS TO THE AMBIENT TEMPERATURE
1270 C DURING THE CALIBRATION RUN AT TIME 0 (THE INITIAL READING).
1280 C
1290 C DATA IS TO BE READ IN AS FOLLOWS:
1300 C (EACH LINE OF INFORMATION BELOW MUST BE KEYED IN AS A SEPARATE
1310 C LINE WITH COMMAS PLACED AFTER EACH VALUE)
1320 C BATCH #, MONTH, DAY, YEAR, PAGE #, NOTEBOOK #,
1330 C INITIAL SAMPLE TEMP., MASS OF H2O, MASS OF SAMPLE, # OF CYCLES,
1340 C ELAPSED ELECTRICAL "ON" TIME, ELAPSED HEATING TIME
1350 C FINAL COOLIN, HEAT LOSS COEFFICIENT, EQUIV CALORIMETER MASS
1370 C NUMBER OF VOLTAGES TO BE READ,

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```

1380 C      VOLTAGE 1,
1390 C      VOLTAGE 2,
1400 C      VOLTAGE 3,
1410 C      .....
1420 C      VOLTAGE N,
1430 C      NUMBER OF CURRENTS TO BE READ,
1440 C      CURRENT 1,
1450 C      CURRENT 2,
1460 C      CURRENT 3,
1470 C      .....
1480 C      CURRENT N,
1490 C      NPTS1,NPTS2, MASS OF BOTTLE, TMAX
1500 C      THETA1(I),TAMB1(I), THETA IS THE TEMP IN DEWAR
1510 C      .....
1520 C      THETA1(NPTS1),TAMB1(NPTS1)
1530 C      NOW ENTER THETA2(I),TAMB2(I)
1540 C      .....
1550 C      THETA2(NPTS2),TAMB2(NPTS2)
1560 C      TIME 0, TAMB2(0) CONTINUE IN 1 MINUTE INTERVALS TO
1570 C      TIME AT MAXIMUM TEMPERATURE DURING CALIB. RUN, TAMB2(MAX)
1580 C      ALL DATA IS NOW ENTERED AND IS READY FOR MANIPULATION
1590 C
1600 C      LINES 1603 AND 1604 REFER TO DEWAR #1,1607 AND 1608 - DEWAR #2
1601 C      READ(6,/)CALNUM
1602 C      IF(CALNUM.GT.1)GO TO
1603 C      MCAL=92.18
1604 C      K1HL=0.6384
1605 C      GO TO 2
1606 C      1 CONTINUE
1607 C      MCAL=128.175
1608 C      K1HL=0.9585
1609 C      2 CONTINUE
1610 C      READ(6,/)BATCH,MON,DAY,YR,PAGE,NTBK,TINIT,MH2O,MSAMP,CYCLE
1620 C      READ(6,/)ETIME,HTIME,CIME
1650 C
1790 C      NV REPRESENTS THE NUMBER OF VOLTAGE READINGS
1800 C      READ-IN OF NV VOLTAGE READINGS IN VOLTS
1810 C
1820 C
1830 C      NA REPRESENTS THE NUMBER OF CURRENT READINGS
1840 C      READ-IN OF NA CURRENT READINGS IN AMPS
1850 C
1860 C      READ(6,/)NV
1870 C      ESUM=0
1880 C      DO 115 I=1,NV
1890 C      READ(6,/)EE(I)

```

```

1895 115 CONTINUE
1900 DO 117 I=1,NV
1910 ESUM=ESUM+EE(I)
1915 117 CONTINUE
1920 E=ESUM/NV
1930 READ(6,/)NA
1940 ASUM=0
1950 DO 116 I=1,NA
1960 READ(6,/)AMP(I)
1965 116 CONTINUE
1970 DO 118 I=1,NA
1980 118 ASUM=ASUM+AMP(I)
1990 AMPS=ASUM/NA
2000 C
2010 C
2020 C
2040 C
2050 C THE MASS OF THE CALORIMETER IS CONSTANT = MCAL AND REPRESENTS THE
2060 C EQUIVALENT MASS OF WATER
2070 C
2080 C K1HL IS THE HEAT LOSS COEFFICIENT
2100 C
2110 READ(6,/)NPTS1,NPTS2,AMBOT,T2MAX
2112 C NPTS2=# OF TAMB VALUES FOR CALIBRATION RUN
2113 C AMBOT=MASS OF SAMPLE BOTTLE IN GRAMS
2114 C NPTS1=# OF TAMB VALUES FOR COOLING RUN
2180 DO 200 I=1,NPTS1
2190 READ(6,/)THETA1(I),TAMB1(I)
2195 200 CONTINUE
2220 C
2230 C
2240 C AVERAGE AMBIENT TEMP. IS CALCULATED BELOW FOR TIME 1 TO TIME 40
2250 C THIS IS FOLLOWED BY THE HEAT LOSS CALCS. FOR THE SAME TIME
2260 C
2270 C
2280 TSUM=0.0
2290 DO 10 I=1,NPTS1
2300 TSUM=TSUM+TAMB1(I)
2305 10 CONTINUE
2310 TAVG1=TSUM/NPTS1
2320 QHL1=K1HL*CTIME*((THETA1(1)+THETA1(NPTS1))/2-TAVG1)
2610 C CALCULATION OF THE TOTAL HEAT FOR THE SAMPLE
