University of Dayton
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ADVANCED PHASE CHANGE MATERIALS AND
SYSTEMS FOR SOLAR PASSIVE HEATING AND COOLING
OF RESIDENTIAL BUILDINGS

Final Technical Report
Covering the Period of
29 May 1986 through 15 July 1988

Grant No. DE-FG03-86SF16308

Prepared By:
Ival O. Salyer
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Prepared For:
U.S. Department of Energy
Oakland, CA 94612

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1. INTRODUCTION AND SUMMARY

During the last three years under the sponsorship of the DOE Solar Passive Division, The University of Dayton Research Institute (UDRI) has investigated four phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current and most promising series of candidate phase change materials, C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultrapure C-16 to C-18 alkyl hydrocarbons (PCM) from ethylene polymerization that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price of \$1.86/lb (technical grade) and \$9.68/lb (98% pure grade). These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, a series of crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at the much lower cost of \$0.26/lb to \$0.50/lb from petroleum refining (Witco, Shell, Exxon, Union). These petroleum-based paraffins have melting points ranging from 15-80°C, and a quoted price of \$0.26/lb to \$0.50/lb for tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated, "neat" and in "blends."

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. We have defined four economic and effective methods of packaging the candidate PCM in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer, and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

The four processes are as follows:

1. Direct incorporation of PCM into the wet mix of building materials;
2. Direct incorporation into rubber or plastics medium for floor and wall tiles;

3. Indirect incorporation by first swelling the PCM into crosslinked polyethylene pellets or powder which are then incorporated into building materials;
4. Direct incorporation by imbibing (percolating) the melted PCM into the open spaces in porous building materials.

As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3), the building material is less likely to burn. However, in process 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard after ignition will continue to burn slowly until the PCM is exhausted. In process 2, where the PCM is compounded into rubbers and plastics, the resulting composite will also burn, unless the polymer matrix is made fire retardant with effective additives.

We have preliminarily addressed the flammability problem in these four processes by incorporating a state-of-the-art fire retardant system consisting of chlorinated paraffin and antimony oxide into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in process 4. Accordingly, more research on this specific process and on the whole area of fire retardance was carried out. This was a subject of major emphasis in the last year's research, and further work is required to scale-up and optimize the processes developed.

However, other areas were also intensively investigated. We continued laboratory tests of both pure and lower cost commercially available linear alkyl hydrocarbon PCM to define materials that could provide the most cost-effective performance for solar passive applications. We completed extensive thermocycling tests of small-scale samples of building materials containing PCM, and prepared model samples for tests by others. Finally, we continued our efforts towards commercializing the results for home heating and cooling through demonstrations of processes 3 and 4 in the laboratories of a major U.S. manufacturer of plasterboard, and aggressive marketing of the technology elsewhere in the U.S. and abroad.

Additionally, in separate research, we have developed several promising spin-offs of the PCM technology that may reach commercial fruition considerably sooner than the application in building materials. These spin-off

applications include use in tableware for keeping food and drinks hot or cold, citrus tree wraps to prevent overnight freezing, and hot and cold packs for medical therapeutical uses.

Several patent applications have been filed in the United States and abroad on the technology developed in the research. Five U.S. patents have been issued and others are pending. One license agreement has been completed with a major Japanese company that is exclusive for Japan. At least three option/license agreements are in the active state of negotiation, and at least one will be completed within the next few months.

On an overall basis, the research to date can be said to constitute a major breakthrough in thermal energy storage technology that can in the near future become commercialized in a variety of applications. Successful commercialization of building materials can affect substantial energy conservation, and thereby, perhaps, minimize the "greenhouse effect" as well.

Details of the research are contained in Section 2, "Discussion of Technical Approaches," and in the attached copies of the individual Monthly Progress Reports.

2. DISCUSSION OF TECHNICAL APPROACHES

The major part of the research during this contract period was directed toward the following three objectives.

- Find, test, and develop low-cost effective phase change materials (PCM) that melt and freeze sharply in the comfort temperature range of 73-77°F for use in solar passive heating and cooling of buildings.
- Define practical materials and processes for fire retarding plasterboard/PCM building products.
- Develop cost-effective methods for incorporating PCM into building construction materials (concrete, plasterboard, etc.) which will lead to the commercial manufacture and sale of PCM-containing products resulting in significant energy conservation.

2.1 Phase Change Materials Development

2.1.1 Basic Studies of Pure Linear Alkyl Hydrocarbon

Extensive work with 99% pure n-hydrocarbons obtained from Humphrey Chemical Company confirmed the earlier observations that these expensive "C-18" crystalline alkyl hydrocarbon PCM are the most effective PCM systems available for thermal energy storage for applications in the 0° to 80°C temperature range.

The research also established the little or no supercooling (~2°C) of the PCM at the relatively low rate of heating and cooling that may be expected during their actual usage. Selective blending of pure normal hydrocarbons showed that sharp transitions and minimum loss of latent heat are obtained in blends of as many as four adjacent homologues. These blends melt and freeze at the temperatures projected for pure linear alkyl hydrocarbons of the calculated average chain length. This gives us the ability to "tailor" blends for intermediate temperature ranges, as well as to check the suitability of lower cost commercially available PCM.

Interestingly, odd carbon atom pure paraffins show a pronounced solid-state transition at chains as short as C-9. This type of transition is encountered only in even carbon chains of the lengths of C-22 and longer.

2.1.2 Evaluation of Humphrey Chemical Company Technical Grades of Linear Alkyl Hydrocarbons

The ultrapure alkyl hydrocarbon PCM evaluated above are not obtained by refining of petroleum, but rather by polymerizing ethylene. The products obtained by this process consist primarily of even-numbered carbon atom PCM which have little or no solid-state secondary transition at carbon chain lengths of 16 to 22 carbon atoms. In preparing these PCM, the ethylene is polymerized by Chevron, Shell, or Ethyl to an olefin that contains a terminal double bond. The olefin is subsequently hydrogenated by Humphrey Chemical Company to form saturated linear alkyl hydrocarbon PCM that are sold without purification as "Technical Grades." The technical grades (\$1.86/lb) are then fractionally distilled to make more expensive (\$10.00/lb) products of 98-99% purity.

The Humphrey Technical Grades are available in chain lengths of 14 to 24 carbon atom lengths. Because of the absence of solid-state transitions due to odd carbon chain length compositions, the technical grades tend to have significantly higher heats of fusion and crystallization than the lower cost products from petroleum refining. For this reason, we conducted a thorough evaluation of the Humphrey Technical Grades of PCM since it was believed they could be cost effective at the selling price of about \$0.70/lb (projected about two years ago), with even lower prices foreseen as possible for large-scale production quantities.

Differential Scanning Calorimeter (DSC) analysis at 2°C/minute rate of heating and cooling showed that Humphrey Tech Grade C-18 has a melting and freezing temperature near the comfort temperature range of 73-77°F, and stores and releases about 50 cal/gm heat of fusion and crystallization.

However, during the last two years, the cost of the ethylene monomer starting raw material has escalated rapidly to more than double its earlier price. Accordingly, the selling price of all products made from ethylene has also risen dramatically resulting in Humphrey Tech Grade C-18 listing to sell for about \$1.86/lb, a figure that might require prohibitively long pay-back times through energy savings in home heating and cooling.

Therefore, much emphasis has, in the last year, been placed on cooperative research with petroleum refiners, such as Witco, with the objective of defining a more cost-effective PCM for home heating and cooling applications.

2.1.3 Cooperative Research With Witco Chemical Company to Develop Improved PCM in the Temperature Range for Residential Heating and Cooling From Petroleum Refining Operations

As pointed out in Paragraph 2.1.2, the "purer" alkyl hydrocarbons from ethylene polymerization are considerably more expensive than the corresponding by-products of normal petroleum refining. Accordingly, one of our projects of emphasis during the project period was collaborating with Witco Chemical Company to develop lower cost PCM in the C-16 to C-18 range which are not now commercially available.

We participated with Witco in developing an effective process for commercial manufacture of K-61, a PCM that is a likely candidate to be used for solar heating and cooling of buildings because of its transitions near the comfort range. DSC and gas chromatographic analyses of different fractions from distillation versus solvent crystallization were carried out. It was observed that fractions from crystallization precipitates mostly the higher molecular weight linear hydrocarbons leaving the lower and branched homologues in solution. This is reflected in higher heats of fusion and crystallization (46-48 cal/gm) as compared to the unfractionated products (35-44 cal/gm).

A five-gallon supply from a larger lot of solvent fractionated K-61 (prepared by Chevron for Witco) was found to compare favorably with regard to thermal energy storage characteristics with that of small laboratory samples of K-61 previously obtained from Witco. This is important in indicating that scale-up of the solvent fractionation process for eventual commercial production is feasible.

2.1.4 Evaluation of Fatty Acid Ester PCM for Solar Passive Applications

In the event of a major crisis in the Mideast that could curtail the supply and escalate the price of petroleum, a renewable indigenous source, such as the fatty acid esters, could become of interest. For this reason, as well as to obtain background data on research elsewhere (e.g.,

Canadian Mines and Resources), we have determined the chemical composition and thermal energy storage properties of U.S. commercial grades of butyl stearate.

The chemical composition of the butyl stearate was determined by chromatographic analysis to be butyl stearate/butyl palmitate (67/33). The thermal energy storage properties were analyzed by DSC at several rates of heating and cooling. The butyl stearate was found to melt and freeze near 20°C, and to store and release about 35 cal/gm. Esters with shorter side chains melt at somewhat higher temperatures (e.g., methyl ester, ~38°C).

This "impure" grade of butyl stearate is projected to sell in the United States for about \$0.70/lb. A purer grade obtained by distillation of the mixed esters is projected to sell for \$1.10/lb. The fatty acid esters could undergo hydrolysis with long-term exposure in cementitious building materials, and they may also support mold growth. Thus, on the basis of overall cost/performance, the fatty acid esters are less desirable than the alkyl hydrocarbon PCM, unless petroleum should suddenly become less available and less competitive in price. Further, the products can only cover a very limited range of temperatures.

We have done, for the same reason as above, DSC analysis on three commercially available fatty acid esters from Japan that are derived from palm oil. These esters (Thermotops) can store and release thermal energy in the same limited range of temperatures as the esters from animal fats. However, because of their higher palmitic ester content, their thermal energy storage capacity is significantly lower.

2.1.5 Effect of Rate of Heating and Cooling on Thermal Energy Storage Properties as Determined by DSC Analysis

As a matter of standard practice, we have for economy ordinarily run all our DSC analysis on thermal energy storage materials at 10°C/minute rate of heating and cooling. In practical end-use applications, the rates of heating and cooling would be considerably lower than this. At 10°C/minute rate of heating and cooling, we also noted a significant difference in the melting temperature (T_m) and freezing temperature (T_f).

Accordingly, to obtain a better evaluation of these rate effects, we ran DSC measurements on the Humphrey Tech Grade of C-18 and butyl

stearate at 10, 5, 1, and 0.1°C/minute rate of heating and cooling. The results were interesting in showing that for both C-18 and butyl stearate the melting and freezing temperatures closely approach the same temperature at slower rates of heating and cooling (e.g., 1.0 and 0.1°C/minute). These results are of considerable practical importance since, in solar passive applications, the rate of change in temperature is not likely to exceed 0.1°C/minute (6°C/hour). Further, it indicates that with truly congruent melting and freezing, a single material, such as Humphrey C-18 or butyl stearate, could be effective in both winter heating and summer cooling.

2.2 Fire Retardance of Solar Passive Building Materials Containing Alkyl Hydrocarbon PCM

Most of these experiments were directed at making PCM-imbibed plasterboards fire retardant. Chlorowax 70S and antimony oxide, the cheapest and most common fire retardants, are not soluble in hydrocarbon PCM, and so cannot be used to fire retard plasterboard during incorporation of PCM by percolation. After examining a number of halogenated organic compounds from Ethyl Corporation and Great Lakes Corporation, Ethyl's BCL-462 (dibromoethyldibromocyclohexane) was found to be soluble with the hydrocarbon PCM in all proportions. This was considered a breakthrough since, in combination with submicron particle-size antimony pentoxide, this has the potential of fire retarding plasterboards simultaneously with percolation of the PCM. Several plasterboard samples percolated with Witco 45A/BCL-462 in the ratio of 75/25 showed improved fire retardance in laboratory experiments.

Encouraging fire retardance in imbibed plasterboard was also obtained using a soluble halogenated alkyl hydrocarbon from Ferro Chemical Company. Ferro's Bromochlor 50 was soluble in our PCM at room temperature, and their Bromochlor 70 at the standard 80°C percolation temperature. Further comparison experiments are planned to determine whether the Bromochlor fire retardants in combination with antimony oxide are equal or better than the BCL-462 with which we have more extensive experience. In follow-up experiments with the soluble fire retardant, BCL-462, it was found that up to 49% Witco 45A/BCL-462 combination can be incorporated in plasterboards by sequential percolation in PCM and BCL-462. By varying the duration and order of immersion, different ratios of these components can be incorporated in

plasterboard. A number of these combinations showed potential for improved fire retardance.

In very recent experiments, we found that solubility of the fire retardant in the PCM is not a requirement if the sequential percolation method referred to above is used to adjust the amount of PCM absorbed as well as to preferentially locate the fire retardant on the surface.

From the Dow Chemical Company, we have obtained two phosphate ester fire retardant compounds, FYROL CPF (trichloroisopropyl phosphate) and FYROL CEF (trichloroethyl phosphate). Neither of these compounds are soluble in alkyl hydrocarbon PCM. In sequential percolation experiments, we found that we could control the PCM uptake by varying the PCM and FYROL percolation time. Best results were obtained with the FYROL CEF in that we obtained excellent resistance to initial ignition, quick extinction after the flame was removed, and little smoke or fumes emitted.

Experiments were also carried out to fire retard plasterboard by in-situ incorporation of insoluble (and cheaper) fire retardants during the manufacturing process.

In order to introduce fire retardants by the in-situ process, it was necessary to duplicate the commercial process to prepare low-density plasterboards. Preliminary experiments showed that it was possible to match the density of commercial plasterboards by adjusting the amount of foaming agent.

In parallel experiments, it was considered that it may be possible to fire retard plasterboards by lowering the amount of PCM absorption by using PCM diluted in a solvent as the imbibing medium. Accordingly, samples with varying PCM content from 2%-23% by weight were prepared by percolation of PCM in heptane and methylene chloride. The samples containing 18% PCM extinguished in five seconds. This is a very encouraging development since plasterboards with significant thermal energy storage and reduced flammability can be made by varying the solvent/PCM ratio to reduce the PCM content.

Subsequently, it was found that use of solvent diluent to limit PCM uptake could be avoided entirely. The plasterboard was first percolated for a very short time (e.g., one minute) to obtain about 20% composite weight

PCM uptake, then followed by post heating to equilibrate the surface concentrated PCM throughout the interior of the board. Thereby, we obtained a lower and non-wicking average concentration of PCM throughout the board. This is a very promising approach which should be followed up if there is continuing commercial interest in developing the percolation process.

Importantly, the approach of limiting the total quantity of PCM to below the critical level required to support combustion has also been investigated by our Japanese licensee using HDPE/PCM pellets incorporated into the wet mix of the plasterboard. They have evaluated the burning characteristics of plasterboard containing 20% and 40% wt of the PCM in the HDPE/PCM pellets with very encouraging results. At the lower PCM concentration, the plasterboards would not ignite. At the 40% PCM level, the plasterboard burned slower than plywood. Off-gas products were also monitored in their tests.

Another method of fire retarding plasterboard containing either imbibed or in-situ incorporated PCM was briefly investigated during the last quarter of the current contract period. We investigated the thermal energy storage properties of halogenated alkyl hydrocarbons (1-bromo octadecane and 1-bromo hexadecane) supplied by Humphrey Chemical Company. DSC analysis at 2°C/minute showed the 1-bromo octadecane to melt and freeze at about 23°C and to have a heat of fusion and crystallization of about 42 cal/gram. This approach is interesting since the PCM would be composed entirely of an inherently fire retardant chemical. Unfortunately, this Humphrey chemical is also expensive and sells for about \$3.08/lb, a price that would require an excessively long energy pay-back time if used for home heating and cooling applications.

In any continuing research, we therefore plan to place most emphasis on obtaining low-but-useful concentrations of PCM in plasterboard, preferably by the in-situ HDPE/PCM pellet approach. However, we would also continue to develop the solvent-free imbibing of low-but-useful PCM concentrations into plasterboard that provide non-wicking fire retardant products.

We would continue to devote some effort to the sequential imbibing of PCM followed by imbibing of a fire retardant. In this approach, we would use sequential percolation in a second immersion bath consisting of the

combination of a soluble halogenated fire retardant, plus the submicron particle-size antimony oxide or an immersion bath of FYROL CEF (trichloroethyl phosphate).

2.3 Further Developments on Containment Methods

In further studies on permeation, it was possible to swell about 90% K-61 PCM and about 81% NP-15 in Marlex 6006 (10 mrad). NP-15 melts and freezes below room temperature and can be potentially useful for cool storage and breeze deck deicing.

In the above experiments with NP-15 and HDPE pellets, it was observed that washing with poorer solvents (MEK > ethanol > methanol) increased the ultimate weight gain of swelled pellets. This indicates that washing removes the swelled wax from the top layer of the pellets. This has been confirmed by DSC experiments from different layers of the swelled pellets.

The above observation about the removal of swelled wax by washing with MEK is of minor consequence for the pellets, but it has a major impact for the HDPE powders. We would like to imbibe HDPE powders with PCM since the small particle size of the powder would be less detrimental to the strength of the building material. However, earlier work showed no weight gain for HDPE powder swelled in Witco 45A at 150°C for two hours and washed with MEK. Follow-up work during this period with methanol rinsing showed substantially higher weight gain for 45A imbibed with Marlex 6006 powder. Only minor effect of the level of gamma irradiation between 4-8 mrad was noted on imbibed weight or DSC determination of PCM (provided the samples were washed with methanol). This conclusively proves that because of the smaller size, a good solvent like MEK washes away most of the imbibed PCM in powders. Further research is necessary to develop an effective gamma irradiation crosslinking process for HDPE powders than can subsequently be swelled to approximately 80% wt PCM.

The second method attempted is crosslinking of HDPE by chemical methods (e.g., peroxide and vinyl triethoxy silane). Some samples of LDPE, HDPE and polypropylene prepared by one or the other of these methods, and subsequently swelled in paraffinic hydrocarbon, have been tested by us for thermal energy storage and were found to contain up to 85% hydrocarbon, an amount comparable to crosslinking by gamma irradiation.

Prior work shows, potentially, the peroxide method will be cheaper than gamma irradiation. Accordingly, a series of samples were recently made by extrusion crosslinking with dicumyl peroxide at different concentration levels at Springborn Laboratories. Some of these also contained antimony pentoxide to simultaneously fire retard the pellets (after they are subsequently permeated with PCM/BCL-462 solution). Pellet sizes can also be adjusted to obtain smaller sizes. Further research on swelling of these pellets, analysis of thermal energy storage, and subsequent incorporation into building material is planned.

In further efforts aimed at reducing the cost of the crosslinked HDPE/PCM pellets, we evaluated incorporating the PCM into the liquid melt of HDPE. By simply mixing the PCM into the molten HDPE at a temperature of about 150°C, we were able to incorporate to obtain up to 85% of composite weight of PCM. The melts were manually cut into pellets and later extruded to obtain small hard pellets that are apparently stable to room temperature thermocycling.

Significant cost savings can be realized in this process since the irradiation crosslinking is eliminated. This modification is claimed in patent applications, and should be further investigated in the continuing research.

The work was also directed to alternatives to the containment methods already described. One of the methods attempted was microencapsulation. Preliminary data showed good encapsulation and thermal energy storage, but projected encapsulation costs are very high (\$5.00-\$10.00/lb).

2.4 Stability of PCM to Repeated Cycles of Melting and Freezing

One of the most important criteria of PCM for use in Solar Passive heating and cooling of buildings is the ability to undergo many repeated cycles (e.g., 1000X) of melting and freezing without degradation of thermal energy storage properties. To test the stability of the alkyl hydrocarbon PCM to such thermocycling, samples of the PCM, PCM in HDPE pellets, and PCM in building materials were placed in small glass vials in an automated oven and cycled between -20°C and +80°C for 1000 cycles.

This thermocycling portion of this experiment has been completed. The preliminary results were very encouraging since there was no visually apparent degradation of the PCM themselves or the building products containing them. The HDPE/PCM pellets showed little or no oozing out of the pellets. There was no visible PCM "running out" of imbibed (percolated) plasterboard samples. DSC analysis of the products was scheduled but not completed due to unavailability of contract funds. The samples are stored, and therefore could still be analyzed if the necessary funds become available.

2.5 Technology Transfer to Industry

Transfer of the PCM technology to the building products industry was continued throughout the current contract period. A technical presentation made at the 20th Intersociety Energy Conversion Engineering Conference (IECEC) in August 1985 led to many subsequent inquiries. We have placed our principal (almost entire) effort on interesting the large manufacturers of plasterboard here in the United States. The potential for use of the PCM in concrete was also evaluated to some extent and should be further investigated.

We did demonstrations of the wet mix HDPE/PCM pellet process in the laboratories of United States Gypsum Corporation (USG) and the National Gypsum Company (NGC).

We received an option offer from USG that we did not accept. The offer was later withdrawn after USG went through extensive restructuring and cutbacks in personnel and research funding.

During the last year, we have had an active research program with NGC to work with them in a joint program to evaluate the HDPE/PCM pellets incorporation into the wet mix of plasterboard and imbibing (percolation) into finished plasterboard. This work is still continuing and is nearing a decision that will be determined by the projected economics (energy saving pay-back time). The work was supported entirely by NGC and details are therefore proprietary. However, NGC's Senior Vice President, Joe Keller, has expressed stronger interest in the HDPE/pellet process for many reasons (little added capital equipment, easier to fire retard, etc.).

However, during the current contract period, we have also, with separate funding, investigated the potential of the alkyl hydrocarbon PCM for applications other than for heating and cooling of houses.

The use of the PCM in tableware for keeping hot foods and drinks at the correct temperature, cold foods cold, is of strong interest to two separate industrial organizations. An option/license agreement is anticipated to be finalized in the very near future.

Another application for the alkyl hydrocarbon PCM technology is in medical therapy (hot packs and cold packs). Four companies are currently interested in this technology.

A combination of an insulative PCM "wrap" for citrus trees to prevent overnight freezing is also of current interest to a large Florida manufacturer of frost protection products.

Other potential applications include preventing overnight freezing of bridge decks, PCM-containing textiles, and waterproofing of cementitious materials (concrete, plasterboard, etc.).

We have negotiated a license for the phase change technology with a large Japanese enterprise that is exclusive for Japan and excludes the North American continent. They expect to have their first products on the market early in 1989.

Additional details on most of the above aspects of the PCM technology are contained in the copies of the individual Monthly Progress Reports attached.

3. CONCLUSIONS

1. Taken together with the prior DOE/UDRI sponsored research, the linear alkyl hydrocarbon phase change materials (PCM) defined in this program constitute a major breakthrough in thermal energy storage materials for the human comfort temperature range (e.g., 73-77°F), and for temperatures immediately above and below this.
2. It is unlikely that PCM which are more cost-effective than the linear alkyl hydrocarbons derived from petroleum refining (\$0.50/lb, 35 cal/gm) for home heating and cooling applications can be found. Importantly, these PCM are non-toxic; and stable to hydrolysis, thermocycling, and prolonged storage.
3. It is also unlikely that PCM having equal or higher thermal energy storage than the ultra pure linear alkyl hydrocarbons derived from polymerization of ethylene (\$1.86 to \$10.00/lb, 50-60 cal/gm) for the near ambient and higher temperatures can be found at any price.
4. Practical processes have been defined and demonstrated whereby these PCM can be incorporated into building construction materials including plasterboard and concrete. Currently, incorporating PCM in the form of HDPE/PCM pellets into the wet mix of plaster is preferred over the imbibing (percolating) into finished plasterboard. If the technology can be successfully commercialized in the United States, major energy conservation should result with significant attendant benefits including reducing U.S dependence on imported oil and diminishing the CO₂ "greenhouse" effect. Commercialization of the technology for home heating and other applications now appears certain to occur this year (1989) in Japan, but will occur later in the United States.
5. The problem of fire retardance in plasterboards containing the alkyl hydrocarbon PCM has been addressed effectively, but much further research remains to be done. Regulating the PCM content to a level that will not support combustion (about 20% composite weight) appears to be the most practical solution, but may require use of thicker plasterboards (e.g., 5/8" or 3/4") to supply adequate storage. However,

effective fire retardant additives were also defined, as well as processes for incorporating them into plasterboard.

6. To anticipate the future possibility of an acute petroleum shortage, alternate PCM from renewable and other resources (e.g., fatty acid esters) have also been defined and methods of "containment" developed for them.
7. There have been several important potential spin-offs of the technology for other applications including tableware, medical hot and cold wraps, and insulative wraps to prevent overnight freezing of citrus trees, etc. These applications can and probably will be commercialized in the United States soon, and well before the use of the PCM for heating and cooling of residential buildings.

Other spin-offs of the technology that are further from commercialization include preventing the overnight freezing of highway bridge decks, textile wearing apparel, and waterproofing of concrete.

8. Of both theoretical and practical interest, we have obtained differential scanning calorimeter data on an extensive series of ultrapure (98% to 99%) alkyl hydrocarbons, and on synthesized blends of these pure PCM. We found pronounced secondary solid-state transitions early in odd-number carbon chains (e.g., C-9), and later (e.g., C-22) in even-number carbon atom chains. We have also determined the effect of rate of heating and cooling on the measured melting and freezing temperatures of pure alkyl hydrocarbons, commercial products (which are blends), and fatty acid esters. Importantly, these data establish clearly that the alkyl hydrocarbon PCM melt and freeze congruently at rates of heating and cooling that are well within the range of temperature change that would be encountered in actual applications. Additionally, it was found the commercial paraffins that are blends of up to four chain lengths nonetheless melt and freeze sharply at the temperature predicted from their average chain length, provided the blends are nearest "neighbors" in the homologous series. This single melting temperature is of critical importance to the use of the lower cost commercial alkyl hydrocarbon PCM blends derived from petroleum refining.

9. As mentioned in Section 2.5, we have filed comprehensive patent applications covering important aspects of the phase change technology in both the United States and abroad. There are five issued U.S. patents and several more pending. One foreign license has been negotiated, and several U.S. licenses are in the negotiation stage.
10. Although major progress has been made in the total DOE-sponsored research, this progress could have been significantly greater were it not for the problems of low funding, and lapses in funding, in a program where DOE repeatedly stated they planned to continue in order to achieve commercialization of the technology. These "hiatus" in funding detracted from the efficiency of the program, and created severe personnel management and morale problems. If the program is to be continued to address the remaining outstanding problems, and to achieve commercialization, it is sincerely hoped that this can be accomplished without the protracted funding lapses, or low levels of funding encountered repeatedly in the research to date.

4. RECOMMENDATIONS FOR FUTURE RESEARCH

4.1 Phase Change Material Containment

As described in Section 1, we have developed four different methods of processes for containing linear alkyl hydrocarbon phase change materials (PCM) in cementitious products for solar passive heating and cooling of residential buildings. The process of greatest current interest for commercialization in plasterboard is the one wherein HDPE/PCM pellets are incorporated into the wet mix of plaster and concrete, and the process of continuing but secondary interest is where the PCM is incorporated into the plasterboard or concrete by immersion into liquid PCM (imbibing, percolation). We believe further research and development on both processes, in collaboration with plasterboard and concrete building materials manufacturers, is necessary.

4.2 Chemical Crosslinking of Polyethylene Pellets, Sheets, Films, and Moldings With Vinyl Triethoxy Silane

We have in prior research evaluated the use of vinyl triethoxy silane (VTES) coupling agent as a method to crosslink high-density polyethylene and polypropylene. This modification, after hydrolysis crosslinking, should result in Si-O crosslinks that provide strong adhesive bonding to plaster and concrete, and thereby significantly enhance the physical properties of the product. We recommend that this alternate crosslinking be reevaluated to determine its relative merit and cost effectiveness compared to electron-beam or gamma-irradiation crosslinking.

4.3 Incorporation of PCM Into Uncrosslinked Polyethylene

We have in recent research found that it may be possible to incorporate the PCM into uncrosslinked HDPE pellets with significant reductions in raw material costs effected thereby. We recommend further investigation of this lower cost process be undertaken in any continuing research.

4.4 Fire Retardance

Another important issue that requires continuing research is that of fire retardance. The relative merit of the two approaches (reducing the PCM content below that which will support combustion and fire retardant

additives) needs significant further research and development, including large-scale fire tests.

4.5 Government Assistance to Promote Technology Transfer, and Commercialization of the PCM Technology in Plasterboard

The PCM technology is at a critical state of development insofar as transfer of the technology for heating and cooling of buildings is concerned. The principal issue to be resolved for application of the technology in home heating and cooling is economic pay-back time in energy cost savings. Thus, financial (DOE) and technical assistance (UDRI) is needed for the one petroleum refiner (Witco) who is preparing to produce a low-cost (\$0.50/lb) alkyl hydrocarbon PCM which melts and freezes sharply at 75°F. Government support for this part of the technology transfer process is crucial to successful transfer of the residential heating and cooling technology to industry by making a cost-effective PCM commercially available. There is no other significant market foreseen for these room-temperature melting paraffins.

The second issue where government assistance would materially speed transfer of the PCM technology for heating and cooling of buildings is through demonstrating unequivocally the energy savings and added comfort of the PCM installed in one or more houses. Theoretical analysis now scheduled will not convince the homeowner to undergo the added expense of the PCM system. Preferably, two identical houses should be built in two or three selected climate zones in the United States in which families can live for a two-year cycle, interchanging after the first year; all energy costs would be monitored and the added "comfort" features evaluated. With these data, the economic pay-back time can be accurately determined and cost effectiveness established with certainty.

Upon completion, most of the government's investment could be recovered through sale of the houses.

4.6 More Extensive Evaluation of the Alkyl Hydrocarbon PCM Technology in Concrete Building Materials

Primarily at the direction of our DOE Contract Monitor, the principal and almost exclusive emphasis in the research during the last two contract periods was placed on developing methods (processes) for incorporating the

alkyl hydrocarbon PCM into plasterboard. Concrete and hollow-core concrete blocks are also major building materials for use in residential housing. Due to the mass of concrete building materials, a small percentage of PCM by weight (e.g., 5%) can achieve equivalent or greater storage than 35% wt in plasterboard. Additionally, depending on the process used, the concrete can be simultaneously waterproofed as in plasterboard.

In view of the above, we recommend that further investigation of the use of alkyl hydrocarbon PCM in various forms of concrete building materials, especially hollow-core concrete blocks, be included in continuing DOE-sponsored research.

4.7 Further Investigation of Alternatives to the Alkyl Hydrocarbon PCM From Petroleum

Whether they are obtained from petroleum refining operations or the polymerization of ethylene, the ultimate source of the current alkyl hydrocarbon PCM is fossil fuels (petroleum and natural gas). There is no question, at the present rate of consumption, these resources will gradually become depleted. The question is exactly when will the total world demand exceed the total world supply by a significant amount. There is also no doubt when this occurs, the resulting crisis will be an order of magnitude greater than the short-lived OPEC-generated shortage in 1977. At that future time, the price of hydrocarbon raw materials will rapidly escalate toward the selling price of more-valuable-than-fuel products made from them.

Since the above scenario is certain to occur, it is strongly recommended that the study of alternate PCM from non-fossil fuel resources we have already briefly investigated should be continued and expanded. The fatty acid esters, alcohols, and saturated hydrocarbons which can be derived from these indigenous renewable resources should receive intensive effort in continuing DOE-sponsored research to develop the most cost-effective systems.

APPENDIX

MONTHLY PROGRESS REPORTS, NOS. 1-20
JUNE 1986 - FEBRUARY 1988

MONTHLY PROGRESS REPORT NO. 1
CONTRACT NO. DE-FG03-86SF16308
COVERING JUNE, 1986

1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research, on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase-change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends."

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

In the first process, the PCM's (alkyl hydrocarbons) can be added directly into the wet mix of cementitious materials at concentrations up to

5% wt (cement) and 10% wt (plaster). However, considerable reduction in the strength properties of the cement and/or lengthening of the setting time is encountered. In one modification of this process, the cementitious products can also be made waterproof.

In the second process, the PCM's are first mechanically dispersed into rubbers, such as natural rubber, and plastics, such as polyethylene, using Banbury mixer or roll mill, at concentrations greater than 50% wt. These PCM "concentrates" can potentially be used directly, in sheet form, as floor or wall tiles and may be especially useful for retrofit use in buildings where they could be adhered to existing walls and floors.

In the third process the PCM is imbibed into small pellets of HDPE by swelling at elevated temperatures. The resulting small hard pellets contain up to 80% wt PCM, and should be easy to incorporate into the wet mix of cementitious materials with minimum reduction in strength properties.

The rubber or HDPE pellets from the second and third process above can potentially be used as an effective low-cost pellet bed heat exchanger; to heat or cool the air, or liquid medium, in solar passive hybrid applications.

In the fourth process, the PCM in liquid form is percolated directly into the open space in porous building materials (cement, plaster bricks). This process also has the attendant advantage that the porous products are simultaneously waterproofed. The process has obvious potential applications in waterproofing cement for other applications as well (i.e., highway bridge decks).

As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3). The building material will not burn. However, in process No. 4, where

the PCM is percolated into plasterboard (in high concentrations), the plasterboard after ignition will continue to burn slowly until the PCM is exhausted.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self extinguishing. However, there are difficulties in applying this technology effectively in process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will initiate extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

This month's work consists of reexamining the thermal energy storage data of pure hydrocarbon phase change materials (PCM) and blends. This was taken up because of the availability from Humphrey Chemical of the whole series of normal paraffinic hydrocarbons of 99% purity. The results of this investigation were written in the form of an extended abstract and was submitted to the North American Thermal Analysis Society. A copy of this abstract is attached for a brief description of this month's work. The full paper, which will include more data that are being processed now, will be presented at the 15th Annual Conference of North American Thermal Analysis Society to be held on September 21-24, 1986 at Cincinnati, Ohio.

ANALYSIS OF CRYSTALLINE PARAFFINIC HYDROCARBONS FOR
THERMAL ENERGY STORAGE BY DSC

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ABSTRACT

Thermal energy storage potential of crystalline paraffinic hydrocarbons for solar-passive heating in residential building has been studied by differential scanning calorimetry (DSC). The DSC parameters chosen are melting temperature (T_m), crystallization temperature (T_c), supercooling ($T_m - T_c$), latent heat of fusion (ΔH_f), and latent heat of crystallization (ΔH_c). Pure hydrocarbons having a narrow distribution of carbon chain lengths, blends of pure hydrocarbons, as well as less pure commercial waxes, were studied. DSC data are explained on the basis of different crystal symmetries of "odd" and "even" carbon chains. The reasons for lower thermodynamic values of blends and commercial paraffins are indicated.

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INTRODUCTION

Extensive use of DSC has been made by the present authors¹ to determine the thermal energy storage potential of paraffinic hydrocarbons. Most commercial materials are, however, blends of normal hydrocarbons and have lower transition temperatures and enthalpies than those of the pure hydrocarbons. The present investigation aims at understanding the thermodynamic data of the pure materials and selected blends in order to be able to predict the thermal energy storage potential of commercial blends available at a much cheaper price.

EXPERIMENTAL

Instrumentation

Thermodynamic values were determined with a DuPont DSC module coupled with a DuPont 9900 system, controller-programmer. The data were generated at 10°C/min. under 100 ml/min. flow of nitrogen between -40°C and 70°C. An average of three data points were reported. The transition temperature recorded is that of the "peak" and not the "onset" temperature.

Material

The paraffinic hydrocarbons used were C₁₂ to C₂₄ normal aliphatic hydrocarbons, supplied by Humphrey Chemical Company. These hydrocarbons were identified as being 99% pure and were used without further purification. The purity of C₁₈, C₂₂ and C₂₄ hydrocarbons

was checked by a Gas Chromatograph fitted with an OV-17 column and a flame ionization detector, and was found to be over 99% pure.

DISCUSSION

Thermal energy storage properties of normal alkanes depend on their purity. Purity and chain length also determine the crystalline form in the solid state. In the discussion that follows attempts have been made to explain the variation of thermodynamic values (temperature and heats of transition) of hydrocarbons differing in chain length and blend composition by their known predisposition to different solid state crystalline patterns.²

Crystalline Structure of n-Alkanes

Carbon-carbon bond lengths and bond angles of n-alkanes are maintained by strong forces. On the other hand, rotation of C-H bonds can occur readily. As a result, the carbon-hydrogen units of the chain can assume a variety of positions differing in energy. In the case of normal alkanes the arrangement giving minimum energy is that in which the chain takes the form of a flat zig-zag of carbon atoms. An assembly of these zig-zag chains, nucleating from a melt or solution, can crystallize in four characteristic geometric forms. These are identified by Broadhurst³ as α_H , β_O , β_T , and β_M . The symbols α and β designate, respectively, the high and low temperature phases and the subscripts H, O, T, and M indicate the type of crystalline structure. Thus, the symbols α_H , β_O , β_T , and β_M identify, respectively, the hexagonal, orthorhombic, triclinic and monoclinic crystal structures. The structures differ in the inclination of the chain axes to the end group planes. The chain axes are perpendicular to the end group planes in the α_H and β_O structures and are inclined to the end groups planes in the β_T and β_M forms. The latter two forms give rise to closer packing. The packing arrangement assumed being the closest possible fitting together under a particular set of conditions. This closest packed arrangement gives the minimum free energy.

The α_H form is stable just below the freezing point in the "odd" alkanes from C₉-C₄₃ and in the "evens" from C₂₂-C₄₂. The β_O or orthorhombic structure is the stable low temperature phase of the odd n-alkanes from C₉ and above and is a high temperature phase of C₃₀ and perhaps of all "evens" above C₃₂. In addition, this is the low temperature form assumed by mixtures of normal alkanes and therefore is the usual

form for normal alkanes of questionable purity. The β_T or triclinic structure is assumed by all "even" carbon alkanes from C_4 to C_{20} without any intermediate α_H transition. With C_{22} , C_{24} , and C_{26} a transition from the liquid into β_T occurs via α_H . The β_M structural form is assumed by the "even" alkanes above and possibly including C_{24} and C_{26} upon cooling from the α_H or β_0 phases.

Correlation With Experimental Data

From the foregoing discussion, it is apparent that C_{12} to C_{24} alkanes studied in this investigation differ in crystalline form depending on "odd" or "even" number of carbon atoms in the carbon chains. The even carbon chains below C_{20} , can crystallize directly into the β_T form, and thus should have only one transition. The reverse is true for the "odd" carbon chains. They crystallize from the melt in the α_H form and later change to the β_0 form on further cooling. Two transitions are therefore expected for "odd" carbon chain normal alkanes. This is borne out in Figure 1 which plots DSC melting (solid $\rightleftharpoons$ liquid) and transition temperatures (solid $\rightleftharpoons$ solid) of C_{12} - C_{24} normal alkanes vs. the number of carbon atoms in the chain. The denser packing of the "even" carbon chains manifests itself in slightly higher melting temperatures. The "odd" "even" difference in melting temperature diminishes as the carbon chain length increases.

The transition temperature vs. carbon chain length for "odd" carbon alkanes follows a parallel curve, separated from the melting point curve by almost a constant difference of 12°C . Figure 2 compares the fusion and crystallization temperatures. There is a difference of 6 - 8°C between the temperatures of the two curves, indicating some supercooling. Slight supercooling is expected for pure melts because of the lack of impurities serving as nucleation sites. Since the latent heat of solidification opposes the formation of nuclei, supercooling could favor nucleation by increasing the density and degree of molecular ordering in the liquid and by providing a medium for absorbing the latent heat of solidification. Again, the solid $\rightleftharpoons$ solid transition temperature (cooling) follows a parallel curve, separated by the crystallization and fusion temperature by about 10 and 18°C , respectively. It is interesting that C_{26} and C_{22} and C_{24} show two peaks during solidification (indicating a $\alpha_H \rightleftharpoons \beta_T$ transition) and only one peak during melting (Figure 1).

Figure 3 plots the heats of transition for the even and odd carbon alkanes. ΔH_f for even carbon

chains is higher than even the combined total for melting and solid $\rightarrow$ solid transitions for the odd chains. Total heats of transition for both odd and even carbon chains seem to increase with the increasing number of carbon atoms, but this has to be confirmed further by inclusion of higher members of n-alkanes.

Binary Systems of Blends

A binary system of blends can either form a solid solution, a eutectic, or something in between. The requirements for solid solutions are, similarity in (1) form, (2) dimension, and (3) crystal symmetries. In other words, an "odd" or "even" carbon chain pair who are near neighbors and isomorphous would be expected to form a solid solution. An odd-even pair or those separated by a few carbon chains will not. These expectations are, more or less, borne out by the examples shown in Figures 4, 5 and 6 for C₁₆-C₁₈, C₁₇-C₁₉ and C₁₆-C₂₀ hydrocarbon blends, respectively. C₁₆-C₁₈ pair differ from the others. Presumably, the blends can not fit into the β_T (triclinic) structure of the pure components and form orthorhombic subcell⁷, in the mid-range concentration. Hence, ΔH_f is lower.

Commercial Blends

Table 1 shows the DSC analysis of five commercial blends, used by the authors as phase change materials (PCM). These materials are mostly blends of up to ten components from C₁₂-C₂₆ hydrocarbons in different proportions. As expected, both T_m and ΔH_f are lower than the pure components and the temperature span is wider. Because of the impurities, supercooling is lower than that of pure compounds. Another factor that would give lower T_m and ΔH_f is the presence of uncertain amounts of side chain alkanes. However, only two peaks are observed in the DSC curves, indicating some amount of solid solution. Surprisingly, approximate values of T_m or ΔH_f could be calculated from the composition and the known literature values of the pure components. Since the commercial paraffins are already blends having lower enthalpy, intermediate blends of these show very little further lowering of enthalpy.

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LEGENDS FOR FIGURES

- Figure 1. DSC Melting Peak Temperature of 99% Pure n-Alkanes vs. Number of Carbon Atoms in the Chain.
- Figure 2. DSC Melting and Crystallization Peak Temperature of 99% Pure n-Alkanes vs. Number of Carbon Atoms in the Chain.
- Figure 3. Heat of Transition of 99% Pure n-Alkanes vs. Number of Carbon Atoms in the Chain.
- Figure 4. Thermal Energy Storage Properties of C₁₆-C₁₈ n-Alkane Blends.
- Figure 5. Thermal Energy Storage Properties of C₁₇-C₁₉ n-Alkane Blends.
- Figure 6. Thermal Energy Storage Properties of C₁₆-C₂₀ n-Alkane Blends.

TABLE 1
MELTING AND FREEZING TEMPERATURES AND HEAT
OF FUSION AND CRYSTALLIZATION OF LOW
MELTING WITCO PARAFFIN WAXES

	T _m °C	T _c °C	T _m -T _c °C	ΔH _f CAL/GM	ΔH _c CAL/GM
1. WITCO LLN	40.0	34.7	5.3	51.1	49.2
2. WITCO 45-A	31.4	26.3	5.1	41.2	40.0
3. WITCO K-61	24.0	19.8	5.2	48.4	47.8
4. WITCO K-51	17.4	12.3	5.1	47.6	47.2
5. WITCO 85010-1	*7.6	*4.0	3.6	30.4	31.0

MONTHLY PROGRESS REPORT NO. 2
CONTRACT NO. DE-FG03-86SF16308
COVERING JULY, 1986

1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research, on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends".

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

In the first process, the PCM's (alkyl hydrocarbons) can be added directly into the wet mix of cementitious materials at concentrations up to 5% wt (cement) and 10% wt (plaster). However, considerable reduction in the strength properties of the cement and/or lengthening of the setting time is encountered. In one modification of this process, the cementitious products can also be made waterproof.

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As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3). The building material will not burn. However, in process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard

after ignition will continue to burn slowly until the PCM is exhausted.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will initiate extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

1. To determine the concentrations of commercially available fire retardants that will inhibit the flame propagation of Witco LLN wax.
2. Swelling studies of crosslinked Marlex 6006 (10 m-rad gamma) in Witco K-61 hydrocarbon PCM.
3. Thermal energy storage properties of some new supplies of n-alkyl hydrocarbon PCM.
4. Evaporation rates of Witco waxes.

3. TECHNICAL DESCRIPTION OF CURRENT RESEARCH

- 3.1 To determine the concentration of commercially available fire retardants which will inhibit the flame propagation of Witco LLN wax.

A limited amount of work to determine flammability of plasterboard that contain hydrocarbon phase change material, has been carried out during the earlier phases of this project (Final Report, Contract No. DE-AC03-82-CE30755). However, a lot more screening experiments need to be done in order to decide the best material (or a combination) and the concentration that will be needed to impart flame retardance to hydrocarbon treated plasterboard. These screening experiments were carried out by melt blending the PCM and different proportions of fire retardants, and pouring the melted blend onto a steel strip which was then ignited over a bunsen burner. The experimental details are described in Appendix 1. The screening experiments are discussed under the following subtitles. LLN was used as PCM because of its availability in large quantities and that it was used in the earlier experiments.

3.1.1 LLN/Chlorowax 70S

Tables 1 and 2 report the flame retardance experiments of Witco LLN/Chlorowax 70S wax. It should be noted, that LLN and Chlorowax 70S are not miscible with one another. Samples were held both horizontally and vertically to the flame in different experiments (see Figure Appendix-1). As much as equal proportions of PCM and Chlorowax 70S are necessary for effective flame retardance where the sample is held vertically. Improved fire retardance properties are observed in horizontal experiments (Table 2). It becomes increasingly more difficult to ignite the wax as the proportion of Chlorowax in the blend increases. Also, the flame travelled less and less and extinguished faster. Above 70% Chlorowax the paraffin/Chlorowax blend could not be ignited, and above 50% it became self-extinguishing. The horizontal experiments are more relevant to flame propagation in actual fire

TABLE 1
FIRE RETARDANCE PROPERTIES OF
WITCO LLN/CHLOROWAX 70S
(Sample Held Vertically)

<u>Blend Ratio LLN/C1 70</u>	<u>Hardness (1-5)</u>	<u>Time to Extinguish</u>	<u>Color of Smoke</u>	<u>Type of Smoke</u>
9:1	1	doesn't extinguish	black	strong, thick
8:2	1	doesn't extinguish	black	strong, thick
7:3	2	didn't extinguish	grey-black	moderate
6:4	2.5	didn't extinguish	grey-black	moderate
5:5	3	12 sec.	dark grey	moderate
4:6	4	8 sec.	dark grey	moderate
3:7	5	3 sec.	grey	light
2:8	5	didn't burn when removed from flame	grey	light
1:9	5	didn't ignite	none	none

All melted samples were observed to be homogeneous. LLN precipitates out if allowed to settle.

TABLE 2
FIRE RETARDANCE PROPERTIES OF LLN/CHLOROWAX 70S
(Samples Held Horizontally)

<u>% 70S</u>	<u>Phase Separation</u>	<u>Ignite in 5 sec.</u>	<u>Time to Ignite</u>	<u>Flame Traveled</u>	<u>Time to Extinguish</u>	<u>Smoke</u>
10	yes	no	15 sec.	2 in.	5 sec.	white
20	yes	no	25 sec.	2 in.	3 sec.	white
30	yes	no	29 sec.	1 in.	3 sec.	white
40	yes	no	40 sec.	1 in.	1 sec.	white
50	yes	no	40 sec.	1 in.	1 sec.	white
60	yes	no	40 sec.	1 in.	when flame was removed	white
70	yes	no	45 sec.	1 in.	when flame was removed	white
80	yes	no	----- didn't ignite-----			
90	yes	no	----- didn't ignite-----			

situations. It is encouraging that even 10% Chlorowax would improve the fire retardance of the wax.

3.1.2 LLN/Antimony Oxide/Chlorowax 70S

In the second set of experiments, reported in Tables 3 and 4, a stock of 2:1 ratio of Chlorowax 70S:antimony oxide was mixed first. Different proportions of this mixture were then added to LLN as detailed in Appendix 1. It may be observed that only 20% by weight of the mixed flame retardant (FR) is effective in extinguishing the flame in vertical experiments. As expected, improved fire retardance properties are observed in horizontal experiments (Table 4). However, the improvement as compared to Table 2 (Chlorowax only) is minimal. Because antimony oxide powder cannot get into the already formed plasterboards this combination cannot be used in permeation process, and will only be effective where PCM is introduced as an ingredient in plasterboard manufacture.

3.1.3 LLN/Saytex Flame Retardants

The flame retardants that were obtained from Ethyl Corporation and their chemical composition are as follows:

Saytex BCL-462
Dibromoethyldibromo
cyclohexanane

Saytex HBCD
Hexabromocyclo
dodecane

Saytex 102
Decabromodiphenyl
oxide

SAYTEX BN-451

NON-REACTIVE

ETHYLENEBISDIBROMO-
NORBORNANE
DICARBOXIMIDE

The details of preparing the LLN/Saytex flame retardant blends are reported in Appendix 2.

TABLE 3
FIRE RETARDANCE PROPERTIES OF LLN/CHLOROWAX 70S/
ANTIMONY OXIDE COMBINATION
(Sample Held Vertically)

<u>Blend Ratio LLN/FR</u>	<u>Hardness (1-5)</u>	<u>Time to Extinguish</u>	<u>Color of Smoke</u>	<u>Type of Smoke</u>
95:5	1	didn't extinguish	black	very strong & thick
90:10	1	didn't extinguish	black/grey	heavy
85:15	1.5	didn't extinguish	very dk. grey	heavy
80:20	2	24 sec.	grey	moderately heavy
75:25	2	22 sec.	grey	moderate
70:30	2	12 sec.	grey	moderately thin
65:35	2.5	10 sec.	grey	thin
60:40	2.5	8 sec.	grey	moderate
55:45	3	6.5 sec.	lt. grey/white	thin
50:50	3	5 sec.	dk. grey	thin to moderate

When melted, the Witco LLN wax separated to the top of the melt. Phase separation occurred during cooling.

TABLE 4
FIRE RETARDANCE PROPERTIES OF LLN/CHLOROWAX 70S/
ANTIMONY OXIDE (Samples Held Horizontally)

<u>% 70S/ AO</u>	<u>Phase Separation</u>	<u>Ignite in 5 sec.</u>	<u>Time to Ignite</u>	<u>Flame Traveled</u>	<u>Time to Extinguish</u>	<u>Smoke</u>
5	yes	no	15 sec.	3 in.	12 sec.	black
10	yes	no	15 sec.	2 in.	8 sec.	black
15	yes	no	20 sec.	2½ in.	6 sec.	black
20	yes	no	20 sec.	2 in.	5 sec.	black
25	yes	no	20 sec.	2 in.	5 sec.	black
30	yes	no	25 sec.	1½ in.	6 sec.	black
35	yes	no	30 sec.	1 in.	3 sec.	grey
40	yes	no	30 sec.	1/2 in.	4 sec.	grey
45	yes	no	30 sec.	1/2 in.	2 sec.	grey
50	yes	no	30 sec.	---	2 sec.	grey

Table 5 and 6 report the experimental results. It may be observed that only BCL 462 is miscible with LLN in the proportions studied. A 15 percent blend of this with LLN is self-extinguishing. Saytex HBCD (hexabromocyclodecanane) is effective in less quantities (10%), but unfortunately is not miscible. Miscibility is very important for permeating the fire retardant into already formed plasterboard along with the PCM. Further work is planned for a combination of two flame retardants, Chlorowax 70S and BCL 462, in order to minimize cost. It may be observed in Table 6 that LLN by itself did not ignite in horizontal flame test. The procedure was modified by introducing a wick to propagate the flame. However, the wick propagates the flame for too long and fails to discriminate many of the samples.

3.2 Swelling of crosslinked Marlex 6006 (10 m-rad) and Witco K-61 wax.

In continuation of our study of the containment of phase change material in crosslinked polyethylene, further study was made of swelling of crosslinked Marlex 6006 polyethylene in K-61 wax. The K-61 wax has the melting and crystallization temperature at right range (25-30°C) for residential heating and cooling. Table 7 shows the data for DSC analysis. During swelling, small (4g) samples were taken out at 30 min., 1 hr., 2 hr., and 3 hr. periods during swelling. The total time of swelling was 4 hrs. The method of swelling is given in Appendix 3.

The data in Table 7 confirms our earlier conclusions with Witco 45A wax. Around 89% of K-61 wax is imbibed in 4 hrs. The value of 89% by weight gain and 90% by DSC area corresponds very well. As may be observed in Table 7, ΔH_f for the wax increases and that for polyethylene decreases with time. However, the swelling is very slow after 1 hr. when a weight gain of 86% (measured by DSC area) has taken place. Simultaneously, with the increase of swelling a slight lowering of T_m for both the polyethylene and the K-61 is observed with time. Figures 1 and 2 show the DSC analysis for the pure and imbibed materials,

TABLE 5
ETHYL CORP FIRE RETARDANTS (SAYTEX) IN LLN WAX
(Sample held vertically over the flame)

	<u>% FR</u>	<u>Hardness*</u>	<u>Dissolved</u>	<u>Self Extinguishing</u>	<u>Smoke</u>
Saytex BLC-462	10	1	yes	no	white & black
	15	1	yes	yes	white
	20	1	yes	yes	white
	25	1	yes	yes	white
Saytex HBCD	10	1	no	yes	white
	15	1	no	yes	white
	20	1	no	yes	white
	25	1	no	yes	white
Saytex 102	10	1	no	no	black
	15	1	no	yes	white
	20	1½	no	yes	white
	25	2	no	yes	white
Saytex BN-451	10	1	no	no	black
	15	1½	no	no	black
	20	1½	no	no	black
	25	2	no	no	black

* Hardness rating: 1(soft) - 5(hard)

TABLE 6
ETHYL CORP FIRE RETARDANTS (SAYTEX) IN LLN WAX
(Samples held horizontally with the flame)

	<u>% FR</u>	<u>Phase Separation</u>	<u>Ignite in 5 sec.</u>	<u>Time to Ignite</u>	<u>Flame Traveled</u>	<u>Time to Extinguish</u>	<u>Smoke</u>
BLC-462	10	no	no	17 sec.	no	2 sec.	white
	15	no	no	20 sec.	no	immediately	white
	20	no	no	22 sec.	no	immediately	white
	25	no	no	15 sec.	no	immediately	white
Saytex	10	yes	no	15 sec.	no	immediately	white
HBCD	15	yes	no	17 sec.	no	immediately	white
	20	yes	no	25 sec.	no	immediately	white
	25	yes	no	45 sec.	no	immediately	white
Saytex	10	yes	no	16 sec.	no	9 sec.	white
102	15	yes	no	20 sec.	no	8 sec.	white
	20	yes	no	24 sec.	no	7 sec.	white
	25	yes	no	30 sec.	no	3 sec.	white
Saytex	10	yes	no	35 sec.	no	2 sec.	white
BN-451	15	yes	no	30 sec.	no	12 sec.	white
	20	yes	no	11 sec.	1/2 in.	19 sec.	black
	25	yes	no	15 sec.	1 in.	43 sec.	black
LLN Wax (Control) horizontal	0	N/A	no	didn't	no	---	none
LLN Wax (Control) vertical	0	N/A	no	20 sec.	yes	burned till wax was gone (about 3 min.)	white

TABLE 7

DSC ANALYSIS OF THERMAL ENERGY STORAGE OF MARLEX 6006
(10 mrad, N₂) SWELLED IN K-61 WAX AT 150°C FOR DIFFERENT TIMES

Sample Identification and Composition	T _m (°C)	T _c (°C)	T _m -T _c (°C)	ΔH_f cal/gm	ΔH_c cal/gm	Extrapolated to 100%	
						ΔH_f cal/gm	ΔH_f cal/gm
Recrystallized K-61 wax w/o 860708 Recd. July 1986	26.4	20.2	6.2	47.5	46.4		
	27.8	20.4	7.4	46.9	47.3		
Marlex 6006, 10 mrad Gamma	132.4	114.4	18.0	53.6	47.0		
Marlex 6006, Swelled in K-61 @ 150°C, 30 min.	27.6	16.2	11.4	29.2	30.2		
	116.4	102.9	13.5	19.7	18.7		
Marlex 6006, Swelled in K-61 @ 150°C, 1 hr.	30.3	16.6	13.7	40.8	42.0		
	113.2	99.7	13.5	9.5	9.2		
Marlex 6006, Swelled in K-61 @ 150°C, 2 hrs.	28.2	18.1	10.0	40.7	42.6		
	111.8	99.7	12.1	7.1	6.0		
Marlex 6006, Swelled in K-61 @ 150°C, 3 hrs.	29.0	18.2	9.6	41.9	44.3		
	111.3	98.9	12.4	5.0	4.6		
Marlex 6006, Swelled in K-61 @ 150°C, 4 hrs.	28.6	18.7	9.9	42.8	44.5	48.2	50.1
	110.8	99.6	11.6	4.5	4.1	44.7	36.6
K-61 Residue After 4 hrs. Swelling	27.6	18.3	9.3	45.9	45.9		

NOTE: Weight gain after 4 hrs. at 150°C was 88.8%, based on total weight.

Sample: K-61/ RECRYSTALLIZED
 Size: 9.02 mg
 Method: DSC-MELT
 Comment: 5 GALLON DRUM

DSC

File: RUN0858.02
 Operator: TODD SILL
 Run date: 07/14/88 19:20

Sample: MARLEX 6006 10 Mrad
 Size: 4.15 mg
 Method: DSC-MELT

DSC

File: RUN0855.02
 Operator: MLG
 Run date: 07/14/88 12:14

Figure 1. DSC Analysis of K-61 and Marlex 6006 Pellets.

Figure 2. DSC Analysis of Swelled Marlex 6006 Pellets With Time.

respectively. Residual wax after separation of the imbibed pellets shows indications of impurity, but no polyethylene peak is observed.

3.3 Thermal energy storage properties of new supplies of PCM

In our continuous search for alternative sources of PCM, three new samples of waxes were received. These were: (1) Witco K-61 wax, prepared by Chevron, using solvent precipitation method, (2) Quaker State 104/110, and (3) Humphrey Technical Grade n-octadecane. The DSC data are presented in Table 8 and the thermographs are presented in Figures 1, 4 and 5, respectively.

The present supply of 5-gallon sample of K-61 corresponds to the deoiled K-61, supplied earlier by Witco (Table 13 of Final Report, March 14, 1986). Gas chromatographic data, supplied by Witco, is reproduced in Figure 3 and shows 97.7% normal paraffins. The Quaker State 104/110 approximates Witco LLN (Table 4, final report) in transition temperatures but have lower ΔH_f and higher $(T_m - T_c)$. It also has an extra transition in DSC melting thermograph, indicating nonhomogeneity. The Humphrey Technical Grade has slightly lower transition temperatures and ΔH_f than the 99% pure material to be reported later, but is superior to the other Technical Grades analyzed. $(T_m - T_c)$ is higher but is lowered at a lower rate of heating (2°C/min). The crystallization peak shows a double transition. The resolution is improved at 2°C/min rate of heating. However, only single peak is observed for melting both at 10°C/min and 2°C/min rate of heating. The same characteristics were observed for the 99% pure n-octadecane which will be reported later.