2620 C
2630 C HLBOT1= HEAT GAINED BY SAMPLE BOTTLE IN PART 1
2635 HLBOT1=0.46*AMBOT*(THETA1(NPTS1)-TINIT)
2640 QSAMP1=(MH20+MCAL)*(THETA1(1)-THETA1(NPTS1))-QHL1-HLBOT1
2650 C

```

```

2660 C
2670 C      CALCULATION OF THE TOTAL HEAT PER GRAM OF THE SAMPLE
2680 C
2690 C
2700      QPERG1=QSAMP1/MSAMP
2710      DO 45 I=1,NPTS2
2720      READ(6,/)THETA2(I),TAMB2(I)
2725 45 CONTINUE
2730      TSUM=0.0
2740      DO 40 I=1,NPTS2
2750      TSUM=TSUM+TAMB2(I)
2755 40 CONTINUE
2760 C
2770 C
2780 C      CALCULATION OF AVERAGE AMBIENT TEMP. DURING ELECT. HEATING
2790 C
2800 C
2810      TAVG4=TSUM/NPTS2
2820 C
2830 C
2840 C      CALCULATION OF ELECTRICAL HEAT INPUT TO THE CALORIMETER
2850 C
2860 C
2870      QELEC=E*AMPS*ETIME*60/4.184
2880 C
2890 C
2900 C      CALCULATION OF HEAT LOSS DURING COOLING BY METHOD 2
2910 C
2920 C
2930      Q2HL=QHL1+K1HL*HTIME*((T2MAX+THETA2(1))/2-TAVG4)
2940 C
2950 C
2960 C      CALCULATION OF TOTAL HEAT FOR SAMPLE BY METHOD 2
2970 C      HLBOT2= HEAT GAINED BY SAMPLE ROTTF IN PART 2
2980 C
2985      HLBOT2=0.46*AMBOT*(T2MAX-TINIT)
2990      QSAMP2=QELEC-Q2HL+(MH2O+MCAL)*(THETA1(1)-T2MAX)-HLBOT2
3000 C
3010 C
3020 C      CALCULATION OF HEAT PER GRAM OF SAMPLE BY METHOD 2
3030 C
3040 C
3050      QPERG2=QSAMP2/MSAMP
3060 C
3070 C
3080 C      CALCULATION OF THE THEORETICAL HEAT OF THE SAMPLE BY
3090 C      METHOD 1 FOLLOWED BY FRACTION 1 (F1)
3100 C

```

```

3110 C
3120 Q1TH=(0.42*(32-TINIT)+60+0.79*(THETA1(NPTS1)-32))
3130 F1=60/Q1TH
3140 C
3150 C
3160 C CALCULATION OF THE THEORETICAL HEAT OF THE SAMPLE BY
3170 C METHOD 2 FOLLOWED BY FRACTION 2 (F2)
3180 C
3190 C
3200 Q2TH=(0.42*(32-TINIT)+60+0.79*(T2MAX-32))
3210 F2=60/Q2TH
3220 C
3230 C
3240 C CALCULATION OF THE CHANGE IN ENTHALPY BY METHOD 1 (ENTH1)
3250 C
3260 C
3270 ENTH1=QPERG1*F1
3280 C
3290 C
3300 C CALCULATION OF THE CHANGE IN ENTHALPY BY METHOD 2 (ENTH 2)
3310 C
3320 C
3330 ENTH2=QPERG2*F2
3340 C
3350 C
3360 C CALCULATION OF THE PERCENTAGE OF THEORETICAL BY METHOD1 (POT 1)
3370 C
3380 C
3390 POT1=ENTH1/54*100
3400 C
3410 C
3420 C CALCULATION OF THE PERCENTAGE OF THEOR. BY METHOD 2 (POT 2)
3430 C
3440 C
3450 POT2=ENTH2/54*100
3460 F1=F1*100
3470 F2=F2*100
3480 C
3490 C
3500 C PRINTOUT OF ALL VALUES TO BE USED AS A CHECK
3510 C AND OUTPUT OF ALL COMPUTED DATA
3520 C
3530 WRITE(5,161)CALNUM
3531 161 FORMAT(/,10X,'***** THIS IS CALORIMETER NUMBER ',I2,' *****')
3540 WRITE(5,400)QSAMP1,QSAMP2,ENTH1,POT1
3550 400 FORMAT(/,10X,'QSAMP1 = ',F9.3,3X,'QSAMP2 = ',F9.3,3X
3560 1,'ENTH1 = ',F7.3,3X,'POT1 = ',F7.3)

```

```

3570      WRITE(5,405)QPERG1,QPERG2,ENTH2,POT2
3580 405 FORMAT(10X,"QPERG1 = ",F9.3,3X,"QPERG2 = ",F9.3,3X,
3590 1"ENTH2 = ",F7.3,3X,"POT2 = ",F7.3,///)
3600      WRITE(5,101)BATCH
3610 101 FORMAT(10X,"BATCH NO.",F7.2)
3620      WRITE(5,102)MON,DAY,YR
3630 102 FORMAT(10X,"DATE",I2,"/",I2,"/",I2)
3640      WRITE(5,103)PAGE
3650 103 FORMAT(10X,"PAGE NO.",I3)
3660      WRITE(5,104)NTBK
3670 104 FORMAT(10X,"NOTEBOOK NO.",I4)
3680      WRITE(5,105)CYCLE
3690 105 FORMAT(10X,"CYCLES",I4)
3700      WRITE(5,106)CTIME
3710 106 FORMAT(10X,"FINAL COOLING TIME",I4,X,"MINS.")