3.4 Evaporation rates of Witco waxes.

One of the concerns of the plasterboards, imbibed with phase change materials, is the loss of PCM with time by evaporation. The following experiments were performed to determine the relative evaporation rates of the different Witco hydrocarbon phase change materials.

TABLE 8
DSC ANALYSIS OF THERMAL ENERGY STORAGE
PROPERTIES OF NEW SUPPLIES OF PCM

<u>Sample Identification and Composition</u>	<u>T_m (°C)</u>	<u>T_c (°C)</u>	<u>T_m-T_c (°C)</u>	<u>ΔH_f cal/gm</u>	<u>ΔH_c cal/gm</u>
Witco K-61 (recrystallized) w/o 860708, Code 860055, Recd. July 1986	26.4	20.4	6.2	47.5	46.4
Quaker State 104/110 Hydrofinished filtered wax	42.6	34.6	7.9	47.7	47.5
Humphrey Technical Grade N-Octadecane	28.0	19.5	8.5	52.9	52.6
Humphrey Technical Grade N-Octadecane (2°C/min.)	26.2	22.4	3.8	49.9	49.6

RT	AREA	AREA TYPE	AR/HI	AREA%
8.11	3298	PC	0.048	0.110
9.83	26246	PC	0.048	0.110
11.92	217629	PC	0.051	0.872
14.35	574850	PC	0.056	0.872
16.02	5770	PC	0.055	0.192
17.02	750500	PC	0.061	24.934
18.81	14982	PC	0.059	0.498
19.86	742690	PC	0.063	24.675
21.72	23138	VB	0.061	0.769
21.90	4346	BB	0.058	0.144
22.78	450260	PC	0.064	14.959
24.67	12351	VC	0.063	0.410
24.94	4948	BB	0.063	0.164
25.72	150550	PC	0.063	5.082
28.66	28379	PC	0.066	0.943

77.715

TOTAL AREA= 3009900
MULT FACTOR= 1.000E+00

RUN # 203
WORKFILE ID: C
WORKFILE NAME:
MAR/19/86 08:55:10

Figure 3. Gas Chromatographic Analysis of Chevron K-61 (#860055).

Sample: QUAKER STATE 104/110

Size: 4.35 mg

Method: DSC-MELT

Comment: HYDRO FINISHED FILTERED WAX

File: RUND879.02

Operator: ED DYKE

Run date: 07/24/86 08:31

DSC

Figure 4. DSC Analysis of Thermal Energy Storage of Quaker State 104/110.

(A)

Sample: n-OCTADECANE
Size: 4.78 mg
Method: DSC-MELT
10°C/MIN

DSC

File: RUN0894.02
Operator: ED DYKE
Run date: 07/31/86 11:31

(B)

Sample: n-OCTADECANE
Size: 4.63 mg
Method: DSC-MELT
Comments: HEATING RATE 2°C/MIN

DSC

File: RUN0895.06
Operator: ED DYKE
Run date: 08/01/86 07:45

Figure 5. DSC Analysis of Thermal Energy Storage of Humphrey Technical Grade Octadecane. A. 10°C/min, B. 2°C/min.

Figures 6 and 7 show the thermogravimetric curves of Witco LLN, 45A, K-61, K-51 and NP15 waxes, both in nitrogen and in air. The peak temperature in DTG curves decreases with the average carbon chain length and melting temperature of the waxes, as would be expected. Although these waxes are blends of different n-alkanes in different proportions, only one peak is observed, showing the homogeneity of the blends. The peak temperatures in these cases probably relate to boiling temperatures of the carbon chains in the blend.

Figures 8 and 9 show the evaporation loss of different Witco hydrocarbon waxes in nitrogen and air as determined by isothermal thermogravimetry at 50°C for 16 hours. The air or nitrogen flow was 50 cc/min. As may be observed, the relative weight loss follow the pattern expected with hydrocarbon chain length, melting temperature and boiling temperature. Much less loss is observed with nitrogen than with air, which is hard to explain.

Figure 10 shows the evaporation rates of Witco waxes at different temperatures by continual air sweep. The relative rates follow the same pattern as isothermal thermogravimetry, although the loss is much less. This would be expected since the sweep is not continual here vs. continuous flow in thermogravimetry. Also, the thermogravimetric experiments were prolonged for a longer time.

It may be mentioned that Cox Chart for vapor pressure of normal paraffin hydrocarbons show a vapor pressure of only 2×10^{-6} psia and 7.5×10^{-5} psia, respectively, at 25 and 50°C. So the actual loss by surface evaporation of hydrocarbon PCM from building materials is expected to be negligible.

Immediate Future Plans

1. Determine the fire retardance of Witco LLN containing 20% of BCL 462/70S in selected ratios.

LLN

45A

K-61

K-51

NP-15

Figure 6. Thermogravimetry of Witco Hydrocarbon Waxes in Nitrogen.
Rate of Heating 10°C/min.

LLN

45A

23

K-61

K-51

NP-15

Figure 7. Thermogravimetry of Witco Hydrocarbon Waxes in Air.
Rate of Heating 10°C/min.

Sample: WITCO HYDROCARBONS
 Size: 4.88 mg
 Method: TGA-ISOTHERMAL IN NIT
 Comment: 16 HR @ 50 C ISOTHERMAL
 File: A:RUN0078.12
 Operator: MARY
 Run date: 10/18/85 17.03

TGA

Figure 8. Evaporation Loss of Different Witco Hydrocarbon Waxes in Nitrogen As Determined by Isothermal Thermogravimetry at 50°C.
 TGA V1.1F Dupont 9900

Sample: WITCO HYDROCARBONS
 Size: 4.76 mg
 Method: TGA-ISOTHERMAL
 Comment: ISOTHERMAL @ 50 C-18 HR / AIR

TGA

File: A: RUN0082.11
 Operator: MARY
 Run date: 10/23/85 16:00

Figure 9. Evaporation Loss of Different Witco Hydrocarbon Waxes in Air, As Determined by Isothermal Thermogravimetry at 50°C.

-*- 45 Wax
 -+- Octadecane
 -o- R-61 Wax
 — Kenwax 15

Figure 10. Evaporation Rates of Witco Waxes by Continual Air Sweep.

2. Determine the fire retardance properties of soluble fire retardant BCL 462 in plasterboard permeated with Witco 45A PCM.
3. Determine the highest concentration of 45A PCM that will not continue to burn after ignition.
4. Prepare and evaluate ground pellets of irradiation crosslinked Marlex 6006 HDPE that are permeated with K-61 PCM.
5. Determine by sieve screen analysis the particle size distribution of crosslinked Marlex 6006 powder and ground "powder" of Marlex 6006.
6. Determine the thermal energy storage properties of extended range of 99% pure n-alkanes and blends obtained from Humphrey Chemical.
7. Determine the thermal energy storage properties of PCMs and pure n-alkanes at a slow rate of heating and cooling.
8. Determine the effect of "annealing" on ΔH_f and ΔH_c of PCMs.
9. Prepare plasterboards using the proprietary method obtained from U.S. Gypsum.
10. Determine the solubility characteristics of two presumably crosslinked HDPE in xylene, at 5% wt. and 120°C.
11. Evaluate PCM removal from 45A PCM permeated, ground crosslinked Marlex 6006 powder with methanol and ethanol at 25°C and 35°C, respectively.
12. Prepare 1000g quantity and evaluate the thermal energy storage properties of "ground" and whole pellets of 10 m-rad gamma crosslinked Marlex 6006 HDPE that is permeated with Witco 45A PCM.
13. Prepare 1000g quantities of crosslinked Marlex 6006 powder that is irradiated at a lower dosage of gamma rays by Neutron Products.
14. Prepare microencapsulated capsules of PCMs using the expertise of a local firm.

APPENDIX 1

PROCEDURE FOR TESTING LLN/CHLOROWAX OR LLN/CHLOROWAX/ ANTIMONY OXIDE FIRE RETARDANCE

A. LLN/Chlorowax 70S

1. 10 grams of a 9:1 mix of LLN and Chlorowax 70S were prepared by weighing out 90 grams of homogenized Witco LLN into a 30 ml beaker on a Mettler balance. 1 gram of Chlorowax 70S was then weighed into a paper cup on the same Mettler balance, and poured into the beaker with the LLN wax. This mixture was melt-blended on a hot plate for five minutes at 80°C.
2. While still melted, the mixture was examined for homogeneity and recorded.
3. The melted blend was then poured over a strip of steel about 23 cm long, 1 cm wide, and 0.2 cm thick and allowed to cool on a metal tray.
4. The above steps were then repeated with ratios of 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, or 1:9.
5. The hardness of the mixtures was determined by scraping each of the hardened melts with a metal pick, and recording the hardness in relation to the other melts on a scale of 1 to 5, with 1 being the softest.
6. A bunsen burner was then set up and the samples ignited as shown in Figure 11 in a hood that was well ventilated.
7. The burning was carried out in two ways: (a) The sample strip held vertically over the bunsen burner; (b) The sample strip clamped horizontally and the wax lighted by the flame of the burner, held at the edges. In (a) each metal bar was held over the flame until it was ignited for five seconds, or until all the wax had dripped off. In (b) the flame was held over the sample until it was ignited and the time for ignition was recorded.
8. The bar was then removed from the flame and allowed to burn itself out. The time until the flame extinguished was recorded, as well as the type and amount of smoke emitted.
9. All data from this test was compiled in a table included with the report.

B. LLN/Chlorowax 70S/Antimony Oxide

10 gram samples of LLN/Chlorowax 70S/Antimony Oxide were tested as follows:

Verticle
Flame
Test

(A)

Horizontal
Flame
Test

(B)

Figure 11. Vertical and Horizontal Flame Tests.

1. 200 grams of Chlorowax 70S and 100g of Antimony Oxide were weighed into separate 500 ml beakers, and mixed by combining both into another 500 ml beaker by adding in small quantities.
2. This 2:1 mixture of Chlorowax 70S/Antimony Oxide was then combined with the LLN wax in the same manner as the plain Chlorowax 70S as described in Steps 1-3 in A.
3. These procedures were used to make blends at the ratios at 95:5, 90:10, 85:15, 80:20, 75:25, 70:30, 65:35, 60:40, 55:45, and 50:50 of LLN/Chlorowax and Antimony Oxide.
4. These samples were then ignited as described above and the data recorded as stated in steps 5-9 in A.

APPENDIX 2

Work Order No. 860729-1 to 16

Work performed by: Mary Galaska

Procedure:

Small (10g) blends were prepared that contained 10%, 15%, 20%, and 25% of an Ethyl Corporation fire retardant in LLN wax. The four fire retardants used were BCL-462, HBCD, 102, BN-451. The blends were melt mixed for five minutes at 80°C, then poured onto a 1/2" metal strip and allowed to cool.

The fire retardance was tested by igniting the strips with a bunsen burner (samples held vertically and horizontally, as in Appendix 1) and noting the time to self-extinguishing and the nature and amount of smoke emitted.

The three fire retardants that did not dissolve at 80°C were heated to 150°C for an additional five minutes but still did not dissolve. They were stirred vigorously before being poured onto the metal strips.

APPENDIX 3
METHOD FOR SWELLING OF CROSSLINKED
MARLEX 6006 IN K-61 WAX

Work Order: 860708-3,4,5,6 Pellets

Performed By: Ed Dyke/Mary Galaska

Date: 8/21/86

Procedure:

500g of homogenized K-61 wax and 5g of Santowhite powder were weighed into a metal beaker and heated to 150°C with constant stirring under a ventilated hood. 100g of irradiation crosslinked 10 Mrad pellets was poured into the wax and heated at 150°C for four hours. The pellets swelled very quickly and it was necessary to add an additional 600g K-61/Santowhite (1 phr). The wax was heated to 150°C before it was added to the swelled pellets. Approximately 4.0g samples were taken at 0, 1/2, 1, 2, 3, and 4 hour intervals. The samples were cooled to about 50°C, washed in a beaker with excess MEK (warmed to 50°C), and filtered through a Buchner funnel without a filter paper. They were washed again in the funnel with the warm MEK. The samples were air dried in a hood overnight. Each batch was analyzed by DSC for thermal energy storage.

Original Wt.	100g
Final Wt.	893.6g
% Wt. Gain	88.81%

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ADVANCED PHASE CHANGE MATERIALS AND
SYSTEMS FOR SOLAR PASSIVE HEATING AND COOLING
OF RESIDENTIAL BUILDINGS

Monthly Progress Report No. 3
Covering the Month of August 1986

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1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research, on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends".

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

In the first process, the PCM's (alkyl hydrocarbons) can be added directly into the wet mix of cementitious materials at concentrations up to 5% wt (cement) and 10% wt (plaster). However, considerable reduction in the strength properties of the cement and/or lengthening of the setting time is encountered. In one modification of this process, the cementitious products can also be made waterproof.

In the second process, the PCM's are first mechanically dispersed into rubbers, such as natural rubber, and plastics, such as polyethylene, using Banbury mixer or roll mill, at concentrations greater than 50% wt. These PCM "concentrates" can potentially be used directly, in sheet form, as floor or wall tiles and may be especially useful for retrofit use in building where they could be adhered to existing walls and floors.

In the third process the PCM is imbibed into small pellets of HDPE by swelling at elevated temperatures. The resulting small hard pellets contain up to 80% wt PCM, and should be easy to incorporate into the wet mix of cementitious materials with minimum reduction in strength properties.

The rubber or HDPE pellets from the second and third process above can potentially be used as an effective low-cost pellet bed heat exchanger; to heat or cool the air, or liquid medium, in solar passive hybrid applications.

In the fourth process, the PCM in liquid form is percolated directly into the open space in porous building materials (cement, plaster bricks). This process also has the attendant advantage that the porous products are simultaneously waterproofed. The process has obvious potential applications in waterproofing cement for other applications as well (i.e., highway bridge decks).

As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3). The building material will not burn. However, in process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard

after ignition will continue to burn slowly until the PCM is exhausted.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will initiate extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

The present month's work consists of the following:

1. Fire retarding of linear alkyl hydrocarbon PCM via dispersed or dissolved halogenated additives.
2. Fire retardance of plasterboard percolated with PCM.
3. Crosslinked high density polyethylene, pellets and powder absorbers for alkyl hydrocarbon PCM.
4. Further investigations on the thermal energy storage properties of n-alkyl hydrocarbons.

3. TECHNICAL DESCRIPTION OF CURRENT RESEARCH

3.1 Fire Retarding of Linear Alkyl Hydrocarbon PCM Via Dispersed or Dissolved Halogenated Additives.

3.1.1 Experiment Number 860729-1 to 16 (Supplement)

In the July Progress report, we reported on the evaluation of four Ethyl Corporation brominated fire retardant additives, in Witco LLN phase change material. The additives were incorporated into the LLN by melt blending at concentrations of 10, 15, 20, and 25% wt. The melt mixed blends of PCM and fire retardant was then poured on strips of metal where they solidified, on cooling to room temperature. The metal strips were then ignited with a bunsen burner, and the type of smoke, and time to extinction observed, with the specimen in both the vertical and horizontal positions. The identity, and chemical composition of the Ethyl Corporation brominated fire retardant compounds is as follows:

- BCL-462, dibromoethyldibromocyclohexane
- HBCD Hexabromocyclodecane
- Saytex 102, decabromodiphenyloxide
- Saytex BN-451, ethylenebisdibromonorboranedicarboximide

In the July vertical tests, the first three compounds (BCL-462, HBCD, and Saytex 102) provided self-extinguishing compositions, even at the lowest concentration (10%) tested. In the horizontal test, all four additives made self-extinguishing compositions (at some concentration), with, however, the BCL-462 and HBCD being the best. Surprisingly, a control of 100% LLN was also self-extinguishing in the horizontal test.

Since paraffin candles do not propagate a flame, without a wick, it was decided to perform a second series of horizontal tests with a cotton wick placed in the center of the wax strip, and projecting about 1/4" beyond.

The procedure used in the prior and current month's experiment is contained in Appendix 2 of the July Progress Report.

The results obtained in this month's experiments are summarized in Table 1, herein.

The results in the horizontal test, with a wick, were very similar to those obtained last month in the horizontal test without a wick. The BCL-462 made the LLN self-extinguishing, even at the lowest (10%) concentration. However, the other three fire retardants (HBCD, Saytex 102, and Saytex BN-451), were less effective, or totally ineffective, as fire retardants.

Importantly, it was also noted during the melt blending that the BCL-462 was completely soluble in the LLN at all the concentrations tested, whereas none of the other three were soluble even at the lowest (10%) concentration tested. This finding is especially significant. The soluble fire retardant will not settle out, or be strained out, when percolating the PCM from solution into plasterboard, by our standard immersion process. Until now, we have found that insoluble fire retardants (e.g. Chlorowax 70-S plus antimony oxide) were "strained out" at the liquid/solid interface of the plasterboard. Thus, fire retardant compositions could not be obtained when using this specific process.

3.1.2 Experiment Number 860815-1 to 4

This experiment was planned to define the lowest concentration of BCL-462 in LLN phase change material that will provide a self-extinguishing composition. Accordingly, melt mixed blends of LLN/BCL-462 were prepared at concentrations of 10, 7.5, 5.0, and 2.5%. The melt solutions were poured onto metal strips, a cotton wick installed (as before), and the samples ignited in the horizontal position. The time to ignite, the extent of flame travel, type of smoke, and time to extinguishment were all noted

The procedure used to prepare the samples is described in Appendix 1, and data are contained in Table 2.

As shown in Table 2, only the sample containing 10% of BCL-462 provided a self-extinguishing composition (time to extinction 11 seconds). All the lower concentrations continued to

burn until the paraffin was exhausted, and the flame traveled the full 4-1/2" length of the metal strip. Although 10% of BCL-462 is sufficient to make LLN self-extinguishing, separate experiments this month have shown that higher concentrations of fire retardant will be required in percolated plasterboard samples.

3.1.3 Experiment Number 860804-1 to 10

Since Chlorowax 70-S is significantly lower in cost than Saytex BCL-462, blends of the two fire retardants were tested in the expectation that a mutually soluble lower cost formulation might be found. Accordingly, five ratios of BCL-462/Chlorowax 70-S (1/3, 1/2, 1/1, 2/1, and 3/1) were tested at total concentrations of 20 and 25%, respectively. Compatibility of the two fire retardant materials in the melt was observed. Fire retardance was tested in both the vertical and horizontal positions - without a cotton wick. In the melt solubility tests, it was noted that the Chlorowax 70-S did not dissolve, but rather formed a cloudy colloidal suspension at all the ratios tested.

The procedure used in preparing the blends is contained in Appendix 2, and the results of the fire tests in Table 3. In the more rigorous verticle test, the 20% concentration samples, in the BCL-462/70-S; 2/1, and 3/1 were self-extinguishing; whereas, the 25% samples were not self-extinguishing. Our only explanation of this apparent inconsistency is that fire tests of the go/no-go type often give inconsistent results in the "borderline" fire retardant compositions.

In the less rigorous horizontal test, all of the compositions were self-extinguishing, and those containing BCL-462/Chlorowax 70-S ratios of 1/1, 2/1, and 3/1 were not ignited in the standard 10 seconds ignition period.

Although the results were "interesting", the lack of complete solubility of the Chlorowax 70-S in the LLN-PCM would make percolation of these compositions into plasterboard difficult

or impossible. No further work with these specific FR blend compositions is planned.

3.1.4 Experiment Number 860815-5 to 8

Of the four brominated fire retardants tested to date, only BCL-462 (dibromoethyldibromecyclohexane) is soluble in the paraffin PCM's at concentrations above 10% wt. Since HBCD (hexabromocyclododecane) (like BCL-462) is a brominated alkyl compound. It was believed that it might be soluble in LLN, and similar paraffins, at lower and still effective, concentrations. Therefore, melt mixed blends of LLN with HBCD were prepared, at 80°C, containing 10, 7.5, 5.0, and 2.5% wt. HBCD fire retardant. It was observed that at all concentrations tested (including 2.5%), the HBCD just settled to the bottom and would not dissolve.

The procedure used in the preparation of this series of LLN-HBCD blends is contained in Appendix 3. However, we still have to test one other Ethyl Corporation brominated fire retardant compound, Saytex 105. A series of five different brominated fire retardant compounds recently received from the Great Lakes, Chemical Company will also be tested for solubility. When tests of the entire series of FR compounds is completed, we should be able to correlate the chemical composition, and solubility parameter, of the fire retardant compound with its solubility in the linear alkyl hydrocarbon PCM's.

3.2 Fire Retardance of Plasterboard Percolated With PCM

3.2.1 Experiment Number 860709-1 to 5

It is known from prior research, that plasterboard percolated with linear alkyl hydrocarbon, to concentrations above 30% weight, will continue to burn after ignited until the PCM is substantially depleted. It is also known that the paper cover on the plasterboard supplies a wicking function that promotes continued burning. It should be noted, however, that the burning in

this instance is not catastrophic (like gasoline), but a slow steady burning, like a wax candle.

It was therefore postulated that a lower concentration of the PCM in the plasterboard, might be spread in such a thin layer that wicking to surface would be prevented. Therefore, an experiment was devised wherein Witco 45-A PCM, was dissolved in concentrations of 25%, 50%, and 75% wt. in low boiling heptane solvent, in an attempt to obtain a graduated series of PCM concentrations in percolated plasterboard. It was hoped thereby to define a lower, and still effective, thermal energy storage concentration that inherently would not support combustion.

Solutions of 45-A/heptane were prepared at ratios of 100/0, 75/25, 50/50, 25/75, and 0/100. Weighed samples of plasterboard were immersed separately in each solvent combination for 10 minutes. After percolating for 10 minutes the samples were removed from the solution, weighed, then vacuum dried for 48 hours to remove the low boiling heptane solvent, then reweighed. Just before the burning test, one of each duplicate specimen had the paper cover removed, to eliminate any wicking effects of the paper.

The procedure used to prepare and test the samples is contained in Appendix 4. The data on weight gain before and after "drying" is contained in Table 4, and the results of the burning tests in Table 5. The weight gain data showed that there was apparently a preferential absorption of the PCM over that of heptane solvent. The PCM pickup varied only from about 30 to 25% wt. in this series where the PCM content decreased from 100% to 25%. Thus, the desired range of graduated PCM concentrations was not obtained. It was also found that control samples, with no PCM and a paper cover retained some heptane (4.6% wt.) even after the 48 hours vacuum drying.

The results in the horizontal burning tests showed that all the samples (except the control that contained no PCM) continued to burn for times up to 10 minutes. The 45-A/heptane (25/75) burned for a shorter 3-1/2 minutes, while the control with

no PCM did not ignite. Considering the high, and nearly constant PCM content of all the samples (except the control), the results were not surprising. However, "preferential" PCM absorption from the heptane solvent solutions was unexpected, and the reasons for this phenomenon are not readily apparent.

3.2.2 Experiment Number 860804-10 to 30

After reviewing the results obtained in experiment 860709-1 to 5 above, a second series of tests was planned to further investigate the burning of plasterboard containing various concentrations of Witco 45-A PCM, applied from solvent solutions. Accordingly, in this experiment, higher ratios of heptane solvent to 45-A PCM were used. Additionally, we included a series made with non-burning methylene chloride solvent, in the same ratios as those used in the heptane series. The 45-A PCM/solvent ratio was 5/95, 10/90, 15/85, 20/80, and 25/75, in both heptane and methylene chloride solvents.

The procedure used in the sample preparation and testing was identical to that used in 860709-1 to 5 above, and is described in Appendix 4. The 45-A PCM pickup data, for both solvent systems is contained in Table 6, along with the results of the burning tests.

As in the prior experiment above, the data in Table 6 shows a preferential absorption of the PCM, even in the very dilute solutions that were used in this experiment. Low PCM absorption (less than 30% wt.) was obtained only in solutions containing 85% and higher concentrations of either heptane or methylene chloride.

The data from the burning tests show that the results are influenced primarily by the PCM concentration, and less by the type of solvent used (heptane versus methylene chloride). When applied from heptane, a PCM concentration of 8.0% was self-extinguishing when the flame was removed. Concentrations of 18% and 23% PCM extinguished themselves in 1 minute 41 seconds, and 1 minute 51 seconds, respectively.

The results obtained with the PCM absorbed from methylene chloride solvent solutions had shorter times to extinguishment at PCM concentrations up to 23% wt. (30 seconds at 23% PCM). However, the time to extinguishment at PCM concentrations greater than 23% weight was at least as long as for the same PCM percentages applied from heptane solvent. Collectively, the results of experiments 860709-1 to 5 and 860804-10 to 30, lead to several important conclusions:

- PCM concentrations of about 10% weight in plasterboard, applied from a solvent solution, are immediately self-extinguishing when the flame is removed.
- PCM concentrations up to about 25% weight are self-extinguishing in 30 seconds (methylene chloride solvent), and in about 2 minutes (heptane solvent).
- Shorter times to extinguishment were obtained in low concentrations of PCM applied from methylene chloride solvent, but not at a high PCM concentration (e.g. >23% wt.).
- The low boiling solvent removal by the 48 hour vacuum procedure was effective in that little or no residual solvent remained in the sample.

We still have no good explanation for the disproportionate absorption of PCM from relatively dilute low boiling solvents. We now need to see if equivalent short times to extinguishment can be obtained in PCM concentrations up to 25% weight in plasterboard, applied from neat (100%) PCM, by using very short percolating times.

3.2.3 Experiment Number 860812-1 to 6

In continuing the investigation of fire retardance in plasterboard, 2" squares of commercial plasterboard were percolated with PCM (LLN or 45-A), containing various concentrations of Ethyl Saytex BCL-462, plus stearic acid wetting agent.

The 2" squares of plasterboard were weighed and immersed in the PCM/BCL-462/stearic acid for 10 minutes at 80°C. The ratios of the PCM (LLN or 45-A)/BCL-462/stearic acid were: 85/10/5, 80/15/5, 75/20/5, and 95/0/5. The samples were then removed from the percolating bath, and reweighed to determine the total PCM pickup. The percolated specimen were then mounted in

the horizontal position and ignited with a Bunsen burner for 10 seconds, and the time to extinguishment noted. The samples were then reignited, as long as necessary, to obtain continued burning, and the second time to final extinguishment also noted.

The procedure used in preparing these samples is detailed in Appendix 5. The PCM pickup data is contained in Table 7. The results obtained in the burning tests are summarized in Table 8.

In the fire tests, all of the samples, except the control that contained no fire retardant, were immediately self-extinguishing. Additionally, the LLN samples that had the surface paper removed failed to ignite in 10 seconds. Reignition tests, however, showed very long times to extinguishment, with somewhat shorter time to extinguishment in the samples which had higher BCL-462 concentration and/or had the surface paper removed prior to fire test. The overall conclusions from this series of tests emphasize:

- At the high PCM concentrations in these samples of plasterboard, at least 20% wt., and possibly 25% wt. of BCL-462 will be required to obtain a self-extinguishing composition. More work is necessary to establish the exact percentage of fire retardant required.
- The paper surface used on all plasterboard certainly makes fire retarding more difficult in plasterboard containing organic PCM. It is possible that a surface rinse with a non-burning solvent (e.g. methylene chloride) could reduce the adverse effect of the paper, and this possibility will be evaluated.
- Other fire retardants may be more effective than BCL-462. Some alternate fire retardant materials from Great Lakes Chemical Company are on hand and will be evaluated. One additional Ethyl Corporation fire retardant (Saytex 105) also remains to be tested.
- The approach of using a lower, but still effective storage concentration, of PCM also deserves further study.

3.3 Crosslinked High Density Polyethylene, Pellets and Powder Absorbers for Alkyl Hydrocarbon PCM

3.3.1 Experiment Number 860708-3 to 6 and 860708-3 to 14

The objective of this experiment was to continue and complete work started last month, wherein it was desired to compare the uptake in crosslinked Marlex 6006 pellets, and powder, of Witco K-61 PCM. In Table 7 of the July Progress Report, we tabulated the data on permeation of Witco K-61 PCM into gamma irradiation crosslinked (10 m-rad) pellets of Marlex 6006 HDPE. In that experiment, the total weight gain of K-61, after permeating for 4 hours in K-61 at 150°C, was 88.8% based on total sample weight. Further the DSC analysis of the thermal energy storage of both the K-61 and HDPE, by DSC analysis was consistent with the weight gain of PCM.

This month we continued the work on PCM uptake in crosslinked HDPE (10 m-rad gamma) using finely divided powder obtained by grinding the same crosslinked Marlex pellets in a laboratory micronizer. The sieve screen analysis of this ground powder is reported in a separate experiment.

The ground powder of the crosslinked HDPE was permeated with Witco K-61 PCM for a total of 4 hours at 150°C, with samples being removed for DSC analysis at intervals of 1/2, 1, 2, 3 and 4 hours. A total of 68.01% of K-61 PCM was permeated into the crosslinked powder in four hours. This is significantly less than the 88.8% uptake by the whole pellets.

The DSC analysis of the permeated powder samples taken at the 1/2, 1, 2, 3 and 4 hour time interval is reported in Table 9. The procedure used in the permeation is described in Appendix 6.

We now know that when permeated, finely divided, HDPE powder is rinsed with MEK solvent after permeation, as has been our standard practice to date, much of the permeated, soluble, PCM is removed. This almost certainly accounts for the lower (68 vs. 88%) PCM retention in the powder. Accordingly,

plans were made to study solvent rinses other than warm MEK, and this has been done in a later experiment this month.

3.3.2 Experiment Number 860716-1 to 4

As noted above, and in last month's Progress Report, the permeation of Witco K-61 PCM, into gamma irradiation crosslinked Phillip Marlex 6006 was investigated using both whole pellets, and "powder" (ground pellets). This experiment had two objectives: (1) to permeate whole pellets, and powder, of crosslinked Marlex 6006 with Witco's hydrocarbon PCM, and (2) to prepare approximately 1000 grams of the permeated pellets and powder for further evaluation in concrete, plaster, etc. To prevent oxidation of the PCM during the relatively long permeation, for 4 hours at 150°C, 1 phr of Santowhite Powder antioxidant was added to the PCM melt, as in the experiment reported above.

In view of the problem of PCM removal from permeated powder, noted above, this experiment was confined to permeation of the pellets, pending resolving of this difficulty. Additionally, it was decided that it would be easier to prepare ten 100 gram batches in the laboratory glassware equipment, than to make a single large batch. This modification of the procedure had the added advantage that the reproducibility of the laboratory permeation process could simultaneously be verified. Since Witco's 45-A PCM was available in quantity, these large scale experiments were carried out with this PCM instead of K-61. The procedure used in the permeation process is described in Appendix 7. The analysis of PCM pickup in each of the ten batches is contained in Table 10. At this time the DSC analysis of the samples has not been completed, and will be reported next month.

As shown by the data in Table 10, the pickup of the 45-A PCM in the ten separate batches was very uniform indeed, and varied only from a low of 87.94% to a high of 89.19%. These values of PCM pickup are also very close to those obtained in the permeation of crosslinked pellets of Marlex 6006 with Witco K-61 PCM, reported previously.

3.3.3 Experiment Number 860729-1 and 2

In view of some of the difficulties noted above in retention of permeated PCM in powders of crosslinked Marlex 6006 (either from polymerization or grinding), it was decided to determine the particle size distribution of these two types of "powders" by sieve screen analysis. The sieve screen analysis was performed using a selected set of standard screens having mesh sizes of 20, 40, 70, 100, 250, 325, and thru 325 (pan). The powder samples were placed on top of the largest screen, and shaken in a Ro-Tap sieve shaker for 30 minutes. Afterward, the PCM powder retained on each screen was weighed, and the percent retained on each screen computed. The procedure used is described in Appendix 8, and the data are contained in Table 11.

There are significant differences in the particle size distribution of powder from ground pellets, and the powder intermediate from the Phillips polymerization process, with the ground pellets being considerably smaller in average particle size. As seen in Table 11 and Figure 1, almost 90% of powder-from-process is retained on the 40 and 80 mesh screens, and thus has a relatively narrow particle size distribution. In contrast, the powder-from-ground pellets has a smaller average particle size distribution with 56.92% being finer than 70 mesh. The particle size distribution is also broader with significant quantities of powder retained on the 40, 70, 100, 250, 325, and pan. From the standpoint of PCM removal, during rinsing of permeated HDPE, the powder from process should be better than that obtained by grinding the permeated pellets. More importantly, both of them are smaller than desired. Accordingly, we will evaluate changes in the pellet grinding procedure aimed at producing powder in the range of 20 to 40 mesh size. However, we have also scheduled, and completed this month, evaluation of alternate solvents for rinsing away the surface PCM that should remove less of the permeated PCM. This is reported below.

3.3.4 Experiment Number 860729-6 to 9

In view of the extensive removal of permeated linear alkyl hydrocarbon PCM, with the methyl ethyl ketone rinsing procedure used heretofore, it was decided to evaluate methanol and ethanol as solvents to be used for rinsing-away the surface PCM, from permeated HDPE powders - of any type. An experiment was devised wherein permeated HDPE ground powder was extracted for two hours, at room temperature with methanol and ethanol, respectively. Afterward, the HDPE powder was filtered off, dried, and weighed. The solvent filtrate was then evaporated to dryness, and the residue weighed. The procedure used is detailed in Appendix 9, and the data are contained in Table 12.

From the data in Table 12, it was concluded that washing for 2 hours in methanol at room temperature removes only 9.43% of the initial permeated powder weight. Most of this 9.43% is found in the residue obtained after evaporating the methanol to dryness.

On the other hand, washing the permeated powder for 2 hours in ethanol removes about 52% of the initial weight of the permeated HDPE powder. Again, a major part of the PCM that was extracted was recovered as residue after the ethanol was evaporated to dryness. Further, it was also observed that the ethanol extracted powder contained small lumps of PCM, and was somewhat sticky; whereas the methanol extracted powder yielded a dry free flowing powder.

From this experiment we concluded that methanol extraction at room temperature would likely be a more useable surface rinse than either ethanol, or the MEK rinse previously used. Further experiments will be done to test this conclusion. Additionally, we plan to prepare smaller pellets by extrusion crosslinking of the lower cost Marlex HDPE powder-from-process, and this experiment is scheduled for next month.

3.3.5 Experiment Number 860813-1 and 2

We have previously observed large differences in the relative permeability to PCM of crosslinked HDPE powder-from-process and crosslinked powder obtained by grinding crosslinked pellets. The process powder was crosslinked by irradiation with gamma, in N₂, to a total dose of 5 m-rads. The ground powder was irradiated with gamma, in N₂ to total dose of 10 m-rad. On this basis the pellets should be more highly crosslinked than the powder. However, we have consistently observed that the PCM uptake of the pellets (e.g. 88%), was always higher than that of powder-from-ground pellets (e.g. 68%), or the crosslinked powder-from-process (e.g. 0-20%).

In order to determine the relative degree of crosslinking in the two HDPE powders, we set up an experiment to measure the gel content of the two powders, and an uncrosslinked control, in xylene solvent, at 120°C. One gram each of the two powders, and the uncrosslinked control, was heated with stirring in 50 ml of xylene, for 1 hour. At the end of this time the samples were observed for solution properties. The solutions (partial or complete) were then filtered hot, and the insoluble gel dried and weighed. The xylene solvent solution was evaporated to dryness, and the residue also weighed. The experimental procedure used is described in more detail in Appendix 10, and the experimental data are contained in Table 13.

From these data, it is apparent that the uncrosslinked HDPE powder has, as expected, a very high soluble content (98.7%). However, the powder-from-ground-pellets (10 m-rad gamma) also has a very high soluble content (93.58%), and this was not expected. The powder-from-process (5 m-rad gamma) has lower solubles of only 31.7% (68.3% gel).

If the powder-from-ground-pellets does have a lower level of crosslinking (as indicated in these experiments), this would account for the higher levels of PCM uptake. However, in the form of ground powder, the PCM is readily removed during the normal MEK rinsing, after permeation. This requires further study

of both the gamma irradiation and the after permeation rinsing processes. We also plan to evaluate the alternate peroxide extrusion crosslinking process.

4. FURTHER INVESTIGATION ON THE THERMAL ENERGY STORAGE PROPERTIES OF N-ALKYL HYDROCARBONS

Extensive work has been carried out during the last few months in order to understand the effect of composition on the thermal energy storage properties of n-alkyl hydrocarbons. Although limited studies on this subject were carried out before at the earlier phases of this project, conclusions were rather indefinite because of the limited amount of data and the questionable purity of the single alkanes used. Recently, we were able to obtain samples of 99% pure linear paraffinic hydrocarbons from C_6 to C_{28} as well as C_{30} , C_{32} , C_{40} and C_{44} from Humphrey Chemical Company. A limited study of thermal energy storage properties of pure paraffins, and blends made therefrom was therefore undertaken. The study was presented at the North American Thermal Analysis Conference at Cincinnati, Sept. 21-24, 1986.

4.1 Comparison With Literature Data

Table 14 summarizes the results for DSC measurements at 10°C per minute rate of heating. The melting point (T_m) and the crystallization temperature (T_c) are determined from the "peak" temperature during heating and cooling cycle, respectively. The results are averages of three measurements. The corresponding DSC thermographs for the single hydrocarbons are illustrated in Figures 2 to 28. A comparison between the DSC data (Table 14) and those obtained from the literature is made in Table 15. Melting temperature by both "peak" and "onset" temperature are recorded. The problem with the literature values are that they are not available from a single source and are probably determined by different techniques. Although the melting temperatures in Table 15 are very near to one another, there are no consistent patterns. However, in all cases, the literature values are lower than the corresponding "peak" temperature for the samples run at $10^\circ\text{C}/\text{min}$.

The "onset" temperatures are very near to the literature value for some low molecular hydrocarbons up to C_{11} and are slightly lower than the literature values in other cases.

4.2 Effect of Rate of Temperature Change

Table 16 presents the data for DSC run at $2^{\circ}\text{C}/\text{min.}$ for a few 99% pure n-alkanes along with some of the commercial phase change materials. Figures 29 to 38 illustrate the nature of the thermographs. As expected the resolution is much better at a lower rate of heating. It is apparent from Table 16 that T_m is lower and T_c is higher at $2^{\circ}\text{C}/\text{min.}$, giving $(T_m - T_c)$ values in the range of $2-3^{\circ}\text{C.}$ $(T_m - T_c)$ is smaller for commercial PCMs than for the pure n-alkanes. For polymeric material, e.g. polyethylene glycol and high density polyethylene, $(T_m - T_c)$ at $2^{\circ}\text{C}/\text{min.}$ has a higher value of 10°C. Figures 39-41 show the DSC thermograph for uncrosslinked Marlex 6006 high density polyethylene at three different heating rates. $(T_m - T_c)$ for HDPE are 14°C and 19°C at 5 and 10°C heating rate, respectively. ΔH_f and ΔH_c show small variations in all the samples. The variation is within reproducibility limits of the experiment.

Table 17 presents the data for octadecane at four heating rates and for hexadecane and Marlex 6006 at three different heating rates. The corresponding thermographs are presented in Figures 39-47. Again, the $(T_m - T_c)$ is smaller as the heating rate decreases. Figures 48 and 49 illustrate how the T_m and T_c get closer with heating rates for samples of n-octadecane (Tech) and n-hexadecane, respectively. The extrapolated values for $(T_m - T_c)$ at zero rate of heating is within 2°C. Table 18 reports these extrapolated values for some selected alkanes and commercial phase change materials. It may be noted that $(T_m - T_c)$ at zero heating rate is smaller for commercial paraffins which are blends than the pure alkanes and is within 1°C for Witco K-61. The extrapolated T_m for pure n-alkanes are $2-4^{\circ}\text{C}$ lower than at 10°C (reported in Table 14), while the extrapolated T_c values are about $2-4^{\circ}\text{C}$ higher. Surprisingly, T_c values decrease at lower rate of heating for PEG 1000 (Figure 50) unlike the n-alkanes. High density

polyethylene (Figure 51) shows an extrapolated ($T_m - T_c$) at zero rate of heating of 9°C.

4.3 Heat of Fusion

Heat of fusion by DSC is consistently higher than the literature value. With one exception (C_{25}) the DSC heat of transition for solid/solid change is also higher than the literature values. The same is true for the total heat of transition, recorded in the last column of Tables 14 and 15. This, along with higher T_m and T_c values discussed earlier, indicates higher purity of the Humphrey samples. In three samples (C_{18} , C_{22} and C_{24}), the purity of the Humphrey material was checked by a Gas Chromatograph, fitted with an OV17 column and flame ionization detector and was indeed found to be over 99% pure. Unfortunately, samples were not available for many of the higher member hydrocarbons. The literature values for the higher homologues are not also readily available in reference sources such as the Handbook of Chemistry and Physics.

4.4 Effect of Chain Length

Going back to the data in Table 14 and Figures 2-28, it is apparent that both T_m (melting temperature) and T_c (crystallization) temperature progressively increases with the carbon chain length. This is amply demonstrated in Figure 52 which plots melting temperature with the number of carbon atoms in the chain. Figure 52 includes a few more of the higher and lower homologues of n-alkanes which were obtained after our June, 1986 report and gives a more complete picture of their characteristics.

4.5 Odd-Even Difference

The odd carbon chains up to C_{20} follow a slightly lower temperature pattern than the curve connecting the even carbon melting points. However, after C_{20} odd and even carbon difference

in melting temperature gradually disappears and the melting temperature of both follow the same curve. Another distinction, between the odd and even carbon chains from C_9 to C_{20} is that the odd carbon chains have solid/solid transition before the melting point (referred to as "secondary" transition in Table 14). The solid/solid transition temperature vs. carbon atoms in chain follow a parallel course to the melting temperature curve except for the carbon chains higher than C_{32} . The "odd-even" alternation also shows up in solid/solid transition temperature between C_{20} and C_{44} carbon atoms, as is evident in both Figures 52 and 53. Again, both odd and even carbon chains between C_{24} - C_{44} have two transitions during crystallization. However, C_{20} and C_{22} show only one transition during melting and two during crystallization.

Figure 53 shows the plot of crystallization and melting temperature along with solid/solid transition during cooling vs. carbon atoms in the chain. Melting and crystallization temperatures follow a, more or less, parallel path, with an average difference ($T_m - T_c$) of 8°C . Solid/solid transition temperatures also follow a similar pattern with an average difference between heating and cooling cycle temperatures of around 7°C . As will be seen later ($T_m - T_c$) of 8°C is higher than the similar data for commercial phase change materials. This would be expected, since the nucleation is more difficult in pure materials, than in the commercial paraffins which are mostly blends. However, as discussed earlier the difference in ($T_m - T_c$) decreases as heating rate decreases and becomes negligible at zero heating rate. Figure 54 plots the heats of fusion (ΔH_f) of the even and odd carbon chains. Except for the linear increase between C_6 and C_{20} , the even carbons show irregular behavior. Odd carbons show less scatter. The reason for this may be explained in Figure 55, which plots the heats of transition for solid/solid transition for both odd and even carbon atoms. The odd carbons show this additional transition all the way from nonane, while the even carbons have this starting from hexacosane (in some cases tetracosane, as in present work). The total heat of transition from the stable solid crystal

form to the liquid is thus divided between the solid/solid and the solid/liquid (melting transition). The former constitutes about 20-30% of the total. The even carbons between C_4 to C_{20} does not show the first transition and thus shows higher heat of fusion, since the total enthalpy is not divided between two transitions. Starting from C_{24} the even carbons start to show the additional solid/solid transition. A metastable phase may also be observed for lower carbon chains (C_{18} , C_{20} , C_{22}) so the heat of fusion decreases. After C_{28} or possibly C_{32} the proportion of total enthalpy required for solid/solid transition diminishes, thus showing the upward trend again for the heat of fusion vs. chain length curve. Unfortunately, not enough of the higher member ($>C_{30}$) carbon chains were available to show the above trends in this study.

The above explanation implies that the total heat of transition (sum of solid/solid + solid/liquid) would follow a regular pattern with carbon chain length. This was found to be true, as shown in Figure 56. The odd and even carbon chains fit in similar curves when the total heat is plotted with carbon chain length. Slightly higher values for the even carbon chains reveals a denser crystalline packing arrangement. A much better linear fit is obtained when molar heat of fusion is plotted vs. number of carbon atoms in the chain (Figure 57). A least square fit of all data shows all the odd carbons below the regression line, whereas most of the even carbons slightly above. Separate plot for the odd and even carbons are shown in Figure 58. The regression equations are only slightly different. The slopes were 1.00 for the even carbon and 0.98 for the odd carbon atoms. The slope represents the value of heat of fusion in kcal/mole per CH_2 group. The value is higher than that in the literature (F.W. Billmeyer, J. Appl. Phys., 28, 1114, 957) and is probably due to higher purity of the samples in this study. Slightly higher value for the even carbons indicates a denser crystalline arrangement which requires more energy to break down.

4.6 Crystalline Structure of n-Alkanes

Carbon-carbon bond lengths and bond angles of n-alkanes are maintained by strong forces. On the other hand, rotation of C-H bonds can occur readily. As a result, the carbon-hydrogen units of the chain can assume a variety of positions differing in energy. In the case of normal alkanes the arrangement giving minimum energy is that in which the chain takes the form of a flat zig-zag of carbon atoms. An assembly of these zig-zag chains, nucleating from a melt or solution, can crystallize in four characteristic geometric forms. Table 19 describes the phase notations commonly used. These are identified by Broadhurst as α_H , β_O , β_T , and β_M . The symbols α and β designate, respectively, the high and low temperature phases and the subscripts H, O, T, and M indicate the type of crystalline structure. Thus, the symbols α_H , β_O , β_T , and β_M identify, respectively, the hexagonal, orthorhombic, triclinic and monoclinic crystal structures. As reported in Table 19, the structures differ in the inclination of the chain axes to the end group planes. The chain axes are perpendicular to the end group planes in the α_H and β_O structures and are inclined to the end groups planes in the β_T and β_M forms. The latter two forms give rise to closer packing. The packing arrangement assumed being the closest possible fitting together under a particular set of conditions. This closest packing arrangement gives the minimum free energy.

The α_H form is closely related to the ordered structure which the molecules had already attained in the liquid just above the freezing point. This is the first solid state structural form obtained by many of the normal alkanes upon cooling from the liquid form. The subcell is hexagonal and the molecular chains are arranged perpendicular to the end group planes and rotate about their long axes. Although crystalline in nature, this state is characteristically plastic, waxy and translucent and resembles the liquid state in several ways.

The β_O form, sometimes called the orthorhombic structural form, is one of the hard forms assumed by many of the pure normal

alkanes and other long chain molecules upon cooling from either the liquid state or the α_H form. As in the α_H form the chains are perpendicular to the end group planes, so that a transformation into this structure from either the ordered liquid or the α_H phase can take place easily when, upon cooling, chain rotation ceases or becomes greatly restricted. The α_H to β_O transition has been identified as a rotational order-disorder transition.

The β_M or monoclinic subcell form is assumed by some "even" carbon alkanes upon cooling from the α_H or β_O form. The chains make an angle of about 61° with the end group planes, representing a displacement of adjacent chains, along their axes of about two carbon to carbon units so that considerable slippage of chains must occur for this low energy phase to form. Rotation of the tilted chain is very restricted. The transition into this phase is a more complex operation than into the α_H or β_O phases.

The β_T or triclinic structure represents the lowest energy state into which the shorter "even" carbon number alkanes enter upon cooling either from the melt or the α_H form. The transition into this state is also complex, because the chain axes are tilted at an angle of 73° with the end group planes, representing a displacement in the direction of the chain axes by a distance equal to about one C-C unit. Rotation of the chains is very restricted.

4.7 Crystal Structure Variation with Carbon Chain Length

Many of the observed variations of melting and transition temperatures and of the heats of transition, either solid/solid or solid/liquid, may be explained by the already published information of crystal structure of the n-alkanes of various carbon chain lengths (W. R. Turner, Ind. Eng. Chem. Prod. Res. Dev. 10(2), 238, 1971). Sometimes more than one structure is assigned to a single carbon chain. This is due to small differences in free energies among the different β forms, the effect of end group packings or the differences in purity, which determine which structure has the lowest free energy.

Table 20 is compiled from the information available in the literature and records the observed variation of crystal structure with carbon chain length. As observed in Figures 52-58 and Table 14 there are subtle differences in transition temperatures and heats of transition between "odd" and "even" carbon chains. This is the so-called "odd-even" alternation of carbon chain melting temperature of normal alkanes below C_{20} and the solid phase transition of the normal alkanes between C_{20} and C_{44} . Figure 59 illustrates the effect of packing density of "even" vs. "odd" normal alkanes. The packing density is much higher for the tilted structures. The "even-odd" differences occur only when the tilted (β_T, β_M) structures are involved and the differences are due primarily to packing differences in the end group layers. When the paraffin chains are packed vertically as in α_H or β_O structures, there is no reason for either the chain group or the end group packing to be any different for even than the odd numbered chains. But when tilted, only the even paraffins have the necessary symmetry for equivalent (apparently low energy packing of both ends). This explains the alternation of melting points below C_{20} , because of the β_T structures assumed by the even carbons. The alternation in transition temperature between C_{20} and perhaps C_{44} does occur because the even paraffins assume the tilted (β_T and β_M) structure.

The melting points of the normal alkanes increase with chain length (reflecting the stronger intermolecular forces) and approach a limiting value representing the melting temperature of an infinitely long chain. This value is in the range of 135-145°C and has been reached very closely by the synthesis of high molecular weight, substantially linear polyethylenes and polymethylenes.

5. BLENDS OF N-ALKANES

The commercial waxes used for thermal energy storage are usually obtained at the refinery by solvent/non-solvent separation from the branched paraffins, required for gasoline, diesel fuel

and motor oil. Further purification is often carried out by solvent crystallization, but the products still contains homologues of a mixture of n-paraffin with a minor amount of branched chain paraffins. A limited study of the blends of pure n-paraffins was undertaken during this investigation to understand the relationship of the thermal energy storage properties with composition. The study was extended from binary blends of odd and even carbon chain paraffins to triblends and ultimately to selected compositions of a number of n-alkanes, to match the gas chromatographic composition of Witco waxes used in this project.

5.1 Conditions for Solid Solutions of Binary Systems of Blends

In the liquid state pairs of n-alkanes are completely miscible. In the solid state, binary system of blends can either form a continuous solid solution, an eutectic or something in between. The requirements for solid solution are similarity in (1) form, (2) dimension, and (3) crystal symmetries. In mixtures of the normal alkanes, the requirement of the similarity in form is met because they are homologues, and the dimensional requirement is met if only a small difference exists in carbon chain length of the components making up the system. The symmetry requirement is not met, however, unless the components have the same type of elementary cells and subcells. Thus, odd carbon chain alkanes having orthorhombic subcell (Table 20) should form continuous solid solutions if they are near neighbors. A mixture of odd and even below C_{26} can never be continuous because of symmetry difference. Even when all the requirements are satisfied, e.g. two even pairs, the end group packing becomes sufficiently disturbed to preclude the formation of tilted chains (mono- or triclinic). The orthorhombic form thus appears as an accommodation device for almost all mixtures of alkanes and those of questionable purity and corresponding breaks in solubility occur. The orthorhombic form which appears in such mixtures, however, differs somewhat from that observed with pure odd alkanes (A.E. Smith, Bull. Amer. Phys. Soc. 6(2), 171, 1961).

According to Kravchenko (V.M. Kravchenko, Acta Physicochim (USSR), 21, 335, 1946) solid solutions form when the molecular length difference is less than 6% and eutectics when the length difference is greater than 15%. Other experimental work suggests that in the C_{18} - C_{35} range the critical difference could be two to six carbon atoms (J.A. Kieras, W.R. Turner, F.W. Melbolder, Amer. Chem. Soc. Div. Petrol. Chem. Preprints, 9(3), 257, 1964).

As for the molecular packing of the crystals a general rule (A.I. Kitaigorodskii and Yu V. Mnyukh, Dokl. Acad. Nauk. (USSR), 121, 115, 1958; Yu V. Mnyukh, Zh. Struct. Khim, 1(3), 370, 1960) suggests that under otherwise similar conditions, a higher percentage of shorter chain normal alkanes will dissolve in a solvent of longer chain normal alkanes without affecting the crystal structure of the latter than in the reverse case where the shorter chain alkane is the solvent. Figure 60, adapted from Mnyukh (1960), illustrates how chain length differences could affect the molecular packing and consequently the mutual solubilities of the alkane pairs. Thus, the crystal structure of a compound will tolerate more contaminant if the latter is shorter chain length than the major component. If A is longer than B as in right illustration of Figure 60, the existence of only a few projections from one layer can interfere with the close packings of adjacent layers.

5.1.1 Blends of "Odd" N-Alkanes

Table 21 and 22 record the DSC analysis data for blends of C_{17}/C_{19} and C_{15}/C_{19} , respectively. Corresponding plots of melting temperature and heat of fusion vs. percent composition of C_{19} are presented in Figures 61 and 62, respectively. In the case of C_{17}/C_{19} , two odd adjacent homologues, all the conditions of formation of solid solution are satisfied. Melting temperature shows a continuous, almost linear change from C_{17} to C_{19} except where C_{17} is the major component, showing agreement with the corollary that the adjacent layer planes are disturbed much more when the minor added component has a longer chain length. The same observation seems to hold good for C_{15}/C_{19} pair in Figure 62.

There is, however, a larger drop of ΔH_f (indicating differences in packing density) in C_{17}/C_{19} as compared to C_{15}/C_{19} pair, which is hard to explain. ΔH_t (heat of solid/solid) transition remains more or less unaffected by the added component.

Earlier workers (M.G. Broadhurst, J. Research, National Bureau Stds., 66A, 241, 1962; R.T. Edwards, TAPPI, 41(6), 267, 1968; R.G. Craig, J.M. Powers and F.A. Peyton, J. Dent. Res., 46) observed that the transition temperature (T_t) (Table 14, T_m , secondary) is affected much more than T_m by impurities. Even when impurities do not prevent a transition from occurring they usually greatly lower the transition temperature and cause increased separation of T_m and T_t . Because of this, solid state transition temperatures are frequently a much more sensitive indicator of impurities than are melting temperatures. This is borne out by the data in Tables 21 and 22. In all the tables data for the solid state transition thermograph are recorded as the secondary or tertiary peak.

One difference between Table 21 and 22 is in the number of secondary peaks. While C_{17}/C_{19} pair shows a single secondary peak at all compositions, the C_{15}/C_{19} pair shows two and sometimes three. This is illustrated in Figure 63 (A & B) for 50:50 composition of both pairs. Also, notice the sharp peak for the adjacent homologue pair vs. the greatly distorted peaks for C_{15}/C_{19} where the dimensional differences are greater. Figure 63B shows signs of the formation of mixed crystals.

5.1.2 Blends of "Even" n-Alkanes

Rather complex phase behavior is reported for the pairs of even alkanes (William R. Turner, Ind. Eng. Chem., Prod. Res. Dev. 10(3), 238, 1971). Even if the chain length differences are less than the critical value, pairs of even alkanes do not form continuous solid solution. Although the pairs of even alkanes below C_{26} and again above C_{26} are homologues, the mixing together of two chains of different lengths disturbs the end group packing to such an extent that the orthorhombic form supplant the triclinic or monoclinic forms of the pure components (A.K.

Kitaigordskii and Yu V. Mnyukh, *Izv. Akad. Nauk (USSR), Otd. Khim. Nauk*, p. 2088, 1959).

Tables 23, 24 and 25 report the DSC analysis of C_{14}/C_{16} , C_{16}/C_{18} and C_{16}/C_{20} , respectively. The thermographs for C_{14}/C_{16} blends are reported in Figures 64-67. As may be observed the two pure components have no solid/solid transition. Only 10% of hexadecane in tetradecane (Figure 64B) gives rise to a second peak, probably due to the formation of orthorhombic structure. As the proportion of the larger chain length, second component increases up to 50%, the distance between the solid/solid and melting peak increases and the former becomes less defined. As the composition reaches 60% hexadecane two solid/solid transitions are observed. At the other end of the curve, even 20% of C_{14} in C_{16} does not show a well defined solid/solid transition, again showing that a larger chain can tolerate minor amount of smaller chains without disturbing the crystal structure. This is also supported by the melting point curves in Figures 68-70. These figures also show the same general characteristics as "odd" alkanes with regard to the variation of heat of fusion with composition. The reason for the slightly different shape of ΔH_f vs. composition curve for C_{16}/C_{18} is not well understood.

All the transition temperatures, both melting and crystallization as well as the secondary transitions in the solid state are plotted vs. composition in Figure 71 as an illustration. The lowering of the secondary transition temperatures during heating and cooling are much larger than the corresponding melting and crystallization peak temperature, as was also observed with "odd" alkanes.

Figure 72 shows a comparison of thermographs of C_{16}/C_{18} vs. C_{16}/C_{20} at 50 percent level. Crystalline pattern seems to be more disturbed with the higher alkane, due to the larger difference of crystalline dimension, as would be expected.

5.1.3 Blends of Odd and Even n-Alkanes

As mentioned before, blends of odd-even pairs of n-alkanes does not form a continuous solid solution. According to

earlier workers, the severity of disturbance to the molecular packing is much more when the "odd" carbon chain is longer (H.W.B. Roozeboom, Z. Phys. Chem. 30, 385, 1899; Yu V. Mnyukh, Zh. Struct. Chim, 1(3), 370 (1960)) than when the reverse is the case. Tables 26 and 27 present the DSC analysis data of two pairs, C_{16}/C_{17} and C_{18}/C_{19} , both of which have higher "odd" carbon chain. However, plots of the data (Figures 73 and 74) do not reveal any unusual disruptions of the chain. DSC thermographs (Figure 75) show sharp transition and melting peaks for both pairs. Unfortunately, no "odd-even" pair was studied where carbon chain length difference is greater than one carbon chain.

5.1.4 50:50 Blends of Larger Alkanes

Binary systems of higher alkanes (above C_{20}) particularly even numbered normal alkanes, are expected to be different in phase behavior from those below. While the odd carbons from C_9 to C_{43} would still crystallize in orthorhombic form, the pure even alkanes below C_{26} and possibly C_{24} would crystallize in triclinic form and those above would have the monoclinic structure. However, when similar length pairs are blended in middle range concentration, they form solids having the orthorhombic modification.

Table 28 presents the DSC data for some 50:50 binary blends of n-alkanes above C_{22} , along with those of the pure alkanes from which they are made. The expected lowering of T_m , T_c , ΔH_f and ΔH_c are observed. Unlike T_m or T_c , the T_t or the transition temperature of the blend is much lower than that of either of the components.