3720      WRITE(5,109)HTIME
3730 109 FORMAT(10X,"HEATING TIME",F5.2,X,"MINS.")
3740      WRITE(5,110)ETIME
3750 110 FORMAT(10X,"ELECTRICAL 'ON' TIME",F5.2,X,"MINS.")
3760      DO 201 I=1,NV
3770 201 WRITE(5,202)I,EE(I)
3780 202 FORMAT(10X,"EE(",I2,") = ",F8.3)
3790      WRITE(5,206) E
3800 206 FORMAT(10X,"AVERAGE VOLTAGE DURING HEATING = ",F8.3," VOLTS")
3810      DO 203 I=1,NA
3820 203 WRITE(5,204)I,AMP(I)
3830 204 FORMAT(10X,"AMP(",I2,") = ",F6.4)
3840      WRITE(5,205) AMPS
3850 205 FORMAT(10X,"AVERAGE CURRENT DURING HEATING = ",F6.4," AMPS")
3860      WRITE(5,120)TINIT
3870 120 FORMAT(10X,"INITIAL SAMPLE TEMPERATURE",F7.2,X,"DEG. C.")
3880      WRITE(5,121)MH2O
3890 121 FORMAT(10X,"MASS OF WATER",F8.2,X,"GRAMS")
3900      WRITE(5,122)MSAMP
3910 122 FORMAT(10X,"MASS OF SAMPLE",F8.2,X,"GRAMS")
3920      WRITE(5,123) THETA1(NPTS1)
3930 123 FORMAT(10X,"EQUIL TEMP OF SAMPLE AND DEWAR=",F7.2,X,"DEG C")
3940      WRITE(5,124)AMBOT
3950 124 FORMAT(10X,"MASS OF SAMPLE BOTTLE=",F7.2,X,"GMS")
4020      WRITE(5,111)T2MAX
4030 111 FORMAT(10X,"MAX TEMP. AFTER ELEC. HTG.",F7.2,X,"DEG. C.")
4040      WRITE(5,140)K1HL
4050 140 FORMAT(10X,"K1HL = ",F10.6," HEAT LOSS COEFF.")
4060      WRITE(5,150)MCAL
4070 150 FORMAT(10X,"MCAL = ",F10.3,X,"MASS EQUIV OF CALORIMETER")
4210      WRITE(5,182)F1
4220 182 FORMAT(10X,"F1 = ",F6.3," REPRESENTS FRACTION 1")
4230      WRITE(5,183)F2
4240 183 FORMAT(10X,"F2 = ",F6.3," REPRESENTS FRACTION 2")

```

The heat for the container, water and Dewar flask are calculated as:

$$Q_i = M_i C_i (T_{\text{final}} - T_{\text{initial}}) \quad (2)$$

where M_i is the mass, C_i is the specific heat and T_{final} and T_{initial} are the final and initial temperatures. The value for Q_{Dewar} is calculated by determining an equivalent water mass for the Dewar in a previous calibration experiment. The $Q_{\text{heat loss}}$ term is calculated by the following equation:

$$Q_{\text{heat loss}} = (k_{hl}) (\Delta t) \left[T_{\text{av}} - T_{\text{room}} \right] \quad (3)$$

where k_{hl} is a heat loss coefficient assumed to be constant for a given calorimeter and determined in a calibration experiment, Δt is the elapsed time over which the loss is being calculated, T_{av} is the average temperature in the calorimeter during the time Δt and T_{room} is the average room temperature during the same period. Thus every quantity on the right hand side of eqn. (1) is known and Q_{sample} can be calculated.

As a check, after the sample has reached thermal equilibrium with the water in the calorimeter, the contents of the Dewar are heated to a temperature close to the initial temperature in the Dewar at the beginning of the experiment and an enthalpic balance is made:

$$\begin{aligned}
 H_{\text{sample}}^{T_{\text{initial}}} + \Delta H_{\text{calorimeter}}^{T_{\text{initial}}} + Q_{\text{elec}} = \\
 \Delta H_{\text{calorimeter}}^{T_{\text{final}}} + H_{\text{sample}}^{T_{\text{final}}} + Q_{\text{heat loss}}
 \end{aligned}
 \tag{4}$$

If T_{initial} and T_{final} for the calorimeter are the same, then:

$$\Delta H_{\text{calorimeter}}^{T_{\text{initial}}} = \Delta H_{\text{calorimeter}}^{T_{\text{final}}}
 \tag{5}$$

Q_{elec} is calculated from the average values for the voltage and current and elapsed time during the heating run:

$$Q_{\text{elec}} = (\bar{V} \cdot \bar{I} \cdot \Delta t \cdot 60) / 4.184
 \tag{6}$$

where $\bar{V}$ is in volts, $\bar{I}$ is in amps, Δt is in minutes and Q_{elec} is in calories. If, in fact, the requirements of equation (5) are not strictly met, a small correction based on the mass of the water and calorimeter is applied.