The effect of the chain dimension on phase distortion is evident in Figure 76-81 and Table 29. In Figure 71 two neighboring "odd" carbon pair, show sharp transitions in melting and freezing peak, with minor indication of two solid/solid transitions. When the chain length difference increases to 4 (C_{23}/C_{27}) and 5 (C_{23}/C_{28}) carbons in Figures 76B and 77A a distorted solid/solid transition results. Other than the difference in dimension, there is also a difference in symmetry in crystal

structure of the components for the C_{23}/C_{28} and C_{23}/C_{32} blends. This may have some contribution for more distorted solid state peaks and (in the case of C_{23}/C_{32}) double melting peaks (Figures 72, A & B). The same is true when Figures 76B and 78A are compared with Figure 77B. However, the distortion is much less for C_{24}/C_{28} and C_{24}/C_{32} (Figures 74 A & B) than for C_{23}/C_{27} (Figures 76A & B) and C_{23}/C_{32} (Figure 77B).

Some workers (W.M. Mazee, Erdol Kohle, 13, 88, 1960) suggest that as the proportion of end group planes decrease with molecular chain length, the areas of incompatibility in a phase diagram becomes smaller with higher molecular weight mixed adjacent homologues. The sharp transition for C_{28}/C_{32} probably can be attributed to this phenomenon. This is also very spectacularly shown in the blends for C_{40}/C_{44} (Figure 80B). While the individual components show a small α_H, β_M transition, the blend shows none. Attempts to resolve the single peak at a low rate of heating and cooling ($2^\circ\text{C}/\text{min.}$) were also unsuccessful (Figure 75C). Above C_{45} the alkane chains can solidify from the liquid in β_M form without going through the α_H form. This is probably what is happening here although the crystalline form in blend may be β_O instead of β_M .

Faust (Thermochim Acta, 26(1), 383, 1978), illustrates the calculation of ΔH_f from carbon number distribution (composition) and literature value (F.W. Billmeyer, Jr., J. Appl. Phys. 28, 1114, 1957). Other authors (unpublished letter from Witco) extended this method to calculate T_m . Table 29 compares the experimental vs. calculated values for the 50:50 blends reported above. Calculated values for both T_m and ΔH_f are higher than experimental, as would be expected from their different crystal form density. The only exception is the T_m value for C_{23}/C_{32} blend which shows double melting peaks and a negative (Cal-Expt) value. The percent difference based on the calculated value for both T_m and ΔH_f seems to increase with the carbon chain difference in the blend and may be an indicator of distortion of crystal structure. As mentioned before, T_t (solid/solid transition temperature) is more sensitive to foreign material than T_m .

The difference between the calculated and experimental T_t values in Table 29 is much larger and also increases with carbon chain difference in most blends. However, such calculation can only be carried out with binary pairs of blends where both have a solid/solid transition as in the examples of Table 28. Also, as discussed before, the crystalline structure and symmetry are different depending on "odd" or "even" carbon which give rise to alternation in transition temperature for pure n-alkanes above C_{20} . Such subtle differences would probably explain the somewhat anomalous relationship in Table 29.

5.1.5 Triblends of n-Alkanes

Figures 82-84 and Table 30 report the DSC analysis of a few selected triblends. It appears from the figures that sharpest transitions indicating homogeneity of the blend are obtained by mixing adjacent homologues ($C_{16}/C_{17}/C_{18}$; $C_{17}/C_{18}/C_{19}$, Figure 82). The further the carbon chains are removed the more diffused are the peaks. Therefore, $C_{16}/C_{18}/C_{20}$ and $C_{17}/C_{19}/C_{21}$ (Figure 83) give sharper peaks than $C_{14}/C_{17}/C_{20}$ and $C_{16}/C_{19}/C_{21}$ triblends (Figure 84). Contrary to expectation, increasing the number of components does not detract from sharpness of the peak. For example the triblend of $C_{16}/C_{18}/C_{20}$ (Figure 83) show sharper transitions than either C_{16}/C_{18} (Figure 72A) or C_{18}/C_{20} (Figure 72B).

Table 31 compares the calculated and experimental values of T_m , ΔH_f and ΔT_t . Percent differences calculated do not seem to correlate as well as the higher alkane binary blends (Table 28).

5.1.6 Synthesizing Commercial Samples From Gas Chromatographic Data

Table 32 compares the DSC data for some commercial samples of n-alkane phase change material with those "synthesized" in the lab, to have a composition comparable to that indicated from the gas chromatographic analysis of the commercial samples. The gas chromatographic composition of the commercial samples and the proportion for the laboratory prepared counterpart are shown

in Table 33. It may be noted in Table 32 that T_m and T_c for both lab prepared and commercial samples are very close. T_m , T_c and ΔH_f are slightly higher for the laboratory blended sample probably because of higher purity of the ingredients (free from side chains) and slightly different composition (absence of minor constituents). However, ΔH_f for both the commercial and lab synthesized blends is lower than the corresponding calculated values, as would be expected. Figures 85-89 illustrate the thermographs of the commercial sample and the corresponding laboratory counterpart, which show very little difference. Surprisingly sharp peaks are observed for both the commercial samples and the lab prepared blends. Thus, intermixing of a number of adjacent homologues in different proportions does not seem to detract from the sharpness of the peak. However, there are some common features which are deduced from the triblends that give sharp peaks ($C_{16}/C_{17}/C_{18}$; $C_{17}/C_{18}/C_{19}$): (1) They are odd/even mixtures of adjacent carbon chains, (2) The middle carbon chain is the major component, so that there is a gradual distribution of adjacent chains on both sides. This is found to be true in the commercial samples studies, as is evident from Tables 33 and Figures 85-89. Figure 90 shows a normal distribution of carbon chains for all the commercial samples. However, compositions having a different distribution pattern have not been studied to confirm the above conclusions.

A calculation of $(\Delta H_f \text{ experimental} / \Delta H_f \text{ calculated}) \times 100$ from the data in Table 32 gives a value of around 90% for all the laboratory blended samples as compared to 80-90% for all the plant samples, except NP-15. K-61 gives a values of 88% which is higher than others while NP-15 gives a very low value of around 57%. The low value is partly because the solid/solid transition is not included in the peak area. The higher deviation from the calculated value for the plant samples also indicates the presence of varying amounts of branched chain paraffins, which do not crystallize. It is interesting that K-61 has the widest distribution of carbon chains (Figure 90), while NP-15 has the least.

6. CONCLUSIONS

1. The study of fire retarding of neat PCM with Ethyl Corporation's Saytex brominated compounds was continued this month to include:
 - Evaluation of the Ethyl fire retardants with a cotton wick added to promote burning,
 - The effect of lower concentrations of soluble Saytex BCL-462, and
 - Blends of BCL-462/Chlorowax 70-S that might provide lower cost.

The results obtained indicated that: BCL-462 is superior to the other Ethyl fire retardants tested; and provides effective fire extinguishment of the neat PCM at concentrations as low as 10% wt. (horizontal bar test with a wick). None of the blends of BCL-462/Chlorowax 70-S were effective in the more vigorous vertical test, but were effective in the horizontal test (with a wick).

2. The self-extinguishing properties of plasterboard percolated with various percentage of PCM was evaluated. Solvent (heptane or methylene chloride) dilution of the percolating solution was used to obtain a gradient range of PCM content. At percolated PCM percentages of 23% wt. and lower, self-extinguishing compositions were obtained, and the type of diluting solvent used (heptane or methylene chloride) had little effect on the results. It remains to be demonstrated whether equivalent fire retardance can be obtained by percolating for shorter times in neat PCM solution to obtain comparable PCM pickup.
3. The fire retardance of plasterboard percolated with solutions of PCM/BCL-462/stearic acid, to higher levels of PCM pickup, was determined. BCL-462 concentrations of 10, 15, and 20% wt. were tested. In one ignition, self-extinguishing was obtained at all BCL concentrations tested. However, all of the samples sustained burning for varying lengths of time after igniting a second time. Removal of the paper cover from the plasterboard has little effect on the self-extinguishing properties of the products. Thus, in plasterboard containing 30% and higher concentrations of PCM, 20% will be the minimum amount of BCL-462 to obtain plasterboard that is self-extinguishing after a second ignition.
4. Study of the permeation, and retention, of K-61 PCM showed that ground pellets did not retain a high percentage of PCM after the "standard" permeation and methyl ethyl ketone rinse cycle. In contrast, the whole pellets of the same crosslinked HDPE absorb and retain very high weight percentage of PCM. We believe the difference in the PCM retained by the ground powder, and the whole pellets, is probably

attributable to the effective removal of PCM from the powder by the MEK rinsing. Alternate rinsing solvents were then investigated as shown below.

5. Methanol and ethanol rinses were evaluated as that might remove less permeated PCM, than the present methyl ethyl ketone rinse. Ethanol removed 51% of the permeated PCM from the powder, and methanol only 9%. The ethanol extracted sample contained clumps of PCM, whereas the methanol extracted powder was free flowing. Further studies with methanol and mixtures of methanol/ethanol are scheduled to define an effective rinse, that removes surface PCM, but not that contained in the interior of the pellet.
6. The reproducibility of the process for permeating PCM into the crosslinked HDPE pellets was studied in the preparation of 10 successive laboratory batches. The lab procedure was found to be very reproducible with the PCM pickup (and retention) varying only from 87 to 89% wt.
7. The percentage of xylene solubles in the two different crosslinked HDPE powders was determined. Unexpectedly, ground crosslinked pellets contained 93.6% of xylene solubles, and the powder from process 31%. These data indicate a much lower level of crosslinking in the powder from ground pellets, such as may result from a crosslinked surface and a much less crosslinked interior.
8. A sieve screen analysis of crosslinked HDPE powder-from-process, and powder from ground crosslinked pellets was performed. The powder from ground pellets had a much smaller average particle size and a broader particle size distribution, than the powder intermediate from the Phillips polymerization process.
9. For binary blends of pairs of "odd" and "even" linear hydrocarbon chains sharp transitions are observed only for adjacent chains. The sharpest transitions are observed for "odd"/"even" adjacent pairs, rather than two of the same kind.
10. A higher homologue n-alkane major component in a blend can tolerate more of the adjacent lower homologue, without reduction of the sharpness of the DSC peaks, than in the reverse case when the shorter chain homologue is the major component.
11. With some exceptions, solid/solid transitions are observed for all blends. More than one primary transition is observed as the carbon chain difference of the pair increases.
12. The solid/solid transition temperature (T_t) is very susceptible to extraneous substances, and thus is a better indicator of purity than T_m .

13. The difference between the calculated and experimental values of T_g in a blend increases with chain length difference of the components, and may indicate presence of non-linear crystalline structures.
14. Mixing a number of adjacent homologues with a normal distribution of the components (as in the commercial samples) does not decrease the sharpness of the peaks of the DSC thermographs.

TABLE 1

TESTS OF FIRE RETARDANCE OF WITCO LLN PCM CONTAINING FOUR
DIFFERENT ETHYL CORPORATION FIRE RETARDANTS
(SAMPLE POSITION HORIZONTALLY, WITH A WICK)

<u>Saytex</u>	<u>Phase</u> <u>Separation</u>	<u>Ignite in</u> <u>5 sec.</u>	<u>Time to</u> <u>Ignite</u>	<u>Flame</u> <u>Traveled</u>	<u>Time to</u> <u>Extinguish</u>	<u>Smoke Flame</u> <u>& Char.</u>
<u>BCL462</u>						
% 10	No	No	75 sec	No	Immediately	Black & White
15	No	No	50	No	4 sec	Black & White
20	No	No	25	No	2 sec	Black & White
25	No	No	30	No	2 sec	Black & White
<u>HBCD</u>						
% 10	Yes	No	25 sec	5 1/2"	10 min	Black & White
15	Yes	No	35	1"	3 m 5 sec	Black & White
20	Yes	No	37	1"	2 m 15 sec	Black & White
25	Yes	No	60	1"	1 m 10 sec	Black & White
<u>102</u>						
% 10	Yes	No	47 sec	7"	10 min	Black & White
15	Yes	No	20	6 1/2"	10 min	Black & White
20	Yes	No	17	6 1/2"	10 min	Black & White
25	Yes	No	32	2 1/2"	7 min	Black & White
<u>BN -451</u>						
% 10	Yes	No	35 sec	4 1/4"	10 min	Black & White
15	Yes	No	25	4 1/4"	10 min	Black & White
20	Yes	No	15	7 1/2"	10 min	Black & White
25	Yes	No	17	7 1/4"	10 min	Black & White
Control	N/A	Yes	3 sec	3 3/4"	10 min	Black

TABLE 2
FIRE RETARDANCE OF WITCO LLN PCM CONTAINING
FOUR DIFFERENT CONCENTRATIONS OF ETHYL CORP.
BCL-462 (SAMPLE HORIZONTAL WITH A WICK)

<u>% FR</u>	<u>Hardness*</u>	<u>Phase Separation</u>	<u>Time to Ignite**</u>	<u>Flame Traveled</u>	<u>Time to Extinguish</u>	<u>Smoke</u>
10	1	no	2 sec.	no	11 sec.	black
7.5	1	no	3 sec.	4-1/2"	10 min.	black & white
5.0	1	no	3 sec.	4-1/2"	10 min.	black & white
2.5	1	no	5 sec.	4-1/2"	10 min.	black & white

* Hardness rating - 1(soft)-5(hard).

** Wick extended 1/4" past metal strip and ignited easily.

TABLE 3

FIRE RETARDANCE OF WITCO LLN CONTAINING MIXTURES OF
BCL-462/CHLOROWAX 70-S IN FIVE DIFFERENT RATIOS
(SAMPLE POSITION VERTICAL AND HORIZONTAL, NO WICK)

VERTICAL

<u>% FR</u>	<u>BCL 462/70-S</u>	<u>Hardness</u>	<u>Phase Separation</u>	<u>Self Extinguishing</u>	<u>Smoke</u>
20	1/3	2	No	No	Black
25	1/3	2	No	No	Black
20	1/2	2	No	No	Black
25	1/2	2	No	No	Black/White
20	1/1	1	No	No	White
25	1/1	1	No	No	Black
20	2/1	1	No	Yes	White
25	2/1	1	No	No	Black
20	3/1	1	No	Yes	White
25	3/1	1	No	No	Black

HORIZONTAL

<u>% FR</u>	<u>BCL 462/70-S</u>	<u>Ignite in 5 sec</u>	<u>Time to Ignite</u>	<u>Flame Traveled</u>	<u>Self Extinguishing</u>	<u>Smoke</u>
20	1/3	No	15 sec	No	Yes	White
25	1/3	No	27 sec	No	Yes	White
20	1/2	No	12 sec	No	Yes	Black
25	1/2	No	26 sec	No	Yes	White
20	1/1	No	didn't ignite	-	-	None
25	1/1	No	didn't ignite	-	-	None
20	2/1	No	didn't ignite	-	-	None
25	2/1	No	didn't ignite	-	-	None
20	3/1	No	didn't ignite	-	-	None
25	3/1	No	didn't ignite	-	-	None

TABLE 4

WITCO 45-A PCM PICKUP IN PLASTERBOARD PERCOLATED IN
SOLUTIONS OF 45-A/HEPTANE

45-A/Heptane Composition (%)		100/0	75/25	50/50	25/75	0/100
1. PCM Wt. Gain after 10 min Percolating %	A.	32.73	32.20	30.95	28.37	25.37
	B.	32.69	32.11	29.80	27.95	24.21
2. PCM Wt. After Drying #1 24 hrs. %	A.	30.81	31.13	30.24	29.90	5.99
	B.	30.98	31.57	29.35	30.43	0.04
3. PCM Wt. After Drying #1 48 hrs.	A.	30.17	30.52	30.24	27.07	4.56
	B.	30.38	30.91	28.93	27.26	0.04

TABLE 5
FLAME TEST RESULTS
PLASTERBOARD PERCOLATED WITH 45-A, 45-A/HEPTANE AND HEPTANE

<u>Mixture</u>	<u>Paper On</u>	<u>Paper Off</u>
(45-A/Heptane)		
100%	Burned about 10 min. until majority of wax was burned out and all paper gone	Burned about 10 min. until most of wax was burned out
75/25	Burned about 10 min. until most of wax and paper burned away	Burned about 10 min. until wax was burned away
50/50	Burned with unsteady flame for only 5 min., only 1/4 of square burned	Burned for 8 min. until most of wax was gone from top side of the square
25/75	Burned out entirely in 3 min	Burned out quickly in about 3 1/2 min
0/100	Did not continue burning once out of direct flame	Did not ignite

TABLE 6

WITCO 45-A PCM PICKUP AND FIRE RETARDANCE OF PLASTERBOARD
PERCOLATED IN SOLUTIONS OF 45-A/HEPTANE
AND 45-A/METHYLENE CHLORIDE

45-A/Heptane Composition (%)	5/95	10/90	15/85	20/80	25/75
1. PCM Wt. Gain After 10 min. Percolating Plus 48 hrs. Vacuum Drying (%)	8.32	18.50	23.14	29.54	29.52
2. Extinguishment Time	Immediately	1' 41"	1' 51"	2' 16"	2' 26"
45-A/Methylene Chloride Composition (%)	5/95	10/90	15/85	20/80	25/75
1. PCM Wt. Gain After 10 min. Percolating Plus 48 hrs. Vacuum Drying (%)	10.86	18.60	23.27	28.62	29.56
2. Extinguishment Time	Immediately	18"	30"	5' 23"	10' 28"

TABLE 7

WITCO 45-A/BCL-462/STEARIC ACID PICKUP IN PLASTERBOARD
PERCOLATED WITH THE FIRE RETARDANT COMPOSITIONS

45 A/BCL 462/Stearic Acid

<u>Sample #</u>	<u>Ratio</u>	<u>Dry Weight Final % PCM Pickup</u>
1	85/10/5	33.8
2	85/10/5	34.13
3	80/15/5	35.08
4	80/15/5	34.09
5	75/20/5	33.91
6	75/20/5	33.02
Control 1	95/0/5	32.99
Control 2	95/0/5	32.75

LLN/BCL 462/Stearic Acid

<u>Sample #</u>	<u>Ratio</u>	<u>Dry Weight Final % PCM Pickup</u>
7	85/10/5	34.38
8	85/10/5	34.02
9	80/15/5	34.80
10	80/15/5	34.69
11	75/20/5	34.96
12	75/20/5	34.22
Control 1	95/0/5	35.75
Control 2	95/0/5	34.96

TABLE 8
FIRE RETARDANCE TESTS OF PERCOLATED PLASTERBOARD

45A/BCL 462/Stearic Acid									
Sample #	Ratio	Ignite in 10 sec	Time to Extinguish	Time to Ignite and Stay Lit	Flame Traveled	Time to Extinguish	Smoke		
1	85/10/5	Yes	Immed.	30 sec	Yes	375 sec	wh & blk		
2	85/10/5	Yes	Immed.	29	Yes	390	wh & blk		
3	80/15/5	Yes	Immed.	26	Yes	341	wh & blk		
4	80/15/5	Yes	Immed.	25	Yes	201	wh & blk		
5	75/20/5	Yes	Immed.	30	Yes	160	wh & blk		
6	75/20/5	Yes	Immed.	30	Yes	130	wh & blk		
Control 1	95/0/5	Yes	10 min.	10	Yes	10 min.	wh & blk		
Control 2	95/0/5	Yes	10 min.	10	Yes	10 min.	wh & blk		

LLN/BCL 462/Stearic Acid									
Sample #	Ratio	Ignite in 10 sec	Time to Extinguish	Time to Ignite and Stay Lit	Flame Traveled	Time to Extinguish	Smoke		
7	85/10/5	Yes	Immed.	12 sec	Yes	323 sec	wh & blk		
8	85/10/5	No	Immed.	15	Yes	272	wh & blk		
9	80/15/5	Yes	Immed.	20	Yes	237	wh & blk		
10	80/15/5	No	Immed.	25	Yes	196	wh & blk		
11	75/20/5	Yes	Immed.	30	Yes	155	wh & blk		
12	75/20/5	No	Immed.	36	Yes	58	wh & blk		
Control 1	95/0/5	Yes	10 min.	10	Yes	10 min.	wh & blk		
Control 2	95/0/5	Yes	10 min.	10	Yes	10 min.	wh & blk		

NOTE: Even-numbered samples had paper covers removed.

TABLE 9
PERMEATION AND RETENTION OF WITCO K-61 PCM IN CROSSLINKED
(10 M-RAD GAMMA) GROUND PELLETS (POWDER) OF MARLEX 6006
DSC ANALYSIS

Sample Identification	T _m (°C)	T _c (°C)	T _m -T _c (°C)	Heat of Fusion (cal/g)	Heat of Recryst. (cal/g)
K-61 Recrystallized	26.37	20.17	6.20	47.52	46.35
K-61 Plus PHR Santowhite Powder Marlex 6006	27.79	20.43	7.36	46.93	47.33
Marlex 6006 Whole Pellet	132.37	114.4	17.96	53.35	47.44
Marlex 6006 Ground Pellet	131.31	117.38	13.92	43.64	47.15
1/2 Hour Swell Marlex	27.47 114.05	20.53 103.70	6.93 10.35	27.66 18.33	25.10 18.29
1 Hour Swell Marlex	27.60 112.36	20.92 102.06	6.67 10.30	30.43 13.95	25.49 12.33
2 Hour Swell Marlex	27.29 118.79	20.53 106.89	6.76 11.89	18.94 27.64	17.37 26.68
3 Hour Swell Marlex	26.53 121.83	20.34 109.53	6.74 12.30	12.50 32.47	11.72 31.06
4 Hour Swell Marlex	27.38 119.86	20.37 108.15	6.51 11.70	16.26 26.99	13.81 27.07

TABLE 10
% WEIGHT PCM FOR MARLEX 6006, 10 mrad (GAMMA),
SWELLED 4 HOURS IN WITCO 45A WAX

<u>Batch #</u>	<u>% Weight Gain</u>	eq. = $\frac{\text{Final Wt.} - \text{Initial Wt.}}{\text{Final Wt.}}$
1	88.09	
2	89.19	
3	88.28	
4	88.29	
5	87.99	
6	88.20	
7	88.35	
8	88.33	
9	87.94	
10	87.97	
Average $\bar{x}$ =	88.26	

No experiments were made for swelling the ground powder yet.
When the method of washing the powder is worked out, this work
order will be completed.

TABLE 11
 PARTICLE SIZE DISTRIBUTION OF CROSSLINKED
 MARLEX 6006 POWDER-FROM-PROCESS, AND POWDER-FROM-GROUND-PELLETS

		<u>Diameter</u> <u>(μm)</u>	<u>% Retained/Screen</u>
A. Marlex 6006 powder 5 M-rad	pan	---	0.15
	20	mesh 850	7.30
	40	425	66.19
	70	212	23.46
	100	150	2.40
	250	58	0.23
	325	45	0.27
B. Marlex 6006 ground powder (from 10 M-rad pellets)	pan	---	5.45
	20	mesh 850	1.55
	40	425	13.41
	70	212	22.67
	100	150	32.23
	250	58	16.46
	325	45	8.23

TABLE 12

EXTRACTION OF PCM-PERMEATED POWDER (FROM GROUND PELLETS)
WITH METHANOL AND ETHANOL

<u>Filtered Material</u>				
1.	% Change	MeOH	$\frac{2.0233-1.8325}{2.0233} \times 100\%$	= 9.43% wt. loss
		EtOH	$\frac{1.9140-0.9233}{1.9140} \times 100\%$	= 51.76% wt. loss

Residue Material

2.	MeOH	0.0962 g
	EtOH	0.3923 g

Observations

- * Sample washed in EtOH
- After washing there were two distinct parts
 - one part was a fine white powder which appeared to be pure Marlex.
 - the other part was large clumps which appeared to be almost totally 45A.
- There was a large amount of residue in the filtrate which upon evaporation was yellow in color.
- * Samples washed in MeOH
- After washing, the sample looked very similar to the original starting material. It was just a very slight bit lighter in color as compared to the original material.
- There was a slight amount of residue in the filtrate which upon evaporation was yellow in color.

TABLE 13
DETERMINATION OF XYLENE SOLUBLES IN HDPE POWDERS

<u>Sample</u>	<u>Wt. Residue</u>	<u>% Residue</u>	<u>% Solubles</u>
1. uncrosslinked powder	0.0060g	1.5	98.7
2. 5 M-rad powder	0.2656g	66.4	31.7
3. ground 10 M-rad powder	0.0264g	6.6	93.58

TABLE 14

DSC ANALYSIS OF THERMAL ENERGY STORAGE
OF PARAFFINIC HYDROCARBONS

Sample Identification and Composition	T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)	Total	
						ΔH_f (cal/gm)	ΔH_c (cal/gm)
n-Hexane C_6H_{14}	-90.6	-102.6	12.0	40.5	38.8		
n-Heptane C_7H_{16}	-84.9	-97.5	12.6	38.6	37.3		
n-Octane C_8H_{18}	-52.2	-65.0	12.8	47.7	46.4		
n-Nonane C_9H_{20}	-50.4	-57.4	7.0	33.1	31.5		
	-53.8	-60.3	6.5	11.0	11.4	44.1	42.9
n-Decane $C_{10}H_{22}$	-25.8	-36.0	10.2	50.2	47.8		
n-Undecane $C_{11}H_{24}$	-21.5	-30.2	8.7	36.0	35.8		
	-35.3	-40.3	5.0	11.1	9.9	47.1	45.7
n-Dodecane $C_{12}H_{26}$	-6.9	-15.5	8.6	52.4	51.3		
n-Tridecane $C_{13}H_{28}$	-5.0	-8.8	3.8	38.7	38.5		
	-18.5	-21.7	3.2	9.5	9.8	48.2	48.3
n-Tetradecane $C_{14}H_{30}$	9.0	-0.2	9.2	55.6	55.6		
n-Pentadecane $C_{15}H_{32}$	12.5	4.8	7.7	38.6	42.7		
	-1.1	-6.5	5.4	13.2	9.6	51.8	52.3
n-Hexadecane $C_{16}H_{34}$	21.1	12.2	8.9	56.5	56.5		
n-Heptadecane $C_{17}H_{36}$	25.0	16.5	8.5	42.3	43.8		
	12.7	6.9	5.8	13.7	12.3	56.0	56.1
n-Octadecane $C_{18}H_{38}$	31.2	22.0	9.2	59.1	58.7		
n-Nonadecane $C_{19}H_{40}$	34.4	26.4	8.0	42.6	43.8		
	23.9	18.3	5.6	14.9	13.7	57.5	57.5

TABLE 14
DSC ANALYSIS OF THERMAL ENERGY STORAGE
OF PARAFFINIC HYDROCARBONS
(Continued)

Sample Identification and Composition	T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)	Total	
						ΔH_f (cal/gm)	ΔH_c (cal/gm)
n-Eicosane C ₂₀ H ₄₂							
Primary	39.0	31.3	7.7	60.8	60.8		
Secondary	None	29.9	---	None	Small		
*n-Heneicosane C ₂₁ H ₄₄							
Primary	42.3	35.9	6.4	39.9	45.5		
Secondary	31.4	29.7	1.7	19.0	13.6	58.9	59.1
*n-Docosane C ₂₂ H ₄₆							
Primary	45.9	38.8	7.1	56.0	55.6		
Secondary	None	35.6	---				
n-Tricosane C ₂₃ H ₄₈							
Primary	48.6	43.0	5.6	40.6	45.6		
Secondary	40.3	35.6	4.7	19.8	14.9	60.4	60.5
n-Tetracosane C ₂₄ H ₅₀							
Primary	52.3	46.1	6.2	43.3	42.3		
Secondary	48.5	41.6	6.9	19.1	19.8	62.4	62.1
n-Pentacosane C ₂₅ H ₅₂							
Primary	56.3	47.7	8.6	39.8	42.6		
Secondary	46.4	37.2	9.2	19.9	15.2	59.7	57.8
n-Hexacosane C ₂₆ H ₅₄							
Primary	59.3	50.8	8.5	39.3	38.2		
Secondary	54.1	45.9	8.2	23.4	23.8	62.7	62.0
n-Heptacosane C ₂₇ H ₅₆							
Primary	61.3	53.6	7.7	41.7	42.3		
Secondary	54.1	47.8	6.3	17.6	17.1	62.3	62.4
				3.0	3.0		

TABLE 14
DSC ANALYSIS OF THERMAL ENERGY STORAGE
OF PARAFFINIC HYDROCARBONS
(Concluded)

Sample Identification and Composition	T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)	Total	
						ΔH_f (cal/gm)	ΔH_c (cal/gm)
n-Octacosane $C_{28}H_{58}$							
Primary	64.4	55.4	9.0	46.5	42.2		
Secondary	58.6	49.6	9.0	17.1	20.1	63.6	62.3
n-Triacontane $C_{30}H_{62}$							
Primary	68.1	60.1	8.0	40.3	36.7		
Secondary	63.1	55.4	7.7	22.4	24.7	62.7	61.4
n-Dotriacontane $C_{32}H_{66}$							
Primary	71.9	64.2	7.7	44.2	39.9		
Secondary	66.2	53.6	12.6	20.4	21.5	64.6	61.4
n-Tetracontane $C_{40}H_{82}$							
Primary	83.8	75.8	8.0	61.8	61.5		
Secondary	69.0	61.2	7.8	4.8	2.9	66.6	64.4
n-Tetracontane $C_{44}H_{90}$							
Primary	88.6	80.6	8.0	62.5	59.0		
Secondary	69.6	60.0	9.6	4.5	3.9	67.0	62.9