Thus rearranging equation (4)

$$H_{\text{sample}}^{T_{\text{final}}} - H_{\text{sample}}^{T_{\text{initial}}} = Q_{\text{elec}} - Q_{\text{heat loss}}
 \tag{7}$$

The above calculations are done by a computer. A sample of the output is shown in Table VIII. The terms QSAMP1 and QSAMP2 refer to the calculations of equations (1) and (7) respectively. QPERG1 and QPERG2 are the respective heat values per unit mass (in grams) of sample. The slight discrepancy in values reflects the different

TABLE VIII

***** THIS IS CALORIMETER NUMBER 2 *****

QSAMP1 = 5519.570	QSAMP2 = 5691.943	ENTH1 = 34.582	POT1 =
QPERG1 = 39.352	QPERG2 = 40.581	ENTH2 = 33.642	POT2 =

BATCH NO. 9.10
 DATE 6/ 4/79
 PAGE NO. 55
 NOTEBOOK NO. 198
 CYCLES 4
 FINAL COOLING TIME 88 MINS.
 HEATING TIME 7.44 MINS.
 ELECTRICAL 'ON' TIME 5.44 MINS.
 EE(1) = 120.050
 EE(2) = 120.050
 EE(3) = 120.050
 EE(4) = 120.050
 EE(5) = 120.050
 EE(6) = 120.050
 AVERAGE VOLTAGE DURING HEATING = 120.050 VOLTS
 AMP(1) = 0.7705
 AMP(2) = 0.7705
 AMP(3) = 0.7695
 AMP(4) = 0.7695
 AMP(5) = 0.7695
 AMP(6) = 0.7695
 AVERAGE CURRENT DURING HEATING = 0.7698 AMPS
 INITIAL SAMPLE TEMPERATURE 10.00 DEG. C.
 MASS OF WATER 1200.00 GRAMS
 MASS OF SAMPLE 140.26 GRAMS
 EQUIL TEMP OF SAMPLE AND DEWAR= 30.78 DEG C
 MASS OF SAMPLE BOTTLE= 23.66 GMS
 MAX TEMP. AFTER ELEC. HTG. 35.97 DEG. C.
 K1HL = 0.958500 HEAT LOSS COEFF.
 MCAL = 128.175 MASS EQUIV OF CALORIMETER
 F1 = 87.878, REPRESENTS FRACTION 1
 F2 = 82.900, REPRESENTS FRACTION 2
 TAVG1 = 21.143 DEG. C
 TAVG4 = 21.089 DEG. C
 QELEC = 7209.703 CALORIES

QHL1 = 1027.961 CALORIES
 Q2HL = 1115.576 CALORIES
 Q1TH = 68.276 CALORIES PER GRAM
 Q2TH = 72.376 CALORIES PER GRAM

#QUEUED

#ET=1:32.6 PT=0.4 IO=0.3

#

approaches to the calculations and the various approximations made. Reported values are an average of the two. The data to the right are used in a different application of the program and are of no interest here. The other information listed are pertinent raw data which serve as a check and are included for the sake of convenience.

Since values of the specific heat for the sample are not known precisely, experiments are performed by splitting a batch of the mixture into two halves and measuring the heat content of the first half maintained at a temperature of 50°F (10.0°C) and of the other half maintained at a temperature of 60°F (15.6°C). The difference between the two represent the latent heat of transition stored in the material with a small amount of heat (about 10-15% of the total) due to specific heat effects. The data are normalized to a ΔT of 30°F by assuming a specific heat of 0.35 for the solid and 0.65 for the liquid. Samples for this calorimeter are stored in a sealed plastic bottle. After a calorimetric measurement, the samples are placed in a cycling chamber. The cycling chamber is a freezer which has been modified so that the air temperature varies between 5°F to 75°F in a roughly sawtooth manner, such that a complete thermal cycle lasts eight hours (four hours cooling and four hours heating). Calorimetric data as a function of thermal cycling are presented for two samples in Tables IX and X. The data have been normalized to a standard ΔT of 30°F. The decline in thermal energy storage capacity with cycling is disturbing, however, the fact that initially the performance is high suggests that a thorough analysis of the failure mechanism will lead to a means of maintaining the material's initial acceptable performance.

TABLE IX

THERMAL ENERGY STORAGE CAPACITY
OF 55°F MATERIALS AS MEASURED BY
THE LABORATORY CALORIMETER OVER AN
OPERATING TEMPERATURE RANGE OF 30°F

Cycles	Energy/Lb (Btu/Lb)
1	65.7
1	60.7
6	55.8
11	52.6
20	48.1
98	46.8
102	45.6
135	43.6
151	44.5

TABLE X

THERMAL ENERGY STORAGE CAPACITY
OF A 55°F MATERIAL AS MEASURED BY
THE LABORATORY CALORIMETER OVER AN
OPERATING TEMPERATURE RANGE OF 30°F

Cycles	Energy/Lb (Btu/Lb)
0	70.2
3	64.9
38	53.2
54	52.7
80	47.0
135	40.4
229	37.2
302	35.6
401	37.2

D. Differential Scanning Calorimeter (DSC)

A Mettler TA2000(B) thermal analysis system equipped with a TA34 coolant controller has been used in these studies. The system in this configuration is capable of scanning from -170° to 550°C . The advantage of using a DSC lies in its ability to collect calorimetric data over relatively large temperature ranges in a short period of time (minutes to hours). It does this by using small samples (~ 10 mg) and this fact must be borne in mind when interpreting DSC data. The differential scanning calorimeter records the differences in assimilation of thermal energy between the sample being measured and a reference material. The reference and sample are contained in small individual crucibles and placed on the ends of a thermopile in a well-insulated oven. The temperature of the oven is changed at a precisely controlled rate and the difference in temperature between the reference and sample is recorded. From the area under a peak it is possible to determine the amount of energy involved in an observed thermal transition. In addition, it is sometimes possible to derive values for the heat capacity of the sample from the recorded data.