TABLE 15
COMPARISON OF DSC DATA WITH LITERATURE VALUES

Carbon Atoms in Chain	Melting Temp., °C		Heat of Fusion (Cal/G)		Heat of Transition (Cal/G)		Total (Fusion+Tran), Cal/G	
	DSC	Lit ¹	DSC	Lit ¹	DSC	Lit ¹	DSC	Lit ¹
	Peak Onset							
C ₆	-90.6	-94.5	40.5	36.20 ³				
C ₇	-84.9	-89.5	38.6					
C ₈	-52.2	-56.7	47.7	43.5 ³				
C ₉	-50.9	-55.7	33.1	41.3 ³	11.0		44.1	
C ₁₀	-25.8	-29.8	50.2	48.3 ³				
C ₁₁	-21.5	-26.0	36.0	33.8	11.1	10.5	47.1	44.3
C ₁₂	-6.9	-10.3	52.4	50.3	None	None	None	50.3
C ₁₃	-5.0	-7.2	38.7	37.0	9.5	9.9	48.2	46.9
C ₁₄	9.0	4.8	55.6	54.9	None	None	None	54.9
C ₁₅	12.5	8.8	38.6	39.1	13.2	10.3	51.8	49.4
C ₁₆	21.1	17.4	56.5	54.7	None	None	None	54.7
C ₁₇	25.0	20.9	42.3	40.2	13.7	10.9	56.0	51.1
C ₁₈	31.2	26.8	59.1	58.2	None	None	None	58.2
C ₁₉	34.4	30.3	42.6	40.8	14.9	12.3	57.5	53.1
C ₂₀	39.0	35.0	60.8	59.1	crys.	None		59.1
C ₂₁	42.3	39.0	39.9	38.4	19.0	12.5	58.9	50.9
C ₂₂	45.9	41.5	56.0	37.6	crys.	21.7		59.3
C ₂₃	48.6	46.0	40.6	39.7	19.8	16.0	60.4	55.7
C ₂₄	52.3	46.9	43.3	38.7	19.1	22.1	62.4	60.8
C ₂₅	56.3	51.6	39.8	42.6	19.9	17.7	59.7	60.3
C ₂₆	59.3	51.8	39.3	38.8	23.4	21.0	62.7	59.8
C ₂₇	61.3	57.7	41.7	37.9	17.6/3.0	18.2	62.3	56.1
C ₂₈	64.4	59.3	46.5	39.1	17.1	21.5	63.6	60.6

TABLE 15 (Concluded)
COMPARISON OF DSC DATA WITH LITERATURE VALUES

Carbon Atoms in Chain	Melting Temp. °C		Heat of Fusion (Cal/G)		Heat of Transition (Cal/G)		Total (Fusion+Trans), Cal/G	
	DSC	Lit	DSC	Lit	DSC	Lit	DSC	Lit
	<u>Peak Onset</u>							
C ₂₉		63.4		38.6		17.4		56.0
C ₃₀		65.4		60.8		None		60.0
C ₃₁		68 ²						
C ₃₂	71.9	67.5	44.2		20.4		64.6	
C ₃₃								
C ₃₄								
C ₃₅		74.7 ²						61.1 ³
C ₃₆								
C ₃₇								
C ₃₈								
C ₃₉								
C ₄₀	83.8	80.2	61.8		4.8		66.6	
C ₄₁								
C ₄₂								
C ₄₃								
C ₄₄	88.6	85.2	62.5		4.5		67.0	

1. J.A. Bailey and C. Liao, Final Report NASA-MSFC.

2. Cooperative Agreement NCA8-52, North Carolina State University, 1975.

TABLE 16
DSC ANALYSIS OF THERMAL ENERGY STORAGE FOR SAMPLES RUN AT 2°C/MIN

Sample Identification and Composition	T _m °C	T _c °C	T _m -T _c °C	ΔH _f cal/gm	ΔH _c cal/gm	Total Solid + Liq. ΔH _f + ΔH _c cal/gm	
						ΔH _f cal/gm	ΔH _c cal/gm
n-Hepta decane	Primary	22.1	18.8	3.3	43.0	43.4	55.4
	Secondary	10.7	8.0	2.7	12.3	12.0	55.3
n-Octadecane	Primary	28.0	24.7	3.3	58.0	58.9	55.3
	Secondary	-	-	-	-	-	-
n-Nonadecane	Primary	31.8	28.4	3.4	43.7	45.1	56.7
	Secondary	22.3	19.4	2.9	12.7	11.6	56.4
n-Octacosane	Primary	61.0	58.2	2.8	42.3	44.1	64.1
	Secondary	56.6	52.2	4.4	22.1	20.0	64.4
n-Dotria Contane	Primary	69.6	66.6	3.0	42.6	43.9	59.8
	Secondary	64.6	62.2	2.2	18.0	15.9	59.8
n-Octadecane Humphrey Tech. Grade	Primary	26.2	22.5	3.7	49.0	48.9	48.9
	Secondary	-	17.7	-	-	-	-
Recrystallized K-61 July 86	Primary	25.0	23.2	1.8	-	-	47.3
	Secondary	-2.0	-5.3	3.4	-	-	47.3
Recrystallized 45A (55 Gallon)	Primary	29.8	27.5	2.3	-	-	40.4
	Secondary	7.6	5.3	2.4	-	-	40.4
PEG 1000	Primary	35.9	25.8	10.1	-	-	37.7
	Secondary	-	20.1	-	-	-	37.7
Marlex 6006	Primary	133.3	123.1	10.2	51.9	51.8	51.8
	Secondary	-	-	-	-	-	-

TABLE 17

DSC ANALYSIS OF PHASE CHANGE MATERIALS AT DIFFERENT
RATES OF HEATING AND COOLING

Sample	Rate of Heating °C/min	T _m °C	T _c °C	T _m -T _c °C	ΔH _f cal/gm	ΔH _c cal/gm
Humphrey Tech. Grade Octadecane	2	Primary 26.2	22.7	3.7	49.0	48.9
		Secondary -	17.7			
	5	Primary 27.1	21.2	5.9	50.7	50.7
		Secondary 16.8	16.8			
N. Hexadecane 99% Pure	10	Primary 28.0	19.5	8.5	52.8	52.6
		Secondary 15.0	15.0			
	20	Primary 30.2	18.6	11.5	52.4	51.0
		Secondary 13.7	13.7			
Marlex 6006 High Density Polyethylene	2	18.7	15.0	3.7	58.3	58.0
		19.8	14.0	5.9	58.2	57.9
		21.1	12.2	8.9	56.5	56.5
	5	133.3	123.1	10.2	51.9	51.8
		135.0	120.6	14.4	52.5	51.2
		136.0	117.9	18.1	50.3	50.2

TABLE 18

MELTING AND CRYSTALLIZATION TEMPERATURES OF n-PARAFFINS AT
DIFFERENT RATES OF HEATING AND COOLING

Sample I.D.	20°C/Min			10°C/Min			2°C/Min			Extrapolated 0°C/Min		
	T_m	T_c	$T_m - T_c$	T_m	T_c	$T_m - T_c$	T_m	T_c	$T_m - T_c$	T_m	T_c	$T_m - T_c$
Hexadecane (C_{16})				21.1	12.2	8.9	18.7	15.0	3.7	17.9	15.6	2.3
n-Heptadecane (C_{17})				25.0	16.5	8.5	22.1	18.8	3.3	21.9	19.9	2.0
n-Octadecane (C_{18}) (Pure)				31.2	22.0	9.2	28.0	24.7	3.3	27.2	25.4	1.8
n-Octadecane (C_{18}) (Tech)	30.2	18.6	11.5	28.0	19.5	8.5	26.2	22.5	3.7	25.8	23.4	2.4
n-Nonadecane (C_{19})				34.4	26.4	8.0	31.8	28.4	3.4	31.1	28.8	2.3
n-Eicosane				39.0	31.3	7.7	36.7	32.5	4.2	36.0	32.8	3.2
n-Docosane				45.9	38.8	7.1	43.9	40.5	3.4	43.4	40.9	2.5
n-Octacosane (C_{28})				64.6	55.4	9.0	61.0	58.2	2.8	60.6	58.9	1.7
n-Dotria Contane (C_{32})				71.9	64.2	7.7	69.6	66.6	3.0	69.1	67.3	1.8
Witco K-61 (July 86)				26.4	20.2	6.2	25.0	23.2	1.8	24.7	23.8	0.9
Witco 45A (55 gallon)				30.9	25.5	5.4	29.8	27.5	2.3	29.4	27.9	1.5
PEG-1000				42.9	26.9	16.0	35.9	25.8	10.1	34.0	25.5	8.5
Marlex 6006 HDPE (Pellets)				136.0	117.9	18.1	133.3	123.1	10.2	133	124.4	8.9

TABLE 19
A DESCRIPTION OF THE PHASE NOTATION USED IN
THIS WORK

<u>Phase Notations and Their Characteristics</u>	<u>This Work</u>
Hexagonal Chains are perpendicular to the end group planes. Molecules rotate about long chain axes.	α_H
Orthorhombic Chains are perpendicular to the end group planes. Rotation is greatly restricted. Subcell is orthorhombic.	β_O
Triclinic Chains make an angle of about 73° with the end group planes. Rotation is greatly restricted. Subcell is triclinic.	β_T
Monoclinic Chains make an angle of about 61° with the end group planes. Rotation is greatly restricted. Subcell is orthorhombic.	β_M

TABLE 20
VARIATION OF CRYSTAL STRUCTURES OF N-ALKANES
WITH CARBON CHAIN LENGTH

Identification Carbon Chains	Solid / Liq. Just Below Freezing	Solid / Solid Low Temp. Phase	Reference
<u>Even Carbons</u>			
C_4 to C_{20}	No stable α_H phase	Triclinic (β_T)	Norman & Mathiesen (1960, 1961) ^{16,17}
C_{20} and lower	Metastable form not always detected	Triclinic (β_T)	Hoffman & Smyth (1950) ²¹
C_{22}, C_{24}, C_{26}	Hexagonal (α_H)	Triclinic (β_T)	Norman & Mathiesen (1960, 1961) ^{16,17}
C_{26}	Hexagonal (α_H)	Sometimes mono- clinic (β_M)	Broadhurst (1962) ³
$C_{22} - C_{42}$	Hexagonal (α_H)	Monoclinic (β_M)	Turner (1960) ⁴ , Broadhurst (1962) ³
$>C_{30}$ or C_{32}	Sometimes orthor- hombic	Monoclinic (β_M)	Turner (1960) ⁴
$C_{44} - C_{94}$	Monoclinic (β_M) Sometimes β_O	Monoclinic (β_M)	Turner (1960) ⁴
<u>Odd Carbons</u>			
C_7	Orthorhombic (β_O)	Orthorhombic (β_O)	Westrum & McCullough (1963) ²¹
C_9 to C_{43}	Hexagonal (α_H)	Orthorhombic (β_O)	Turner (1960) ⁴
C_{45} to C_{93}	Monoclinic (β_M) Sometimes β_O	Monoclinic (β_M)	Turner (1960) ⁴

TABLE 21

DSC ANALYSIS OF THERMAL ENERGY STORAGE OF
HEPTADECANE-NONADECANE BLENDS

Sample Identification and Component Ratio	T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)	Total	
						ΔH_f (cal/gm)	ΔH_c (cal/gm)
Heptadecane:Nonadecane C ₁₇ H ₃₆ C ₁₉ H ₄₀							
100:0 Main Secondary	25.0 12.7	16.5 6.9	8.5 5.8	42.3 13.7	43.8 12.5	56.0	56.1
90:10 Main Secondary	24.7 -2.3	17.0 -6.7	7.7 4.4	41.2 5.6	42.1 5.3	46.8	47.4
80:20 Main Secondary	24.7 -4.1	17.5 -8.0	7.2 3.9	40.7 5.2	41.2 5.2	45.9	46.4
50:40 Main Secondary	26.9 -2.1	18.3 -6.6	8.6 4.5	38.9 4.9	39.9 4.9	43.8	44.8
50:50 Main Secondary	27.3 0.1	19.9 -6.0	7.4 6.1	39.5 5.0	39.9 4.9	44.5	44.8
40:60 Main Secondary	28.3 2.9	21.0 -1.6	7.3 4.5	39.1 4.9	40.4 4.9	44.0	45.3
20:80 Main Secondary	31.6 11.4	23.5 7.0	8.1 4.4	39.2 5.1	40.9 4.9	44.3	45.8
10:90 Main Secondary	33.2 17.2	24.4 12.0	8.8 5.2	36.7 5.7	39.6 6.0	42.4	45.6
0:100 Main Secondary	34.4 23.9	26.4 18.3	8.0 5.6	42.6 14.9	43.8 13.7	57.6	57.5

TABLE 22

DSC ANALYSIS OF THERMAL ENERGY STORAGE PROPERTIES
OF C₁₅-C₁₉ HYDROCARBON BLENDS

Sample Identification and Composition	T _m (°C)	T _c (°C)	T _m -T _c (°C)	ΔH _f (cal/gm)	ΔH _c (cal/gm)	Total	
						ΔH _f (cal/gm)	ΔH _c (cal/gm)
Pentadecane:Nonadecane C ₁₅ H ₃₂ C ₁₉ H ₄₀							
100:0 Main	12.5	4.8	7.7	38.6	42.7	51.8	52.3
Secondary Peak	-1.1	-6.5	5.4	13.2	9.6		
90:10 Main	10.5	2.7	7.8	---	---	50.7	50.3
Secondary Peak	-4.9	---	---	---	---		
Tertiary Peak	-11.4	-17.9	6.5	---	---		
80:20 Main	12.1	3.1	8.8	---	---	49.4	48.8
Secondary Peak	-5.1	-15.3	10.2	---	---		
Tertiary Peak	-7.7	---	---	---	---		
Quarternary Peak	-12.7	19.3	6.2	---	---		
60:40 Main	14.6	4.0	10.6	---	---	50.8	49.9
Secondary Peak	-4.9	-14.7	9.8	---	---		
Tertiary Peak	-12.5	---	---	---	---		
50:50 Main	14.8	4.6	10.1	---	---	53.9	51.5
Secondary Peak	-5.7	-14.8	9.1	---	---		
Tertiary Peak	-13.9	---	---	---	---		
Quarternary Peak	20.8	15.3	5.3	---	---		
40:60 Main	13.9	4.5	8.9	---	---	51.1	50.7
Secondary Peak	-5.3	-14.8	9.5	---	---		
Tertiary Peak	-13.5	---	---	---	---		
Quarternary Peak	20.9	17.3	3.7	---	---		

TABLE 22{Concluded)
DSC ANALYSIS OF THERMAL ENERGY STORAGE PROPERTIES
OF C₁₅-C₁₉ HYDROCARBON BLENDS

Sample Identification and Composition	T _m (°C)	T _c (°C)	T _m -T _c (°C)	ΔH _f (cal/gm)	ΔH _c (cal/gm)	Total	
						ΔH _f (cal/gm)	ΔH _c (cal/gm)
Pentadecane:Nonadecane C ₁₅ H ₃₂ C ₁₉ H ₄₀							
20:80 Main	28.1	21.3	6.8	---	---	54.5	54.2
Secondary Peak	20.2	11.0	9.2	---	---		
Tertiary Peak	14.1	---	---	---	---		
Quaternary Peak	-4.8	-14.8	10.0	---	---		
	-14.2	---	---	---	---		
10:90 Main	32.5	22.8	9.6	---	---	54.3	53.1
Secondary Peak	21.6	13.6	8.0	---	---		
Tertiary Peak	12.9	---	---	---	---		
Quaternary Peak	-4.8	-15.4	10.6	---	---		
0:100 Main	34.4	26.4	8.0	42.6	43.8	57.5	57.5
Secondary Peak	24.0	18.3	5.7	14.9	13.7		

TABLE 23

DSC ANALYSIS OF THERMAL ENERGY STORAGE OF
TETRADECANE-HEXADECANE BLENDS

Sample Identification and Composition	T _m (°C)	T _C (°C)	T _m -T _C (°C)	Δ H _f (cal/gm)	Δ H _C (cal/gm)	Total	
						ΔH _f (cal/gm)	ΔH _C (cal/gm)
Tetradecane:Hexadecane C14 H30 C16 H34							
100:0 Main	9.0	-0.2	9.2	55.6	55.6		
90:10 Main Secondary Peak	5.4 -12.3	-3.7 -22.8	9.1 10.5	--- ---	--- ---	51.3	50.2
80:20 Main Secondary Peak	5.3 -23.6	-3.3 -31.8	8.6 8.2	--- ---	--- ---	49.4	48.5
60:40 Main Secondary Peak	8.7 -27.7	-2.9 -34.1	11.7 6.4	--- ---	--- ---	45.1	42.1
50:50 Main Secondary Peak Tertiary Peak	9.3 -24.5 -28.0	-0.1 -29.5 -33.7	9.4 5.0 5.7	--- ---	--- ---	47.6	43.5
40:60 Main Secondary Peak Tertiary Peak	10.9 -8.7 -28.2	2.2 -20.0 -34.1	8.7 11.3 5.9	--- ---	--- ---	48.2	47.0
20:80 Main Secondary Peak	15.9 12.0	6.3 2.7	9.6 9.3	--- ---	--- ---	49.9	48.4
10:90 Main Secondary Peak	18.4 8.2	9.9 ---	8.5 ---	--- ---	--- ---	54.0	52.8
0:100 Main	21.1	12.2	8.9	56.5	56.5		

TABLE 24

DSC ANALYSIS OF THERMAL ENERGY STORAGE PROPERTIES
OF HEXADECANE-OCTADECANE BLENDS

Sample Identification and Ratio	T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)	Total	
						ΔH_f (cal/gm)	ΔH_c (cal/gm)
Hexadecane:Octadecane $C_{16}H_{34}$ $C_{18}H_{38}$							
100:0 Main	21.1	12.2	8.9	56.5	56.5	*	*
90:10 Main Secondary	18.8 -3.5	10.4 -11.0	8.4 7.4	42.8 8.8	42.4 10.6	51.7	53.0
80:20 Main Secondary	18.9 -12.8	11.6 -16.8	7.3 4.0	40.4 9.6	41.6 7.8	50.0	49.4
60:40 Main Secondary	20.1 -10.5	13.8 -14.4	6.2 3.9	40.2 4.5	40.6 4.2	44.7	44.8
50:50 Main Secondary	21.9 -7.6	14.3 -12.1	7.6 4.5	36.3 4.3	36.9 4.2	40.6	41.1
40:60 Main Secondary	23.7 -3.1	15.7 -8.7	8.0 5.6	36.1 3.9	37.3 3.9	40.0	41.2
20:80 Main Secondary	25.7 18.8	19.0 10.0	6.7 8.8	54.0 Small	53.2 Small	*	*
10:90 Main Secondary	27.8 ---	20.5 17.4	7.3 ---	55.3 ---	55.6 Small	*	*
0:100 Main	31.2	22.0	9.2	59.1	58.7	*	*

* None or very small solid/solid transition.

TABLE 25

DSC ANALYSIS OF THERMAL ENERGY STORAGE PROPERTIES
OF HEXADECANE-EICOSANE BLENDS

Sample Identification and Composition	T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)	Total	
						ΔH_f (cal/gm)	ΔH_c (cal/gm)
Hexadecane:Eicosane $C_{16}H_{34}$ $C_{20}H_{42}$							
100:0 Main	21.1	12.2	8.9	56.5	56.5	*	*
90:10 Main	18.9	9.4	9.4	---	---	51.8	51.8
80:20 Main Secondary	18.7 -2.3	9.9 ---	8.8 ---	---	---	49.4	50.5
60:40 Main	21.1	11.6	9.6	---	---	47.9	47.7
50:50 Main	20.7	18.2	2.5	---	---	48.9	48.1
40:60 Main	29.8	22.1	7.7	---	---	51.1	51.1
20:80 Main	34.4	26.4	8.0	---	---	53.2	54.8
10:90 Main	36.0	29.1	6.9	---	---	55.5	55.5
0:100 Main Secondary	39.0 None	31.3 29.9	7.7 ---	60.8 None	60.8 Small	*	*

* None of very small solid/solid transition.

---- Separate peak areas for the melting and solid/solid transitions were not evaluated.

TABLE 26

DSC ANALYSIS OF THERMAL ENERGY STORAGE
OF HEXADECANE/HEPTADECANE BLENDS

Sample Identification and Composition		T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)	Total	
							ΔH_f (cal/gm)	ΔH_c (cal/gm)
Hexadecane/Heptadecane $C_{16}H_{34}$ $C_{17}H_{36}$								
100:0	Main	21.1	12.2	8.9	56.5	56.5	*	*
90:10	Main Secondary	20.1 -4.4	10.2 -9.9	9.9 4.5	---	---	48.3	48.3
80:20	Main Secondary	19.2 -5.2	11.2 -9.9	8.0 4.7	---	---	51.4	51.8
60:40	Main Secondary	20.3 -4.3	12.5 -9.1	7.8 4.8	---	---	51.6	50.5
50:50	Main Secondary	21.5 -3.5	12.5 -8.5	9.0 5.0	---	---	51.2	50.4
40:60	Main Secondary	21.3 -2.7	13.0 -7.0	7.7 4.3	---	---	52.4	52.2
20:80	Main Secondary	23.2 2.2	14.1 -3.8	9.1 6.0	---	---	52.3	52.7
10:90	Main Secondary	23.1 7.0	16.1 1.9	7.0 5.1	---	---	52.5	52.8
0:100	Main Secondary	25.0 12.7	16.5 6.9	8.5 5.8	42.3 13.7	43.8 12.3	56.0	56.1

* No solid/solid transition.

--- Separate peak areas for the melting and solid/solid transitions were not evaluated.

TABLE 27

DSC ANALYSIS OF THERMAL ENERGY STORAGE
OF OCTADECANE-NONADECANE BLENDS

Sample Identification and Composition	T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)	Total	
						ΔH_f (cal/gm)	ΔH_c (cal/gm)
Octadecane-Nonadecane $C_{18}H_{38}$ $C_{19}H_{40}$							
100:0 Main	31.2	22.0	9.2	59.1	58.7	*	*
90:10 Main	29.9	21.5	8.4	---	---	54.9	54.9
Secondary	11.3	6.9	4.4	---	---		
80:20 Main	29.7	22.6	7.1	40.4	42.7	47.1	49.3
Secondary	10.1	6.1	4.0	6.7	6.6		
70:30 Main	31.6	21.6	10.0	---	---	53.1	52.9
Secondary	10.9	5.1	5.8	---	---		
60:40 Main	30.6	23.1	7.5	39.8	41.8	46.3	48.1
Secondary	10.2	5.9	4.4	6.5	6.3		
50:50 Main	31.1	23.4	7.7	---	---	52.9	53.1
Secondary	10.9	6.6	4.3	---	---		
40:60 Main	31.5	23.7	7.8	---	---	52.9	52.8
Secondary	12.0	7.5	4.5	---	---		
30:70 Main	32.0	23.2	8.8	---	---	53.7	53.5
Secondary	12.0	6.8	5.2	---	---		
20:80 Main	32.4	25.4	7.0	---	---	51.1	51.2
Secondary	15.4	10.8	4.6	---	---		
10:90 Main	34.2	25.2	9.0	---	---	54.9	54.9
Secondary	18.9	13.1	5.8	---	---		
0:100 Main	34.4	26.4	8.0	42.6	43.8	57.5	57.5
Secondary	23.9	18.3	5.6	14.9	13.7		

* No solid/solid transition.

--- Separate peak areas for the melting and solid/solid transitions were not evaluated.

TABLE 28

DSC ANALYSIS OF THERMAL ENERGY STORAGE
FOR LARGER NORMAL PARAFFINS AND 50/50 DIBLENDS

Sample Identification and Composition	T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)	Total	
						ΔH_f (cal/gm)	ΔH_c (cal/gm)
C23	Primary Peak	48.6	5.6	40.6	45.6	60.4	60.5
	Secondary Peak	40.3	4.7	19.8	14.9		
C23/C25 50/50	Primary Peak	51.7	7.4	---	---	54.9	54.9
	Secondary Peak	35.4	5.2	---	---		
C25	Primary Peak	56.3	8.6	39.3	38.2	62.7	62.0
	Secondary Peak	46.4	9.2	23.4	23.8		
C27	Primary Peak	61.3	7.7	41.7	42.3	62.6	61.7
	Secondary Peak	54.1	6.3	17.6 3.0	17.1 3.0		
C23/C27 50/50	Primary Peak	54.2	8.9	---	---	51.8	51.5
	Secondary Peak	35.0	6.7	---	---		
C28	Primary Peak	64.4	9.0	46.5	42.2	63.6	62.3
	Secondary Peak	58.6	9.0	17.1	20.1		
C23/C28 50/50	Primary Peak	54.2	8.2	---	---	52.3	51.8
	Secondary Peak	33.4	7.0	---	---		
C23/C32 50/50	Primary Peak	49.9	8.6	---	---	58.7	58.2
	Secondary Peak	40.1	12.2	---	---		
C32	Primary Peak	71.9	7.9	44.2	39.9	64.6	61.4
	Secondary Peak	66.2	12.6	20.4	21.5		

TABLE 28 (Concluded)

DSC ANALYSIS OF THERMAL ENERGY STORAGE
FOR LARGER NORMAL PARAFFINS AND 50/50 DIBLENDS

Sample Identification and Composition	T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)	Total	
						ΔH_f (cal/gm)	ΔH_c (cal/gm)
C24	Primary Peak	52.3	46.1	6.2	43.3	42.3	62.0
	Secondary Peak	48.5	41.6	6.9	19.1	19.8	62.4
C24/C25 50/50	Primary Peak	53.9	46.2	7.7	---	---	55.1
	Secondary Peak	41.3	34.3	7.0	---	---	54.2
C26	Primary Peak	59.3	50.8	8.5	39.3	38.2	62.0
	Secondary Peak	54.1	45.9	8.2	23.4	23.8	62.7
C24/C26 50/50	Primary Peak	54.8	47.5	7.3	---	---	56.3
	Secondary Peak	40.5	35.2	5.3	---	---	56.0
C24/C28 50/50	Primary Peak	54.9	46.4	8.5	---	---	52.2
	Secondary Peak	37.1	31.2	5.9	---	---	51.8
C24/C32 50/50	Primary Peak	51.4	42.5	8.8	---	---	57.1
	Secondary Peak	38.9	33.0	5.9	---	---	57.3
C28/C32 50/50	Primary Peak	66.5	58.2	8.3	---	---	55.6
	Secondary Peak	55.9	48.5	7.4	---	---	55.3
C40	Primary Peak	83.8	75.8	8.0	61.8	61.5	64.4
	Secondary Peak	69.0	61.2	7.8	4.8	2.9	66.6
C40/C44 50/50	Primary Peak	86.1	76.3	9.8	58.6	58.9	*
	Secondary Peak	69.6	60.0	9.6	4.5	3.9	*
C44	Primary Peak	88.6	80.6	8.0	62.5	59.0	62.9
	Secondary Peak	69.6	60.0	9.6	4.5	3.9	67.0

* No secondary transition.

--- Separate peak areas for the main and secondary transition were not evaluated.