A measurement consists of weighing a known amount of sample into a crucible and placing it on the thermopile in the oven along with the reference sample, which is usually an empty crucible. The sample and

reference are brought to the oven temperature and then the experimental scan is initiated. The temperature of the oven is changed at a rate of $1^{\circ}\text{C}/\text{min}$ over the range -20 to 35°C and the temperature difference between the sample and reference are recorded. A complete run consists of a cooling and heating scan between the above temperatures. The area under the peaks is measured and the amount of energy stored or released is computed. The temperature in the oven is known to an accuracy of $\pm 0.5^{\circ}\text{C}$ and is reproducible within $\pm 0.1^{\circ}\text{C}$. The calorimetric measurements are typically accurate to $\pm 2\%$ with a repeatability of $\pm 0.5\%$.

Differential Scanning Calorimeter (DSC) - Sample Calculations

The procedure for calculating the energy involved in a thermal transition consists of integrating the area under the desired recorded peak and comparing the area to that obtained for a known substance, whose thermal characteristics are well known. The manufacturer of the DSC (Mettler Corp.) recommends using indium metal as the calibration standard. The desired equation is:

$$\Delta H_{\text{sample}} = \Delta H_{\text{ref}} \frac{(\text{area of sample peak})}{(\text{reference area})} \quad (1)$$

The reference area is a known area of graph paper which has been measured by the same instrument used to measure the area under the sample peak. The sample peak area and reference area were measured with a K&E Co. compensating polar planimeter and values of 0.6614 and 0.5000, respectively, were obtained (in arbitrary units). The value for ΔH is obtained as follows:

$$\Delta H_{\text{ref}} = (\text{reference area in } \mu\text{V} \cdot \text{sec}) / E_{\text{ref}} \quad (2)$$

The values for the reference area in $\mu\text{V} \cdot \text{sec}$ are obtained from the scan speed of the recorder and the sensitivity reading obtained from the DSC instrument. In this case, the chart paper moved at 1 cm/min and full scale deflection of the pen was 200 μV . The value for E_{ref} was obtained from calibration data recorded earlier.

$$\Delta H_{\text{ref}} = (30,000 \mu\text{V} \cdot \text{sec}) / (54.684 \mu\text{V}/\text{mcal} \cdot \text{sec}) =$$

$$548.6 \text{ mcal} = 0.5486 \text{ cal}$$

Therefore,

$$\Delta H_{\text{sample}} = (0.5486) \frac{0.6614}{0.5000} = 0.726 \text{ cal}$$

The sample's mass was 0.0440 g

$$\Delta H_{\text{sample}}/\text{mass} = \frac{0.726}{0.0440} = 16.5 \text{ cal/g} = 29.7 \text{ Btu/lb}$$

Adding in the contribution for specific heat for a 30°F range and assuming an average specific heat of 0.5 we have:

$$\Delta H/\text{mass} = 29.7 + 15.0 = 44.7 \text{ Btu/lb}$$

Use of Differential Scanning Calorimeter to Study the Effects of
Vibration on Phase Change Material

Differential scanning calorimetry data are shown in Figure 16 for a series of four samples with different thermal and physical histories. All samples were measured under the same conditions, at sample sizes of 40 to 50 milligrams and at a heating rate of 1°C per minute. Samples had been cooled in the instrument to a temperature of -20°C at a cooling rate of $1^{\circ}\text{C}/\text{min}$ before the heating-curve data were collected.

For samples A and B, taken from the upper and lower sections of a control Chub, the heating curves were similar. The onset of melting corresponding to the major thermal effect was in the range of $10\text{--}12^{\circ}\text{C}$ ($50\text{--}55^{\circ}\text{F}$). It is to be noted that the melting temperature is determined by extrapolating the slope of the rise portion of the peak to the baseline. The area under the peak indicates the magnitude of the thermal effect, but the temperature on the chart where the peak is recorded is of no significance.

Samples C and D were taken from the upper and lower sections of a Chub that had been vibrated for a week on the Travelometer. The lower, closely consolidated layer of the vibrated Chub, representing most of the cross-sectional area of the Chub, had a melting curve similar to that of the control (unvibrated) Chub.

All of the samples exhibit secondary thermal transitions which start at a temperature near the freezing point of water.

FIGURE 16
 Differential Scanning Calorimeter:
 Heating Curves for Thermal Energy
 Storage Material from CHUBs

The data indicate that changes occur in the thermal energy storage mixture during an accelerated vibration test. In particular curve C which was taken from the upper layer of the vibrated Chub appears to differ appreciably from the other curves. Note, however, that the extrapolated transition temperature is the same as for the control sample. This suggests that the difference in curve C is due to changes in the thermal conductivity of the material. The fact that the transition temperature is unchanged suggests that the composition of the material is not appreciably changed, however, physical characteristics such as crystal size, etc., may have altered appreciably. This interpretation is consistent with the visual observation described in Section I-F-1.