TABLE 29

CORRELATION OF CALCULATED VS. EXPERIMENTAL VALUES OF
MELTING TEMPERATURE AND HEAT OF FUSION

Sample of 50:50 Ratio of	T_m (°C)			ΔH_f (cal/gm)			Solid $\uparrow$ Solid Transition temperature		
	Exp.	Calc.	Diff. % on Calc.	Exp.	Calc.	Diff. % on Calc.	Exp.	Calc.	Diff. % on Calc.
C ₂₃ /C ₂₅	51.7	52.4	1.3	54.9	60.0	8.5	35.4	43.4	18.4
C ₂₃ /C ₂₇	54.2	54.9	1.3	51.8	61.3	15.5	35.0	47.2	25.8
C ₂₃ /C ₂₈	54.2	56.5	4.0	52.3	62.0	15.6	33.4	49.5	32.5
C ₂₃ /C ₃₂	62.3	60.3	-3.8	58.7	62.5	6.1	40.1	53.2	24.6
C ₂₄ /C ₂₅	53.9	54.3	0.7	54.2	61.0	11.1	41.3	47.5	13.1
C ₂₄ /C ₂₆	54.8	55.8	1.8	56.0	62.5	10.4	40.5	51.3	21.1
C ₂₄ /C ₂₈	54.9	58.3	5.8	51.8	63.0	17.8	37.1	53.4	30.5
C ₂₄ /C ₃₂	51.4	62.1	17.2	57.3	63.5	9.8	38.9	57.4	32.1
C ₂₈ /C ₃₂	66.5	68.2	2.5	55.3	64.1	13.7	55.9	62.4	10.4
C ₄₀ /C ₄₄	86.1	86.2	0.1	58.6	66.8	12.2	None	69.3	---

TABLE 30

DSC ANALYSIS OF THERMAL ENERGY STORAGE PROPERTIES OF HYDROCARBON TRIBLENDS

Sample Identification and Composition	T _m °C	T _C °C	T _m -T _C °C	ΔH _f cal/gm	ΔH _C cal/gm	ΔH _f cal/gm	Calculated ΔH _C cal/gm
25: 50: 25 C ₁₆ : C ₁₈ : C ₂₀	26.4 3.0	19.0	7.4 11.5	47.3 11.6	47.1 11.6	58.9	58.7
C ₁₇ : C ₁₉ : C ₂₁	31.6 4.0	23.8 -1.3	7.8 5.3	49.5 8.0	48.7 8.9	57.5	57.6
C ₁₆ : C ₁₇ : C ₁₈	22.9 -3.1	15.2 -7.5	7.7 11.6	48.7 8.2	50.9 6.0	56.9	56.9
C ₁₇ : C ₁₈ : C ₁₉	28.1 4.4	20.5 0.1	7.6 4.5	50.0 8.0	49.9 7.3	58.0	57.2
C ₁₄ : C ₁₇ : C ₂₀	19.1 2.5	13.6 -18.2	5.5	45.8 11.3	47.5 9.6	57.1	57.1
C ₁₆ : C ₁₉ : C ₂₁	29.6 4.1	23.3 -3.2	6.2 7.3	48.6 8.9	51.5 6.1	57.5	57.6

TABLE 31

CORRELATION OF CALCULATED VS EXPERIMENTAL DSC PARAMETERS OF TRIBLENDS

[illegible]

TABLE 32

COMPARISON OF THERMAL ENERGY STORAGE PROPERTIES
OF WITCO PLANT SAMPLES VS. SYNTHESIZED BLENDS
FROM PURE COMPONENTS

Sample Identification and Composition	T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)	Calculated	
						T_m (°C)	ΔH_f (cal/gm)
Witco LLN, Plant 5 Gallon Can	40.0	35.0	5.0	46.6	42.3	41.7	56.2
LLN Blended from Pure Components	42.4	34.9	7.5	53.3	54.2	43.2	58.3
Witco 45A Lab Crystal- lized (1 Qt. Container)	35.8	29.7	6.1	49.8	46.7	37.4	59.3
45A Blended from Pure Components	35.5	27.5	8.0	53.0	52.8	37.2	58.9
Witco K-61 Lab Sample	24.0	19.8	5.2	48.4	48.4	29.2	54.9
K-61 Blended from Pure Components	27.4	19.2	8.2	49.3	49.9	31.6	57.8
Witco K-51 Lab Sample	17.4	12.3	5.1	47.6	47.2	21.6	53.0
K-51 Blended from Pure Components	19.9	11.6	8.4	51.1	51.7	23.0	55.9
85010-1, Plant Primary 1 Gallon Can Secondary	-24.4 7.6	-26.9 3.6	2.5 4.0	3.6 30.4	3.3 31.0	--- 13.5	--- 53.5
85010-1, Blended Primary from Pure Com- Secondary ponents	9.7 -24.0	2.0 -28.2	7.7 4.2	47.6 ---	47.9 ---	--- 13.7	--- 53.9

TABLE 33
PERCENT COMPOSITION OF PLANT VS. LAB PREPARED HYDROCARBON SAMPLES

'100f Carbon Atom in the Chain	Witco LLN, Plant 5 Gallon Can	LLN Blended from Pure Component	Witco 45A Lab Crystal- lized (1 Qt. Container)	45A Blended from Pure Components	Witco K61 Lab Sample	K61 Blended from Pure Components	Witco K51 Lab Sample	K51 Blended from Pure Components	85010-1 Plant 1 Gallon Can.	85010-1 Blended from Pure Components
C-12									0.56	
C-13									1.12	1.1
C-14							0.53		25.23	26.4
C-15							7.43	7.9	47.09	47.9
C-16			0.11		8.23	8.7	40.26	43.0	19.42	19.7
C-17	0.07		0.90	0.9	25.13	26.5	34.98	37.3	4.83	4.9
C-18	0.71	0.7	11.85	11.8	26.31	27.7	11.03	11.8	0.40	
C-19	3.85	4.0	31.73	31.6	27.53	21.6				
C-20	15.27	16.0	35.94	35.8	10.09	10.6				
C-21	36.10	37.7	18.32	18.2	3.62	3.8				
C-22	28.45	29.7	1.68	1.7	1.03	1.1				
C-23	9.31	9.7								
C-24	2.00	2.1								
C-25	0.38									
C-26	0.06

Figure 1. Distribution of Particle Sizes in Ground Marlex 6006 HDPE and In-Process Powder (Crosslinked 10 mrad).

Figure 2. DSC Analysis of n-Hexane.

Sample: n-HEPTANE 99%
Size: 6.19 mg
Method: DSC- LOW TEMP

DSC

File: RUN0846.02
Operator: ED DYKE
Run date: 07/08/88 13:47
10°C per minute

Figure 3. DSC Analysis of n-Heptane.

Sample: n-OCTANE 99%
Size: 5.45 mg
Method: DSC- LOW TEMP

DSC

File: RUN0847.03
Operator: MTC
Run date: 07/08/88 17.02
100C per minute

Figure 4. DSC Analysis of n-Octane.

Sample: n-NONANE C9 99%
 Size: 4.15 mg
 Method: DSC-MELT

DSC

File: RUN0903.03
 Operator: ED DYKE
 Run date: 08/07/88 08:32

Figure 5. DSC Analysis of n-Nonane.

Figure 6. DSC Analysis of n-Decane.

Sample: n-UNDECANE 99.9%
 Size: 4.34 mg
 Method: DSC SUB-AMBIANT

DSC

File: RUN0803.02
 Operator: ED DYKE
 Run date: 08/25/88 12:20
 10°C per minute

Figure 7. DSC Analysis of n-Undecane.

Figure 8. DSC Analysis of n-Dodecane.

Figure 9. DSC Analysis of n-Tridecane.

Sample: n-TETRADECANE 99%
Size: 4.25 mg
Method: DSC-MELT

DSC

File: RUN0723.02
Operator: TODD SILL
Run date: 06/02/86 18.15
10°C per minute

Figure 10. DSC Analysis of n-Tetradecane.

Sample: n-PENTADECANE 99%
 Size: 3.98 mg
 Method: DSC-MELT

DSC

File: RUN0722.01
 Operator: ED DYKE
 Run date: 06/02/86 16:41
 10°C per minute

Figure 11. DSC Analysis of n-Pentadecane.

Figure 12. DSC Analysis of n-Hexadecane.

Figure 13. DSC Analysis of n-Heptadecane.

Sample: n-OCTADECANE 99%
 Size: 4.43 mg
 Method: DSC-MELT

DSC

File: RUN0719.02
 Operator: ED DYKE
 Run date: 08/02/88 13:25
 10°C per minute

Figure 14. DSC Analysis of n-Octadecane.

Figure 15. DSC Analysis of n-Nonadecane.

Figure 16. DSC Analysis of n-Eicosane.

Sample: n-HENEICOSANE 99%
 Size: 3.12 mg
 Method: DSC-MELT

DSC

File: RUN0718.02
 Operator: ED DYKE
 Run date: 06/02/88 09.04
 10°C per minute

Figure 17. DSC Analysis of n-Heneicosane.

99%

Sample: n-DOCOSANE
Size: 4.02 mg
Method: DSC-MELT

DSC

File: RUN0715.02
Operator: ED DYKE
Run date: 06/02/86 07.47
10°C per minute

Figure 18. DSC Analysis of n-Docosane.

Sample: n-TRICOSANE 99%
 Size: 3.45 mg
 Method: DSC-MELT

DSC

File: RUN0714.02
 Operator: ED DYKE
 Run date: 05/30/86 15:28
 10°C per minute

General VI.0J DuPont 9910

Figure 19. DSC Analysis of n-Tricosane.

Sample: n-TETRACOSANE 99%
 Size: 3.01 mg
 Method: DSC-NELT

DSC

File: RUN0713.02
 Operator: ED DYKE
 Run date: 05/30/86 13:43

Figure 20. DSC Analysis of n-Tetracosane.

Sample: n-PENTACOSANE 99.9%
Size: 4.39 mg
Method: DSC SUB-AMBIANT

DSC

File: RUN0804.02
Operator: D DYKE
Run date: 06/25/86 14:20
10°C per minute

Figure 21. DSC Analysis of n-Pentacosane.

Figure 22. DSC Analysis of n-Hexacosane.

Sample: n-HEPTACOSANE 99.9%
Size: 3.86 mg
Method: DSC-MELT
Comment: HUMPHRY

DSC

File: RUN0806.02
Operator: TODD SILL
Run date: 06/25/88 17:53
10°C per minute

Figure 23. DSC Analysis of n-Heptacosane.

Sample: n-OCTACOSANE 99.9%
 Size: 4.50 mg
 Method: DSC-MELT
 Comment: HUMPHRY

DSC

File: RUN0807.02
 Operator: TODD SILL
 Run date: 08/25/86 19.12
 10°C per minute

Figure 24. DSC Analysis of n-Octacosane.

Sample: n-TRIACONTANE C30 99%
 Size: 3.25 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: RUN0967.02
 Operator: ED DYKE
 Run date: 09/15/86 09:14

Figure 25. DSC Analysis of n-Triacontane.

Sample: n-DOTRIACONTANE 98.9%
 Size: 4.01 mg
 Method: DSC-MELT
 Comment: HUMPHRY

DSC

File: RUN0808.02
 Operator: TODD SILL
 Run date: 08/28/88 16:02
 10°C per minute

Figure 26. DSC Analysis of n-Dotriacontane.

Sample: n-TETRACONTANE 99.9%
 Size: 3.34 mg
 Method: DSC-MELT
 Comments: HUMPHRY

File: RUND809.02
 Operator: TODD SILL
 Run date: 06/26/88 17:38

DSC

Figure 27. DSC Analysis of n-Tetracontane.

Sample: n-TETRATETRACONTANE 99.9%

Size: 2.60 mg

Method: DSC-MELT

Comments: HUMPHRY

File: RUN0810.02

Operator: TODD SILL

Run date: 06/26/86 19:17

10°C per minute

DSC

General V1.0J DuPont 9900

Figure 28. DSC Analysis of n-Tetratetracontane.

Sample: n-HEPTADECANE C17 99%
 Size: 4.59 mg
 Method: DSC-MELT
 Comment: HEATING RATE 2°C/MIN

DSC

File: RUN900.02
 Operator: ED DYKE
 Run date: 08/05/88 11:21

Figure 29. DSC Analysis of n-Heptadecane at 2°C/min.

Sample: n-OCTADECANE 99%
 Size: 3.23 mg
 Method: DSC-MELT 2°C/MIN
 Comment: 2°C/MIN

DSC

File: A: RUN0759.03
 Operator: ED DYKE
 Run date: 06/10/86 10:41

Figure 30. DSC Analysis of n-Octadecane at 2°C/min.

Sample: n-NONADECANE C19 99%
 Size: 4.41 mg
 Method: DSC-MELT
 Comment: HEATING RATE 2°C/MIN

File: RUN0899.02
 Operator: ED DYKE
 Run date: 08/05/88 07:35

DSC

Figure 31. DSC Analysis of n-Nonadecane at 2°C/min.

Figure 32. DSC Analysis of n-Eicosane at 2°C/min.

Figure 33. DSC Analysis of n-Docosane at 2°C/min.

Figure 34. DSC Analysis of n-Octacosane at 2°C/min.

Figure 35. DSC Analysis of n-Dotriacontane at 2°C/min.

Sample: K-61 RECRYSTALLIZED 5-GAL CAN
 Size: 4.23 mg
 Method: DSC-MELT
 Comment: HEATING RATE 2°C/MIN

DSC

File: RUN0902.02
 Operator: ED DYKE
 Run date: 08/06/86 11:58

Figure 36. DSC Analysis of K-61 at 2°C/min.

Sample: PEG 1000 ALDRICH
 Size: 4.20 mg
 Method: DSC-MELT
 Comment: HEATING RATE 2°C/MIN

DSC

File: RUN0910.04
 Operator: ED DYKE
 Run date: 08/18/86 10:45

Figure 37. DSC Analysis of PEG 1000 at 2°C/min.

Figure 38. DSC Analysis of Witco 45A Wax at 2°C/min.

Figure 39. DSC Curve of Marlex 6006 High Density Polyethylene.

Figure 40. DSC Analysis of Uncrosslinked Marlex 6006 HDPE at 5°C/min.

Figure 41. DSC Analysis of Uncrosslinked Marlex 6006 HDPE Pellet at 10°C/min.

Figure 42. DSC Analysis of Humphrey Tech. Grade Octadecane at 2°C/min.

Figure 43. DSC Analysis of Humphrey Tech. Grade Octadecane at 5°C/min.

Sample: n-OCTADECANE (HUMPHREY
 Size: 4.78 mg
 Method: DSC-MET

DSC

File: RUN0894.02
 Operator: ED DYKE
 Run date: 07/31/88 11:31

Figure 44. DSC Analysis of Humphrey Tech. Grade Octadecane at 10°C/min.

Figure 45. DSC Analysis of Humphrey Tech. Grade Octadecane at 20°C/min

Sample: n-HEXADECANE C16 99%
 Size: 3.63 mg
 Method: DSC-MELT
 Comment: HEATING RATE 2 C/MIN

File: RUN0923.02
 Operator: ED DYKE
 Run date: 08/28/86 11.02

DSC

Figure 46. DSC Analysis of n-Hexadecane at 2°C/min.

Sample: n-HEXADECANE C16 99%
 Size: 3.63 mg
 Method: DSC-MELT
 Comment: HEATING RATE 5 C/MIN

DSC

File: RUN0924.02
 Operator: ED DYKE
 Run date: 08/26/86 13:48

Figure 47. DSC Analysis of n-Hexadecane at 5°C/min.

Figure 48. Effect of Rate of Temperature Change Versus Melting and Crystallization Temperature of n-Hexadecane.

Figure 49. Effect of Rate of Temperature Change Versus Melting and Crystallization Temperature of Humphrey Technical Grade n-Octadecane.

Figure 50. Rate of Heating and Cooling Vs. Melting and Crystalline Temperature of PEG-1000.

Figure 51. Rate of Heating and Cooling Vs. Melting and Crystallization Temperature of Marlex 6006 HDPE.

Figure 52. Correlation of Phase Change Temperature During Heating Cycle With Number of Carbon Atoms in the Chain.

Figure 53. Correlation of Phase Change Temperature During Melting and Freezing with Number of Carbon Atoms in the Chain.

Figure 54. Heat of Transition for Solid/Liquid Change During Heating Cycle vs. Carbon Atoms in the Chain.

Figure 55 Heat of Transition for Solid $\leftrightarrow$ Solid Change During Heating Cycle Vs. Carbon Atoms in the Chain.

Figure 56 Combined Heats of Transition and Fusion Vs. Carbon Atoms in the Chain.

Figure 57 Molar Heat of Fusion Vs. Carbon Chain Length of N-Alkanes.

Small circles represent methylene groups; large represent methyl groups which mark layer planes. In β_M phase, "evens" allow more closely fitting layers than "odds" and thus give higher density packing.

Figure 59 Schematic Illustration of Effect on Packing Density of "Even" vs. "Odd" Normal Alkanes.⁸

Shorter chains cause less distortion in crystal structure

Figure 60 Schematic Diagram Showing Effect of Contaminant Chain Length on Layer Stacking in Normal Alkane Crystal (Mnyukh, 1960).⁷

Figure 61 DSC Analysis of Thermal Energy Storage Properties of C₁₇/C₁₉ Blends.

Figure 62 DSC Analysis of Thermal Energy Storage Properties of C₁₅/C₁₉ N-Alkane Blends.

Sample: C17/C19 .50/.50
 Size: 4.17 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A:RUN0736.02
 Operator: ED DYKE
 Run date: 08/04/88 15:49

Sample: C15/C19 0.50/0.50 MIXTURE
 Size: 3.98 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A:RUN0829.02
 Operator: TODD SILL
 Run date: 07/02/88 17:43

Figure 63 DSC Analysis of Odd Carbon Chain Blends. General V1.0J DuPont 9900

Sample: n-TETRADECANE 99%
 Size: 4.25 mg
 Method: DSC-MELT
 Comments: HEATING RATE 10°C/MIN

DSC

File: A:RUN0723.02
 Operator: TODD SILL
 Run date: 08/02/88 18:15

Sample: C14/C16 0.90/0.10 MIXTURE
 Size: 4.78 mg
 Method: DSC-MELT
 Comments: HEATING RATE 10°C/MIN

DSC

File: A:RUN0825.02
 Operator: TIM RESCH
 Run date: 07/01/88 16:55

Figure 64 DSC Analysis of C₁₄/C₁₆ Blends.

Sample: C14/C16 0.80/0.20 MIXTURE
 Size: 3.50 mg
 Method: DSC-MELT

DSC

File: RUN0824.02
 Operator: ED DYKE
 Run date: 07/02/86 14:40

Sample: C14/C16 0.80/0.40 MIXTURE
 Size: 4.84 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A: RUN0823.02
 Operator: ED DYKE
 Run date: 07/01/86 13:37

Figure 65 DSC Analysis of C₁₄/C₁₆ Blends.

Sample: C14/C16 0.50/0.50 MIXTURE
 Size: 4.14 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A: RUN0822.02
 Operator: ED DYKE
 Run date: 07/01/88 12:07

General VI.0J DuPont 9900

Sample: C14/C16 0.40/0.60 MIXTURE
 Size: 4.88 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A: RUN0821.01
 Operator: ED DYKE
 Run date: 07/01/88 09:10

General VI.0J DuPont 9900

Figure 66 DSC Analysis of C₁₄/C₁₆ Blends.

Sample: C14/C18 0.20/0.80 MIXTURE
 Size: 4.75 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10°C/MIN

DSC

File: A: RUN0820.02
 Operator: ED DYKE
 Run date: 07/01/88 08:00

Sample: n-HEXADECANE 99%
 Size: 4.37 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10°C/MIN

DSC

File: A: RUN0721.02
 Operator: ED DYKE
 Run date: 08/02/88 15:52

Figure 67 DSC Analysis of C₁₄/C₁₆ Blends.

Figure 68 DSC Analysis of Thermal Energy Storage Properties of C₁₄/C₁₆ N-Alkane Blends.

Figure 69 DSC Analysis of Thermal Energy Storage Properties of C₁₆/C₁₈ Blends.

Figure 70 DSC Analysis of Thermal Energy Storage Properties of C₁₆/C₂₀ Blends.

Figure 71 Phase Transition Temperatures of C_{14}/C_{16} Blends.

Sample: C18/C18 .50/.50
 Size: 4.71 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10°C/MIN

DSC

File: A: RUN0729.02
 Operator: ED DYKE
 Run date: 08/03/88 13:53

Sample: C18/C20 .50/.50
 Size: 4.36 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10°C/MIN

DSC

File: A: RUN0755.02
 Operator: ED DYKE
 Run date: 08/09/88 13:33

Figure 72 DSC Analysis of 50/50 Blends of "Even" Alkanes.

Figure 73. Thermal Energy Storage Properties of C₁₆/C₁₇ Hydrocarbon Blends.

Figure 74. Thermal Energy Storage Properties of Octadecane-Nonadecane Blends.

Sample: C18/C17 0.50/0.50 MIXTURE
 Size: 4.31 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A: RUN0836.02
 Operator: ED DYKE
 Run date: 07/07/86 09:35

Sample: C18/C19 0.50/0.50
 Size: 4.00 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A: RUN0747.02
 Operator: ED DYKE
 Run date: 06/06/86 13:28

Figure 75 DSC Analysis of 50:50 Blends of Odd/Even n-Alkanes.

Sample: C23/C25 0.50/0.50 MIXTURE
 Size: 3.79 mg
 Method: DSC-MELT
 Comments: HEATING RATE 10C/MIN

DSC

File: A: RUN0815.02
 Operator: ED DYKE
 Run date: 06/30/86 12:29

Sample: C23/C27 0.50/0.50 MIXTURE
 Size: 4.02 mg
 Method: DSC-MELT
 Comments: HEATING RATE 10C/MIN

DSC

File: A: RUN0816.03
 Operator: ED DYKE
 Run date: 06/30/86 14:40

Figure 76 DSC Analysis of 50:50 Blends of Higher Carbon Alkanes.

Sample: C23/C28 0.50/0.50 MIXTURE
 Size: 3.92 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10°C/MIN

DSC

File: A: RUN0811.02
 Operator: ED DYKE
 Run date: 08/27/88 14:38

Sample: C23/ C32 50/50
 Size: 8.83 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10°C/MIN

DSC

File: E: RUN0944.03
 Operator: ED DYKE
 Run date: 09/04/88 09:17

Figure 77 DSC Analysis of 50:50 Blends of Higher Carbon Alkanes.

Sample: C24/C25 0.50/0.50 MIXTURE
 Size: 4.30 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A:RUN0814.02
 Operator: ED DYKE
 Run date: 06/30/86 09:59

Sample: C24/C26 0.50/0.50 MIXTURE
 Size: 3.58 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A:RUN0813.02
 Operator: ED DYKE
 Run date: 06/30/86 08:16

Figure 78 DSC Analysis of 50:50 Blends of Higher Carbon Alkanes.

Sample: C24/C28 0.50/0.50 MIXTURE
 Size: 3.90 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A: RUN0817.02
 Operator: TIM RESCH
 Run date: 06/30/88 18:41

Sample: C24/ C32 50/50
 Size: 5.86 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10°C/MIN

DSC

File: E: RUN0940.05
 Operator: ED DYKE
 Run date: 09/03/88 11:55

Figure 79 DSC Analysis of 50:50 Blends of Higher Carbon Chain n-Alkanes.

Sample: C28/C32 0.50/0.50 MIXTURE
 Size: 3.80 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A: RUN0818.02
 Operator: TODD SILL
 Run date: 08/30/86 18:19

Sample: C40/C44 0.50/0.50 MIXTURE
 Size: 4.00 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A: RUN0812.02
 Operator: TIM RESCH
 Run date: 06/27/86 16:12

Figure 80 DSC Analysis of 50:50 Blends of Higher Carbon Alkanes.

Figure 81. DSC Analysis of 50/50 Blend of C₄₀/C₄₄ at 2°C/min. Heating and Cooling.

Sample: C16/C17/C18 .25/.50/.25
 Size: 3.49 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A:RUN0761.02
 Operator: ED DYKE
 Run date: 08/11/88 14:54

Sample: C17/C18/C19 .25/.50/.25
 Size: 4.04 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A:RUN0768.02
 Operator: ED DYKE
 Run date: 08/17/88 15:24

Figure 82 DSC Analysis of Triblend.

Sample: C18/C18/C20 .25/.50/.25
 Size: 4.74 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A: RUN0764.02
 Operator: ED DYKE
 Run date: 08/17/88 10:03

Sample: C17/C19/C21 .25/.50/.25
 Size: 4.89 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A: RUN0765.02
 Operator: ED DYKE
 Run date: 08/17/88 13:47

Figure 83 DSC Analysis of Triblend.

Sample: C14/C17/C20 .25/.50/.25
 Size: 3.48 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A: RUN0760.03
 Operator: ED DYKE
 Run date: 08/11/88 13:48

Sample: C18/C19/C21 .25/.50/.25
 Size: 4.88 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A: RUN0782.02
 Operator: ED DYKE
 Run date: 08/11/88 18:25

Figure 84 DSC Analysis of Triblend.

Figure 85. DSC Analysis of Plant and Lab Prepared Witco LLN Wax.

Sample: RECRYSTALIZED 45A WAX
 Size: 3.78 mg
 Rate: 100/100 IN HIT
 Program: General Analysis V1.0

DSC

Date: 0-Jan-85 Time: 8:10
 File: 45A.WX DSC DISK 41
 Operator: PAT STEWART
 Plotdate: 0-Jan-85 9:16:17

Sample: 45A LAB
 Size: 3.78 mg
 Method: DSC-HEAT

DSC

File: RUN0351.02
 Operator: ED DYKE
 Run date: 07/09/85 13:42

Figure 86. DSC Analysis of Plant and Lab Prepared Witco 45A Wax.

Sample: K-81 WAX
 Size: 4.88 mg
 Method: 10C/MIN IN NIT
 Comment: 1090-Filename: K-81.02

DSC

File: A: K-81.02
 Operator: PAT STEWART
 Run date: 5-Mar-85 10:41:33

Sample: K-81 LAB
 Size: 4.80 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A: RUN0850.02
 Operator: ED DYKE
 Run date: 07/08/88 09:51

Figure 87 DSC Analysis of Plant and Lab. Prepared K-61 Wax.

Figure 88. DSC Analysis of Plant and Lab Prepared Witco K-51 Wax.

Figure 9. DSC Analysis of Witco 85018-1 Wax (NP-15).

Figure 89. DSC Analysis of Plant and Lab Prepared Witco NP-15 Wax.

Figure 90 Composition Vs. Carbon Chain Numbers in Commercial Paraffin Waxes.

APPENDIX 1

Work Request: 860815-1 to 4

Performed By: Mary Galaska
Date: 8/21/86

Procedure:

Blends of Witco LLN and 10, 7.5, 5.0, and 2.5% Ethyl Corporation BCL-462 fire retardant were prepared by melt mixing at 80°C. The molten blends were poured onto a 1/2" metal strip with a cotton wick down the center. When cooled, the blends were fire tested in the horizontal position in a hood. Observations were made concerning time to ignite, flame travel, time to extinguish and type of smoke.

APPENDIX 2

Work Order: 860804-1 to 10

Performed By: Mary Galaska/Tim Resch

Procedure:

10g blends of Saytex BCL-462 and Chlorowax 70-S in ratios of 1/3, 1/2, 1/1, 0/1 and 3/1 were prepared. These were used to prepare 10g blends of LLN wax and the Fire Retardant Blend in ratios of 20% and 25% FR. Compatibility was observed as the blends were melt mixed at 80°C for 5 minutes. Then they were poured onto 1/2" metal strips and allowed to cool. The strips were given a hardness rating between 1 (soft) and 5 (hard). In a hood, they were ignited with a Bunsen burner and the time to self-extinguishment was noted. The color of smoke was also noted and reported.

NOTE: The Chlorowax 70-S does not completely dissolve. It swells and forms a cloudy colloidal suspension in the LLN wax.

APPENDIX 3

Work Request: 860815-5 to 8

Performed By: Mary Galaska
Date: 8/21/86

Procedure:

10g melt mixed blends of Witco LLN wax and fire retardant Ethyl Corporation HBCD were prepared in the following concentrations: 10%, 7.5%, 5.0% and 2.5% HBCD. The blends were melt mixed at 80°C for 5 minutes then the temperature was raised to 150°C. None of the blends were soluble even at 150°C. The HBCD just settled on the bottom and would not mix in the LLN.

APPENDIX 4

Procedure to determine the highest concentration of 45-A PCM that will not continue to burn after ignition.

1. Ten 2" x 2" squares of USG plasterboard were cut and labelled 100/OA, 100/OB, 75/25A, 75/25B, 50/50A, 25/75A, 25/75B, 0/100A, and 0/100B. These squares were then weighed on an analytical balance, and the weights recorded.
2. The USG platerboard squares were then placed in a dessicator for 24 hours to remove moisture, and reweighed on the analytical balance. These new weights were also recorded.
3. A solution of 950g of 45-A wax and 50g of stearic acid was prepared by taring a metal beaker on a Mettler balance and weighing out the appropriate amounts of 45-A and stearic acid. The combination was then melted on a hot plate and stirred constantly.
4. Into five metal beakers, combinations of 200g 45-A/stearic acid + 0g heptane, 150g 45-A/stearic + 50g heptane, 100g 45-A/stearic + 100g heptane, 50g 45A/stearic acid + 150g heptane, 0g 45A/stearic acid + 200g heptane were added after being weighed out on a Mettler balance. The 45-A wax/stearic acid was supplied from the stock solution formed above. In the beakers containing, 200/0, 150/50, and 100/100 of 45-A/stearic + heptane, 1 phr of oil soluble red dye was added. Due to lack of additional dye, none was added to the 50/50 and 0/100 solutions.
5. The five solutions of PCM/Heptane were then heated to 50°C. At 50°C, the platerboard squares were added to the appropriate beakers: 100/OA and 100/OB in the 200g:0g beaker, etc. The squares were allowed to remain immersed for 10 minutes and then removed and immediately weighed on the analytical balance, and the weights were recorded.
6. The specimens were then placed in a vacuum dessicator and heated to 50°C and held there for 24 hours. After 24 hours, then squares were again weighed on the analytical balance. They were replaced in the dessicator and kept at 50°C under vacuum for 24 more hours. The squares were then reweighed and recorded. The % weight gain was calculated for each square after each weighing following the immersion as follows:

$$\% \text{ wt. gain} = \frac{(\text{final wt.} - \text{wt. of square before immer. in PCM})}{\text{final weight}} \times 100\%$$

% weight gain was calculated and recorded following the initial PCM immersion, the 24 hour dessication, and after 48 hours of dessication.

7. To prepare the squares for flame testing, one square of each solution was stripped of paper from both sides and washed with MEK to remove excess PCM from its surface. The squares were then heated in a vacuum dessicator for 1 hour at 50°C to evaporate remaining MEK.
8. The squares were tested for burning by placing them horizontally in a clamp and igniting them in a hood with a bunsen burner. After igniting the squares for 10 seconds, the flame was withdrawn and the time required for the flame to extinguish was observed and recorded for each square of plasterboard.

APPENDIX 5

Work Request: 860812-1 to 6

Performed By: Mary Galaska
Date: 8/26/86

Procedure:

Twelve 2" x 2" squares of plasterboard were dried in a vacuum dessicator overnight then weighed and labeled. Separate melt mixed percolating baths were prepared containing LLN/BCL-462/stearic acid in the ratios of 85/10/5, 80/15/5, and 75/20/5. Another series was prepared using 45A/BCL-462/Stearic acid in the same ratios. The blends were weighed into metal beakers and heated to 80°C. Duplicate plasterboard samples were immersed in each blend for 10 minutes. After 10 minutes in the bath, the samples were immediately removed and weighed to calculate the percent PCM absorbed. The paper cover was completely removed off of one of the squares of each group. Each sample was mounted horizontally in a hood and ignited for 10 seconds with a bunsen burner. See Table 1 for results.

Controls were included containing LLN/stearic acid and 45A/stearic acid in the ratio of 95/5.