Differential Scanning Calorimetry as a Function of Cycling

Table XI presents data from the differential scanning calorimeter on laboratory samples that were cycled in the Institute's cycling chamber. The data are normalized to the standard ΔT of 30°F. Note that the energy computed from the cooling half of the scan, listed separately from that obtained during the heating portion of the measurement is significantly different. Due to the overlapping nature of the peaks during a heating run (see Figure 16), it is difficult to separate the desired thermal peak from other peaks that are overlapping with it. Similarly, on a cooling run, due to supercooling, several thermal events are present in what appears to be one large peak. For these reasons and the difficulties in obtaining representative samples, differential scanning calorimetry is not considered a good technique for measuring thermal energy storage capacity as a function of thermal cycling.

TABLE XI

DSC DATA

Normalized to $\Delta T = 30^{\circ}\text{F}$ 55 $^{\circ}\text{F}$ Material

Cycles	$\Delta H/m$ (Btu/lb)	
	Cooling	Heating
0	48.3	37.1
0	45.4	60.1
0	40.7	30.7
0	49.7	38.9
0	49.6	42.4
48	36.8	35.5
48	43.1	38.9
48	49.9	37.0
56	49.0	35.7
100	46.1	34.1
101	40.6	31.4
101	42.5	30.5
101	42.7	29.3
101	41.5	28.3

E. Chub Test Results

The thermal energy storage capacity (Btu's per pound) which is of interest is that amount of heat which can be stored under actual field conditions in a practical system. The fact that the system must be carefully specified in order to make meaningful measurements was recognized when the ASHRAE Standard 94-77, "Methods of Testing Thermal Storage Devices Based on Thermal Performance" was developed. The air calorimeter constructed at the Institute of Energy Conversion conforms to this standard and is useful for measuring the heat content of an array of Chubs. It is not surprising, therefore, that the air calorimeter gives the best correlation between laboratory measured capacities and those obtained in Solar One during the summer of 1978 in the first field demonstration of the Chub thermal energy storage material configuration. As mentioned in the description of the air calorimeter, it is calibrated against water as the standard reference material. In one of these calibrations, water contained within Chub film laminate fabricated on the Chub machine was used as the reference.

As a base measurement, the air calorimeter was used to measure the capacity of 183 pounds of 55°F phase change material contained in 1.5-inch diameter plastic tubes. The results of five measurements of the material initially in frozen and thawed states is given in Table XII. Similarly, in Table XIII, a measurement was made of the thermal energy storage capacity of 218 pounds of 55°F phase change material contained

TABLE XII

THERMAL ENERGY STORAGE CAPACITY
AS MEASURED IN THE AIR CALORIMETER

183 Lbs. of 55°F Phase Change Material
 Contained in 1.5-Inch Diameter Tubes

Measurement (#)	Flow Rate fm	Total Energy ^c (Btu x 10 ⁻³)	Total Energy/Lb ^c Btu/lb
1a	183	14.2	77.4
1b	175	13.8	75.2
2a	171	13.3	72.5
2b	181	14.2	77.4
3a	169	14.2	77.4
3b	182	12.6	68.7
4a	173	11.3	61.6
4b	180	11.9	64.9
5a	172	10.9	59.4
5b	181	11.3	61.7

- a) Freezing of thermal energy storage material
- b) Thawing of thermal energy storage material
- c) Includes contributions for specific heat over the normal operating range of 30°F and the latent heat at the transition point

TABLE XIII

THERMAL ENERGY STORAGE CAPACITY
AS MEASURED IN THE AIR CALORIMETER

(218 Lbs. of 55°F Phase Change Material
 Contained in 2-Inch Diameter CHUBs)

Measurement (#)	Flow Rate (fm)	Total Energy ^c (Dtu x 10 ⁻³)	Total Energy/Lb ^c Btu/Lb
1a	181	15.6	71.6
1b	185	17.0	78.0
2a	180	14.0	64.2
2b	178	14.4	66.1
3a	178	12.9	59.2
3b	176	13.2	60.6
4a	178	13.8	63.3
4b	177	14.2	65.1
5a	180	13.2	60.6
5b	177	13.8	63.3

- a) Freezing of thermal energy storage material
- b) Thawing of thermal energy storage material
- c) Includes contributions from specific heat over the normal operating range of 30°F and the latent heat at the transition point

in 2-inch diameter Chubs. The measured thermal energy storage capacities in both of these cases were roughly identical. These values are consistent with, and slightly higher than, previously reported data for the full house testing.⁽²⁾ It should be noted that the data in Tables XII and XIII are for material that had not been previously thermally cycled.

Tables XIV presents results for a portion of the material (206.5 lbs) taken from the 100-cycle test at the end of 71 cycles. Table XV shows data from the air calorimeter for the material cycled 405 times in the accelerated cycle test. The reason for the discrepancy between the two sets of data is not clear at this time.

(2) Experimental Study of Coolness Storage Using Sodium Sulfate Decahydrate, William J. Rice and Joseph J. Sliwowski, ISES Conference, Atlanta, 1979.

TABLE XIV

THERMAL ENERGY STORAGE CAPACITY
AS MEASURED IN THE AIR CALORIMETER

206.5 Lbs. of 55°F Phase Change Material Contained in
 12" Long by 2" Diameter CHUBs After 71 Cycles on the
 Diurnal Test Schedule

Measurement (#)	Total Energy ^c (Btu x 10 ⁻³)	Total Energy/Lb ^c Btu/lb
1a	8.86	42.9
1b	9.43	45.7
2a	8.68	42.0
2b	9.02	43.7
3a	8.75	42.4
3b	9.55	46.2

- a) Freezing of thermal energy storage material
- b) Thawing of thermal energy storage material
- c) Includes contributions for specific heat over the normal operating range of 30°F and the latent heat at the transition point

TABLE XV

THERMAL ENERGY STORAGE CAPACITY
AS MEASURED IN THE AIR CALORIMETER

204 Lbs. of 55°F Phase Change Material Contained in
 12" Long by 2" Diameter CHUBs After Being Cycled
 For 405 Cycles on the Accelerated Test Schedule

Measurement (#)	Total Energy ^c (Btu x 10 ⁻³)	Total Energy/Lb ^c Btu/lb
1a	15.2	74.5
1b	17.8	87.3
2a	14.3	70.1
2b	16.0	78.4
3a	14.5	71.1
3b	14.0	68.9

- a) Freezing of thermal energy storage material
- b) Thawing of thermal energy storage material
- c) Includes contributions for specific heat over the normal operating range of 30°F and the latent heat at the transition point

III. SPECIFICATION AND TESTING

A. For blue Chubs containing 55°F phase change material.

1. Contents

The contents of blue Chubs shall be a uniform mixture of the following components:

Water	41.84	parts by weight
Sodium Sulfate-anhydrous	32.90	parts by weight
Sodium Chloride	6.75	parts by weight
Ammonium Chloride	6.23	parts by weight
Borax - nucleating agent	2.63	parts by weight
Boric Acid - stabilizer	1.75	parts by weight
Min-U-Gel FG - thickener	<u>7.90</u>	parts by weight
TOTAL	100.00	parts by weight

The order of addition and the conditions and temperature of mixing shall be arranged to produce a mixture which has a consistency of 25 to 35 Zahn grams at 25°C, as measured with a Zahn-Gardco Consistency Meter. The consistency meter, and instructions for its use, can be obtained from Paul N. Gardner Company, P. O. Box 6633, Station 9, Fort Lauderdale, FL 33316.

Mixing temperatures should not exceed 160°F. For routine quality control, the differential scanning calorimeter profile of the Chub contents shall match the profile of a standard sample.

2. Dimensions

The standard blue Chub shall have a nominal diameter of 50.8 mm (2.0 inches) and a nominal tip-to-tip length of 508 mm (20.0 inches). The tolerance on Chub length shall be 495 to 508 mm (19.5 to 20.0 inches). Chub length tip-to-tip shall be determined using a metric scale graduated in units of 1 mm. Care should be taken to avoid errors in length measurement due to parallax.

3. Sag

Large variations in the rigidity of the Chub package due to variations in strength, length or filling pressure may lead to difficulties in stacking the Chubs in standard stacking hardware. A pass/fail test for sag in Chubs has been developed using the Chub Sag Tester (Figure 17). This device consists of 102 mm (4 inch) sections of 127 mm (1/2 inch) diameter wooden dowels cemented to a smooth wooden base approximately 51 mm x 102 mm x 508 mm (2" x 4" x 20"). The dowels are aligned parallel to a 102 mm edge of the base, at intervals of 76 mm, 254 mm and 432 mm from one end. The base of the Sag Tester is placed horizontally on an appropriate level surface. When a Chub is laid horizontally across the three parallel dowels, with one end positioned flush with the base of the Sag Tester, no parts of the Chub shall touch the base, i.e., the Chub shall not sag more than 12.7 mm (1/2 inch) at any point. In questionable cases, the sag of the Chub shall be checked at four orientations around its circumference, i.e., with the heat seal up, down, at 90° to the left and at 90° to the right. A Chub shall be considered to have acceptable sag if it passes the test in at least three of the four orientations.

Chub Sag Tester

Sag less than 0.50" is acceptable

FIGURE 17

CHUB Sag Tester

IEC79142

4. Heat Seal Uniformity

A uniform and strong heat seal down the length of the Chub is necessary to ensure retention of the Chub contents during handling and use. For the standard 2-inch diameter Chub, made from a 2-inch wide sheet of laminate, the nominal overlap available for heat sealing is 18 mm.

Heat seals in the Chub package shall have a visually uniform sealed width of at least 10 mm. The seal area shall be essentially free of visible unsealed areas, including wrinkles that traverse the width of the seal area. If an unsealed flap is exposed on the outside of the Chub along the seal area, it must not be peelable as determined by running a thumbnail under the flap and applying moderate inward pressure at the junction of the two layers of film.

5. End Closure

The primary end closure of the Chub package is a clip of heavy wire, comprising one and a half laps around the gathered film. The tightened clip must grip the gathered film so as to achieve a liquid-tight closure without cutting through the film. The ends of the wire clip must be free of sharp burrs. A plastic adhesive or wax, applied to cover the exposed end of the gathered film, serves as a secondary end closure. The end closure must exhibit no visible build-up of white salts, or wet salt solution, around the closure and clip when observed after storage at room temperature for at least seven days.

6. Punctures

An acceptable Chub must be free of pinholes, scratches, or punctures which allow exudation of visible accumulations of white and/or wet salt during handling and storage. These defects are most likely to occur in the creased hemispherical areas at each end of the Chub.

7. Weight

Chub weights shall be determined using a balance sensitive to +1 gram. An Ohaus Heavy Duty Balance, or its equivalent, is suitable. For routine sampling, the weights shall be determined and averaged for at least five percent of the Chubs selected at random in a production lot.

8. Appearance

Chubs ready to be packaged for shipment shall be clean, and free of obvious foreign materials.

9. Color

Chubs for use in cooling applications shall be blue in color. The blue pigmented outer layer of the Chub package shall visually match the standard "Blue" color.

10. Drop Impact

A standardized drop test onto a smooth surface from a height of one meter is used as a measure of the ability of the filled Chub package to withstand dropping and similar abuse during handling as individual Chubs.

An acceptable Chub shall withstand ten drops of one meter onto a smooth hard surface from a horizontal position with the heat seal up, followed by ten similar drops of the same Chub with the heat seal down. For more rigorous testing, to represent extremely rough handling, the test may be continued with the Chub dropped vertically with its bottom end one meter above the smooth flat surface for ten drops, followed by ten vertical drops with the top end of the Chub (as manufactured) down and one meter above the smooth flat surface. In this more rigorous test, the laminate package may become stretched and distorted, so as to be unusable, but should not allow the Chub contents to leak from the package. The more rigorous test will detect weaknesses in the heat seals, and may cause punctures of the laminate by the exposed ends of the wire clips.

11. Delamination

If adhesion between adjacent layers of the laminate, especially those involving the metallized layers, is inadequate, e.g., due to insufficient cure, the laminate layers involved may separate. This will result in a dimpled or bubbly appearance in the laminate, especially adjacent to the cut edge. The Chub contents may then attack the metallized interior layers of the laminate, leading to a marked increase in water vapor transmission rate, and an associated loss of Chub performance.

B. Qualified Chub Fabrication

Based on the specifications of the film laminate developed in cooperation with Du Pont and the use of the Chub Machine (Kartridg Pak, Inc.) by Du Pont to prepare sample Chubs for research evaluation, and the extensive tests conducted both at the University of Delaware and Du Pont, the materials for and the procedure for the preparation of a qualified Chub was completed. Based upon this background, a prototype fabrication facility was set up in 2000 square feet of space located in a building adjacent to the campus of the University of Delaware. In this space, the materials for the preparation of the Chubs were stored, the process machinery for the Chub preparation was installed and used, and the Chubs were inspected, prepared for packaging, and packaged for shipment to a demonstration site. After initial startup and debugging of the process equipment in May 1979, the qualified Chub materials required for life testing under this contract were prepared during the first week of June 1979. These Chubs were 12 inches long by 2-inch diameter. This size was chosen as representative of the Chub thermal energy storage materials which would be used in field demonstrations, but with a size convenient for research testing. The Chubs prepared at the prototype fabrication facility after the first week of June 1979 were all 20 inches in length, which has been adopted as the standard for incorporation into modules (Figure 18) for use in demonstration thermal energy storage systems. During the summer of 1979, approximately 25 tons of Chub thermal energy storage materials were prepared for evaluation in several demonstration systems.

FIGURE 18

CHUB Thermal Energy Storage Module

A schematic diagram for the manufacture of Chubs from materials is shown in Figure 19. The constituent solid materials (sodium sulfate, sodium chloride, ammonium chloride, Borax, boric acid, and Min-U-Gel) are fed in preweighed portions into the reactor mixer. Here hot water is added through a metering pump, the material agitated and homogenized and metered to the Chub machine which forms the final package. This schematic diagrams the flow pattern in a full-scale manufacturing facility. In the facility for the preparation of the qualified Chubs, the material was taken from bags off of skids, weighed on a scale, and premixed, using a ribbon blender such as seen in Figures 20 and 21. The premixed material was added to hot water in the Agi-Mixer (Figure 22) for the dispersion of the materials with the clay gelling agent to create the thixotropic mixture. This can be pumped to a holding kettle such as shown in Figure 23 before going to the Chub machine shown in Figure 24. In the photograph of the Chub machine, the laminate film roll is shown to the upper left, which is fed in flat form and formed into a tube around a mandrel which is heat sealed along the seam. The hydrated salt is inserted into the tube and the tube sealed at each end with a metal clip. The finished product, the Chub (Figure 25), emerges at the bottom of the machine ready for inspection and packaging.

FIGURE 19
Manufacturing Concept

FIGURE 20
Ribbon Blender

FIGURE 21
Ribbon Blender

FIGURE 22
Agi-Mixer

FIGURE 23
Holding Kettle

FIGURE 24
CHUB Machine

FIGURE 25

NOTES:

MATERIALS LIST M/LI

Na ₂ SO ₄	32.89%	MS 1002
Water	41.82%	MS 1001
Borax	2.63%	MS 1007
Boric Acid	1.75%	MS 1003
Minugel	7.89%	MS 1006
NaCl	6.75%	MS 1005
NH ₄ Cl	6.23%	MS 1004
Film		MS 1008
Clamps		MS 1009

PARTS LIST P/LI

Mix	3.25 lb.
Film	147 sq. in.
Clamps	A1 .100" x 1-3/8"L

DRAFTSMAN	JD	UNIVERSITY OF DELAWARE	INSTITUTE OF ENERGY CONVERSION
CHECKER		TITLE 55° CHUB-20"	
DES ENGR			
PROD ENGR		SIZE A	DRAWING NO. P/N-1
QA ENGR			REV.
DEV MGMT		SCALE 3"=1'-0"	SHEET 1 OF 1
PROD MGMT			

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