APPENDIX 6

Work Request: 860708-3,4,5,6 Powder (ground)

Performed By: Ed Dyke/Mary Galaska
Date: 8/21/86

Procedure:

500g of homogenized K-61 wax and 5g of Santowhite powder were weighed into a metal beaker and heated to 150°C with constant stirring and ventilation. 50g of ground irradiation crosslinked 10 M-rad powder was poured into the wax and heated to 150°C for 4 hours. The powder swelled very quickly and it was necessary to add an additional 200g K-61/Santowhite (1 phr). The wax was heated to 150°C before it was added to the swelling powder. Samples (about 1.5g) were taken at 0, 1/2, 1, 2, 3, and 4 hours intervals. The samples were cooled to around 50°C, washed in a beaker with excess MEK (warmed to 50°C) and filtered through a Buchner funnel with a filter paper. They were washed again in the funnel with more warm MEK. The samples were air dried in a hood overnight. Each batch was analyzed by DSC for thermal energy storage.

Original Wt.	50g
Final Wt.	156.3g
% Wt. Gain	68.01%

APPENDIX 7

Procedure for swelling Marlex 6006 10 M-rad pellets in 45-A wax.

1. Five gallons of 45-A wax was removed from the 55-gallon drum and homogenized by melting for 6 hours at 150°C in a circulating air oven and then pouring about 2 inch deep in aluminum trays, and allowed to recrystallize.
2. 1000g of Marlex 6006 pellets were swelled in 10 batches of 100g each. Two batches were made simultaneously in side by side containers.
3. For each batch, a steel beaker was tared on a Mettler balance, and 1500g of the 45-A wax homogenized above was weighed into the beaker.
4. A paper cup was tared on the Mettler balance and 15g of Santowhite powder was weighed into the cup. The Santowhite was then added to the 45-A wax.
5. A 100 ml glass beaker was tared on the Mettler balance, and 100g of Marlex 6006 10 M-rad pellets were weighed into the beaker.
6. The metal beaker was placed on a hot plate, a magnetic stirrer was added, and the wax/Santowhite mixture was melted and heated up to 150°C. The temperature was controlled by manual adjustment of the heater.
7. When the wax/Santowhite reached 150°C, the 100g of Marlex 6006 pellets were added. Throughout the entire swelling procedure, the temperature of the mixture was maintained at 150°C.
8. A sample of wax/Santowhite was removed from the beaker for DSC analysis prior to adding the pellets.
9. Samples of the swelling pellets were removed from the beaker for DSC analysis at 30 min., 1 hr., 2 hrs., 3 hrs., and 4 hrs. Each was washed with warm (50°C) MEK to remove excess wax and filtered with a Buchner funnel.
10. After 4 hrs. of swelling, the beaker was removed from the hot plate and the still hot 45-A/Santowhite/Marlex 6006 mixture was filtered through a Buchner funnel. Upon cooling, the excess 45-A wax was washed with warm MEK three separate times, or until no more wax was visible on the pellets.
11. The washed pellets were then placed in an aluminum tray that was lined with two layers of Kimwipes, spread out, and allowed to dry overnight.

12. The next day, a plastic ziplock bag was tared on a Mettler balance. The swelled pellets were put into the bag for storage, and weighed out on the Mettler balance. The percentage weight gain was recorded.

13. Weight gain was calculated as follows:

$$\% \text{ weight gain} = \frac{(\text{final weight} - \text{initial weight})}{\text{final weight}} \times 100\%$$

APPENDIX 8

Work Request: 860729-1 & 2

Performed By: Mary Galaska
Date: 8/4/86

Particle size determination by standard sieve screen analysis
(ASTM procedure).

Procedure:

Screens were stacked in the following order from bottom to top: bottom receiver pan, No. 325, No. 250, No. 100, No. 70, No. 40, No. 20, and top sieve cover. All six screens and the bottom pan were weighed to the nearest 0.01g. 100g of the powder sample was weighed and placed in the top screen. The cover was secured in place and the stack placed in a Ro-Tap Sieve Shaker for 30 minutes. Then each sieve and the bottom pan was reweighed to determine the amount of powder retained on each level. The particle size distribution can be seen in Table 11.

APPENDIX 9

Start Time: 8:50
Temp. 21°C
Finish Time: 10:50

#1 Ethanol
#3 Methanol

Starting Sample Wt.
1.9140
2.0233

1. Pellets of Marlex 6006 10 M-rad gamma, swelled for 4 hours at 150°C in 45-A, were ground in the Brinkmann grinder.
2. A small sample of powder was taken for DSC analysis.
3. The remaining powder was divided into five parts and placed in beakers which had been previously weighed on the analytical balance.
4. Two of the beakers were placed on hot plates with magnetic stirrers and stir bars were added.
5. The beakers were then filled to the 30 ml line with the solvents being studied: (a) ethanol and (b) methanol.
6. With vigorous stirring, the samples were soaked in the solvents for 2 hours at room temperature (21-22°C).
7. After 2 hours the samples were filtered using a Buchner funnel and filter paper under vacuum.
8. Both the solvent and the powder sample were saved.
9. The powder was allowed to dry in a hood for a minimum of 24 hours before weighing.
10. % weight change was then calculated by the equation:
$$\frac{\text{initial wt.} - \text{final wt.}}{\text{initial wt.}} \times 100\%$$
11. DSC will be run if necessary.

APPENDIX 10

Work Request: 860813-1,2,3
Solubility of Marlex 6006 powders in xylene @ 120°C

Performed By: Mary Galaska
Date: 8/14/86

Procedure:

0.4g of each of the following powders was weighed into separate 100 ml tared beakers:

- (1) Uncrosslinked Marlex 6006 powder,
- (2) 5 M-rad crosslinked Marlex 6006 powder, and
- (3) Marlex 6006 powder ground from 10 M-rad pellets.

19.6g of xylene was added to each beaker to make a 2% solution. The samples were heated to 120°C with constant stirring and held at 120°C for 1 hour. The hot samples were filtered through a preheated suction filter apparatus with a tared filter paper. The beaker was washed two times with hot xylene and this added to the filter. The filter paper was removed, placed on a clean watchglass and allowed to dry in a hood overnight. The filter paper was weighed and the amount of residue was calculated. The solubles were poured into a tared beaker and evaporated to dryness.

MONTHLY PROGRESS REPORT NO. 4
CONTRACT NO. DE-FG03-86SF16308
COVERING SEPTEMBER, 1986

1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research, on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends".

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

In the first process, the PCM's (alkyl hydrocarbons) can be added directly into the wet mix of cementitious materials at concentrations up to 5% wt (cement) and 10% wt (plaster). However, considerable reduction in the strength properties of the cement and/or lengthening of the setting time is encountered. In one modification of this process, the cementitious products can also be made waterproof.

In the second process, the PCM's are first mechanically dispersed into rubbers, such as natural rubber, and plastics, such as polyethylene, using Banbury mixer or roll mill, at concentrations greater than 50% wt. These PCM "concentrates" can potentially be used directly, in sheet form, as floor or wall tiles and may be especially useful for retrofit use in building where they could be adhered to existing walls and floors.

In the third process the PCM is imbibed into small pellets of HDPE by swelling at elevated temperatures. The resulting small hard pellets contain up to 80% wt PCM, and should be easy to incorporate into the wet mix of cementitious materials with minimum reduction in strength properties.

The rubber or HDPE pellets from the second and third process above can potentially be used as an effective low-cost pellet bed heat exchanger; to heat or cool the air, or liquid medium, in solar passive hybrid applications.

In the fourth process, the PCM in liquid form is percolated directly into the open space in porous building materials (cement, plaster bricks). This process also has the attendant advantage that the porous products are simultaneously waterproofed. The process has obvious potential applications in waterproofing cement for other applications as well (i.e., highway bridge decks).

As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3). The building material will not burn. However, in process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard

after ignition will continue to burn slowly until the PCM is exhausted.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will initiate extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

The present month's work consists of the following:

1. Fire Retardance of PCM
 - a. Further work on PCM solubility and fire retardant properties of brominated fire retardants from Great Lakes and Ethyl Corporation.
 - b. Determine the highest concentration of 45A/stearic acid (95/5) PCM in Plasterboard that will not continue to burn after ignition.
 - c. To prepare a total of four 11" x 18" plasterboard panels, two percolated with 45A, two percolated with 45A/BCL462 (75/25) for USG fire retardant test.

2. Containment of PCM

- a. Effect of butyl stearate and stearic acid on percolation of 45A in plasterboard.
- b. DSC analysis of PCM composition sent to Eurand America for microencapsulation.

3. TECHNICAL DESCRIPTION OF CURRENT RESEARCH

3.1 Further Work on PCM Solubility and Fire Retardant Properties of Brominated Fire Retardants

3.1.1 Great River Fire Retardants

In the July Progress Report, we reported on the evaluation of fire retardant properties of some brominated fire retardants from Ethyl Corporation. Subsequently, we obtained a similar supply from Great Lakes Corporation. The technical name and the corresponding chemical structures of these are as follows:

Tetrabromobisphenol A or BA59P

Tetrabromobisphenol A bis(2 hydroxyethylether) or BA50P

Tetrabromobisphenol A-bis(2,3 dibromopropyl ether) or PE68

Tetrabromobisphenol A-bis(allyl ether) or BE-51

BA50-bis(acrylate) or BA43

As may be observed from the structure, Great Lakes BA59P is equivalent to Ethyl Corporation's Saytex RB100. The other Great Lakes fire retardants are different. The common feature of the Great Lakes fire retardants is the tetrabromobisphenol A nucleus (BA59P), which has different types of aliphatic substituents for the different fire retardants mentioned above. None of these, however, have strongly aliphatic substituent to cause it to dissolve in hydrocarbon PCMs. This is evident in Table 1 which records the solubility of the above fire retardants in Witco LLN and NP-15 PCMs. Table 2 shows the results of the horizontal flame test of these wax compositions containing 10 and 20% of the selected fire retardants. The compositions with fire retardants are only marginally better than the control.

3.1.2 Saytex Fire Retardants from Ethyl Corporation

Further efforts to determine suitable wax soluble fire retardants were directed to Ethyl Corporation products. Four of these were investigated and reported in last month's report. This includes BCL 462 which was found to be soluble in Witco LLN at least up to 25 concentration (wt/wt). Ethyl Corporation's Saytex 105 has a structure similar to Saytex BCL 462, with the exception that 105 has a benzene ring instead of cyclohexane and that bromine substitution is not distributed between the aliphatic and aromatic moiety, as in BCL 462, but is altogether on the

TABLE 1
SOLUBILITY OF FIRE RETARDANTS FROM GREAT LAKES
IN WITCO LLN AND NP-15 WAXES

<u>Fire Retardant</u>	<u>% in LLN</u>	<u>Solubility Results</u>
BA-59P	10	did not dissolve - formed fine film on bottom
	20	did not dissolve - formed fine film on bottom
BA-50P	10	did not dissolve - clumped
	20	did not dissolve - clumped
PE-68	10	dissolved completely - clear
	20	did not dissolve completely
BE-51	10	dissolved - cloudy - phase separates when cooled
	20	does not dissolve completely - colloidal suspension
BA-43	10	did not dissolve completely
	20	did not dissolve - clumped

<u>Fire Retardant</u>	<u>% in NP-15</u>	<u>Solubility Results</u>
BA-59P	10	did not dissolve - fine film on bottom
	20	did not dissolve - fine film on bottom
BA-50P	10	did not dissolve - formed oil on bottom
	20	did not dissolve - formed oil on bottom
PE-68	10	did not dissolve
	20	did not dissolve
BE-51	10	most dissolved - cloudy
	20	did not dissolve completely
BA-43	10	did not dissolve - formed oil on bottom
	20	did not dissolve - formed oil on bottom

TABLE 2

HORIZONTAL FLAME TEST FOR GREAT LAKES FIRE
RETARDANTS IN WITCO LLN AND NP-15 PCMs

<u>Fire Retardant</u>	<u>% FR</u>	<u>Ignite in 10 sec.</u>	<u>Time to Ignite</u>	<u>Flame Traveled</u>	<u>Time to Extinguish</u>	<u>Smoke</u>
<u>LLN</u>						
BA-68	10	yes	3 sec.	6-3/4"	10 min.	black - very little
BA-51	10	yes	4 sec.	5-3/4"	10 min.	black - alot
BA-43	10	yes	4 sec.	2-1/2"	10 min.	black - alot
BA-68	20	yes	4 sec.	3-1/4"	10 min.	black - very little
BA-51	20	yes	4 sec.	3"	10 min.	black - alot
<u>NP-15*</u>						
BA-51***	10	yes	2 sec.	9"***	290 sec.	black & white - very little
BA-51	20	yes	2 sec.	9"	412 sec.	black & white - very little
Control	0	yes	1 sec.	9"	369 sec.	white - very little

* Since NP-15 is liquid at room temperature, it soaked the wick but did not stay on the metal strip.

** It burned very rapidly across the entire bar.

*** Phase separated when cooled.

aromatic ring. Saytex 105 was therefore tried for solubility in PCM. The chemical structures of these two fire retardants are as follows:

The results for solubility and fire retardance are reported in Table 3. The solubility data are somewhat encouraging but phase separation takes place on cooling at all concentrations (10-25%) studied. The horizontal flame test data show fire retardance at all concentrations but the degree of retardance as measured by the distance travelled by the flame does not follow the order expected from the fire retardant concentration. The vertical test does not show any fire retardance among the samples. Thus, at this time, we still have only one truly soluble effective fire retardant, BCL 462. We will, however, continue to evaluate other potentially soluble fire retardants, and fire retardant systems, as they become available. The procedure for preparing the samples is reported in Appendix 1.

3.1.3 Determine the Highest Concentration of 45A/Stearic Acid (95/5) PCM That Will Continue to Burn After Ignition

Plasterboards percolated with linear alkyl hydrocarbon, to concentrations above 30% weight, continue to burn after ignition until the PCM is substantially depleted. On the other hand, the control sample of plasterboard will not support combustion, after removal from the flame, if the paper cover is previously removed. It was therefore postulated that a concentration of PCM may be found between the 0 and 30% wt. extremes, where the PCM is so thinly distributed that it will not wick out to burn on the surface.

An experiment was described last month where the plasterboard was soaked for 10 minutes in zero to 100 percent

TABLE 3

SOLUBILITY AND FIRE RETARDANCE OF SAYTEX 105
IN WITCO ILIN PCM

Sample No.	% FR	Solubility @ 80°C	Phase Separation
1	10	dissolved completely	phase separates slightly
2	15	dissolved completely	phase separates on cooling
3	20	dissolved completely	phase separates on cooling
4	25	dissolved completely	quickly phase separates when cooled

Horizontal Flame Test w/Cotton Wick						
Sample Number	% FR	Ignite in 10 sec.	Time to Ignite	Flame Traveled	Time to Extinguish	Smoke
1	10	yes	3 sec.	3/8"	10 min.	black
2	15	yes	2 sec.	3/8"	10 min.	black
3	20	yes	2 sec.	1"	10 min.	black
4	25	yes	2 sec.	1-1/8"	10 min.	black
Control	0	yes	3 sec.	3-3/4"	10 min.	black

<u>*Vertical Flame Test - No Wick</u>						
1	10	no	20 sec.	yes	115 sec.	all had vigorous flame
2	15	no	25 sec.	yes	115 sec.	alot of black smoke
3	20	no	25 sec.	yes	131 sec.	alot of black smoke
4	25	no	24 sec.	yes	115 sec.	alot of black smoke
Control	0	no	20 sec.	yes	180 sec.	alot of black smoke

* Wax melted and dripped down - feeding the flame - The flame burned vigorously until all the wax was gone.

PCM/heptane at 25% intervals of 45A. However, this experiment failed to provide samples with PCM content lower than 27%. As a follow-up of this work, the PCM/heptane solvent ratios were further reduced down to 25/75, 20/80, 15/85, 10/90 and 5/95. A similar series was also made with 45A/methylene chloride solvent. Around 8 and 10% PCM was absorbed at 95/5 composition from heptane and methylene chloride, respectively. The other compositions showed substantially higher PCM pickup from relatively dilute low boiling solvents. This could not be explained.

The same experiment was therefore repeated this month and reported in Table 4. The PCM pickup is substantially lower than those reported before. The data from Table 4 (A and B) are plotted in Figure 1. The table and the figure both show higher PCM pickup from methylene chloride solvent. Table 5 shows the corresponding volume percent composition of PCM in the solvent. These data are plotted in Figure 2 and show a linear relationship between volume percent PCM vs. weight gain for both sets of PCM pickup in heptane and methylene chloride.

Table 6 reports the corresponding horizontal flame tests data. The results show very convincingly, in both sets of data, that in order for the plasterboard to continue burning more than PCM absorption would be necessary. This may be obtained from 90/10 heptane/45A or 95/5 methylene chloride/45A solutions. The higher pickup in methylene chloride is due to higher volume ratio of the PCM in this solvent. Even in higher ratio up to 18%, PCM pickup in both solvents the time to extinction is very short (up to 5 seconds). This is a very encouraging development, since plasterboards with significant thermal energy storage (e.g. 18% wt.) and reduced flammability can be made by varying the solvent/PCM ratio. It remains to be shown whether equivalent fire retardance can also be obtained by using short percolation times to obtain PCM pickup <20% wt.

TABLE 4
PCM ABSORPTION FROM DILUTE SOLUTIONS

A. 45A/Stearic Acid (95/5) + Heptane

% PCM/Heptane	Dry Wt. (g)	After 10 Min.	% Wt. Gain	48 Hr. Vacuum	% Wt. Gain	Avg.
1) 25/75	22.6791	33.2282	31.75	25.2257	11.46	13.05
2) 25/75	24.0538	34.2050	33.70	26.5678	14.64	
3) 20/80	22.1025	30.9370	27.31	24.0670	8.16	8.66
4) 20/80	24.1357	33.2020	28.07	26.5738	9.17	
5) 15/85	24.3398	33.8380	28.07	25.8427	5.82	5.99
6) 15/85	22.7817	32.1050	29.04	24.2736	6.15	
7) 10/90	23.1552	32.8400	29.49	24.2078	4.35	4.37
8) 10/90	22.5864	32.0360	29.50	23.6230	4.39	
9) 5/95	22.5118	31.4040	28.32	23.0545	2.35	2.30
10) 5/95	22.6550	31.1600	27.29	23.1540	2.16	

B. 45A/Stearic Acid (95/5) + Methylene Chloride

% PCM/MeCl	Dry Wt. (g)	After 10 Min.	% Wt. Gain	48 Hr. Vacuum	% Wt. Gain	Avg.
1) 25/75	22.2127	45.3510	51.02	28.9732	23.33	22.78
2) 25/75	22.2865	43.7390	49.05	28.6578	22.23	
3) 20/80	23.3087	42.4840	45.14	28.5140	18.25	18.81
4) 20/80	21.9941	41.4760	46.97	27.2681	19.34	
5) 15/85	22.0713	39.8280	44.58	25.4063	13.13	13.04
6) 15/85	22.4760	39.8510	43.60	25.8199	12.95	
7) 10/90	22.5316	39.6370	43.16	24.6417	8.56	10.12
8) 10/90	21.8867	45.7510	52.16	24.7844	11.69	
9) 5/95	24.1321	43.5100	44.54	25.4638	5.23	6.44
10) 5/95	23.2879	44.6300	47.82	25.2193	7.66	

Concentration of 4SA/Stearic Acid (95/5)
vs % wt gain after 10 min. soak in
PCM / Solvent baths at 80°C.

Figure 1. Weight Concentration PCM in the Solvent
vs. Percent Weight Gain.

TABLE 5
VOLUME CONCENTRATION OF 45A IN THE SOLVENT VS.
PERCENT WT. GAIN OF PLASTERBOARD AFTER 10 MINUTES
SOAK AT 80°C

<u>Weight Ratio 45A/Solvent</u>	<u>Volume Percent 45A in Heptane</u>	<u>% Weight Gain</u>	<u>Volume Percent 45A in Methylene Chloride</u>	<u>% Weight Gain</u>
5/95	4.4	2.30	8.15	6.44
10/90	8.8	4.37	15.8	10.12
15/85	13.3	5.99	22.9	13.04
20/80	17.9	8.66	29.7	18.81
25/75	22.5	13.05	36.0	22.78

Figure 2. Vol. Concentration of 45A in the Solvent vs. Percent Wt. Gain of Plasterboard After 10 Mins. Soak in the Bath at 80°C.

TABLE 6
RESULTS OF FLAME TESTS FOR PLASTERBOARDS
SOAKED IN DILUTE SOLUTIONS OF PCM

% PCM/Heptane	PCM Pick-up (%)	Ignite in 10 Sec.	Time to Ignite	Flame Traveled	Time to Extinguish	Smoke
1) 25/75	11.46	no	54 sec.	no	10 sec.	white
*2) 25/75	14.64	no	didn't	--	---	white
3) 20/80	8.16	no	76 sec.	no	7 sec.	white
4) 20/80	9.17	no	70 sec.	no	2 sec.	white
5) 15/85	5.82	no	84 sec.	no	5 sec.	white
6) 15/85	6.15	no	didn't	no	---	white
7) 10/90	4.35	no	didn't	no	---	white
8) 10/90	4.39	no	didn't	no	---	white
9) 5/95	2.35	no	didn't	no	---	white
10) 5/95	2.16	no	didn't	no	---	white

* Even numbered samples had paper covers completely removed.

% PCM/MeCl	PCM Pick-up (%)	Ignite in 10 Sec.	Time to Ignite	Flame Traveled	Time to Extinguish	Smoke
1) 25/75	23.33	yes	10 sec.	yes-bottom edges	84 sec.	white
*2) 25/75	22.23	no	14 sec.	no	44 sec.	white
3) 20/80	18.25	no	34 sec.	yes-bottom edges	29 sec.	white
4) 20/80	19.34	no	21 sec.	no	5 sec.	white
5) 15/85	13.13	no	31 sec.	no	6 sec.	white
6) 15/85	12.95	no	28 sec.	no	2 sec.	white
7) 10/90	8.56	no	didn't	no	---	white
8) 10/90	11.69	no	39 sec.	no	3 sec.	white
9) 5/95	5.23	no	didn't	no	---	white
10) 5/95	7.66	no	didn't	no	---	white

* Even numbered samples had paper covers completely removed.

3.1.4 To Prepare a Total of Four 11" x 18" Plasterboard Panels, Two Percolated With 45A, Two Percolated With 45A/BCL 462 (75/25) for USG Fire Retardant Test

So far we have used only screening tests developed by us for comparing flammability of the PCM containing building materials. The ultimate test for fire retardance of building material is the ASTM-E119 (Fire Tests of Building and Construction Materials). This test is run by commercial laboratories at a cost of about \$15,000 each. We were informed by U.S. Gypsum that they have a smaller unit which quite accurately approximates this big test, but still it is rather expensive. The next level of testing that USG can use as an indication of probable results on the full scale test is the bench size test using an 11" x 22" sample. This test determines dimensional change and temperature transmission. This is a test that is unique with USG which they offered to run for a few of our samples. Accordingly, four samples of plasterboards of the specified size were made and soaked in PCM for 10 minutes. Two of them are controls and contain 45A PCM only and the other two have, in addition, BCL 462 fire retardant in the ratio of 75/25, PCM/fire retardant. The method of preparation is reported in Appendix 2 and the results are reported in Table 7. Table 7 shows slightly increased weight gain for the samples soaked in PCM/fire retardant combination. A higher weight gain is ascribed to the absorption of the high density BCL 462 fire retardant (density 2.27). This will be confirmed by DSC analysis.

3.2 Containment of PCM

3.2.1 Effect of Butyl Stearate and Stearic Acid on Percolation of Witco 45A in Plasterboard

Stearic acid is normally used as a component in our percolation experiment with hydrocarbon PCM. It is believed to act as a wetting agent to promote percolation of PCM. In order to test this hypothesis percolation experiments with 45A were designed with or without stearic acid in 5 or 10 parts concentration (wt. on 45A). An additional wetting agent, butyl stearate was included to see the difference, if any. The method is

TABLE 7
RESULTS FOR PCM ABSORPTION OF 11" x 22" PLASTERBOARDS
FOR FIRE RETARDANCE TEST AT USG

<u>Sample Number</u>	<u>Bath</u>	<u>Rinse</u>	<u>Dry Weight</u>	<u>After 10 Min. in PCM</u>	<u>% PCM Pickup</u>
1	45A	---	1252.2	1876.8	33.29
2	45A	MeCl	1293.1	1923.2	32.76
3	45A/462 (75/25)	MeCl	1344.1	2091.8	35.74
4	45A/462 (75/25)	---	1320.1	2072.4	36.30

described in Appendix 3 and the results are reported in Table 8. It is apparent that neither stearic acid nor butyl stearate increases absorption of PCM perceptibly. Table 9 shows the DSC analysis. No influence of the two wetting agents on T_m and T_c of 45A is apparent. The values of ΔH_f and ΔH_c are little changed by 10% of either stearic acid or butyl stearate.

Table 9 also includes the solid state T_m and T_c . It is apparent that both of these parameters are lowered by the wetting agents.

Figures 3 and 4 document the DSC analysis of butyl stearate at 2°C and 10°C/min. heating and cooling. Note the double solid/solid transition at 2°C/min. rate of heating and cooling. The ΔH_f and ΔH_c of butyl stearate are adequate (>30 cal/g) to qualify for a PCM. The extrapolated value of T_m and T_c (Figure 5) is 21.5 and 20.2, respectively, which may be in the range required for home heating and cooling. However, the thermal energy storage is lower than for the paraffins, and the anticipated cost higher. Further, hydrolysis to stearic acid and butyl alcohol may be encountered in basic cementitious media (cement, plaster, etc.).

3.2.2 DSC Analysis of PCM Composition Sent to Eurand America for Microencapsulation

One of the disadvantages of including hydrocarbon PCMs into the wet mix of cementitious building material is some sacrifice of physical properties. In order to minimize this deterioration of physical properties, the particle size of the plastics (e.g. HDPE), often used as container of PCM, must be small. This is hard to achieve in HDPE pellets. Swelling of HDPE pellets with PCM, which is our current method to contain PCM in HDPE, increases the size of the particles several folds. In order to solve this problem experiments are planned to contain the PCM in small particle size microcapsules with an outer coating of gelatin by the NCR "microencapsulation" process. An outside source (Eurand America) who has the necessary expertise and equipment for this special process were located. This company

TABLE 8
THE EFFECT OF STEARIC ACID AND BUTYL STEARATE ON PERCOLATION
OF 45A IN PLASTERBOARD

<u>Bath</u>	<u>Original Wt.</u>	<u>Time in Bath</u>	<u>Final Wt.</u>	<u>% Change</u>
45A 100%	21.2406	5 min.	32.0681	33.76
	21.7289	10 min.	34.6114	37.22
45A/Butyl Stearate 95/5	22.8915	5 min.	34.3124	33.28
	21.9582	10 min.	33.9755	35.37
45A/Butyl Stearate 90/10	22.5550	5 min.	33.2739	32.21
	23.1486	10 min.	35.8210	35.38
45A/Stearic Acid 95/5	24.6246	5 min.	36.1854	31.95
	21.3848	10 min.	33.2160	35.62
45A/Stearic Acid 90/10	21.8861	5 min.	32.6358	32.94
	22.8680	10 min.	35.3080	35.23

* DSC Run Numbers: 956.01, 957.01, 958.01, 959.01, 963.01

TABLE 9

DSC ANALYSIS OF 45A CONTAINING STEARIC ACID
AND BUTYL STEARATE

Sample Identification and Composition	T _m (°C)	T _c (°C)	T _m -T _c (°C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)	Extrapolated to 100%	
						ΔH_f (cal/gm)	ΔH_c (cal/gm)
Witco 45A 100/0	30.7	23.8	6.9	42.1	42.9	42.1	42.9
Witco 45A/ Butyl Stearate 95/5	30.5	23.7	6.8	41.5	42.7	43.7	44.9
Witco 45A/ Butyl Stearate 90/10	30.5	23.0	7.5	40.6	40.2	42.7	42.3
Witco 45A/ Stearic Acid 95/5	31.5	23.6	7.9	39.6	40.0	41.7	42.1
Witco 45A/ Stearic Acid 90/10	30.7	23.7	7.0	42.1	44.0	46.8	48.9
Butyl Stearate 100/0 10°C/Min.	23.3	17.4	5.9	35.7	35.8	35.7	35.8
Butyl Stearate 100/0 2°C/min.	21.9	19.5	2.3	36.0	38.0	36.0	38.0
<u>Solid/Solid Transition</u>							
Witco 45A 100/0	8.8	3.7	5.1				
Witco 45A/ Butyl Stearate 95/5	8.1	2.9	6.2				
Witco 45A/ Butyl Stearate 90/10	7.3	2.2	5.1				
Witco 45A/ Stearic Acid 95/5	7.2	1.0	6.2				
Witco 45A/ Stearic Acid 90/10	5.6	0.0	5.6				

Sample: BUTYL STEARATE
 Size: 3.95 mg
 Method: DSC-MELT
 Comment: HEATING RATE 2°C/MIN

DSC

File: A: RUN0920.02
 Operator: MARY
 Run date: 08/22/86 13:37

General V1.0J DuPont 990

Figure 3. DSC Analysis of Butyl Stearate at 2°C/Min. Rate of Heating and Cooling.

Sample: BUTYL STEARATE
Size: 3.95 mg
Method: DSC-MELT
Comment: HEATING RATE 10C/MIN

DSC

File: A: RUN0921.01
Operator: MARY
Run date: 08/25/88 10:34

Figure 4. DSC Analysis of Butyl Stearate at 10°C/Min. Rate of Heating and Cooling.

Figure 5. Rate of Heating and Cooling vs. Melting and Crystallization Temperature of Butyl Stearate.

agreed to prepare small lots of microcapsules for us at no cost. Accordingly, 500 grams of the following compositions were delivered to this company. These are: (1) NP15/butyl stearate, 90/10; (2) 45A/butyl stearate/BCL 462, 70/10/20; (3) K-61/butyl stearate, 90/10. The DSC analyses of these samples are reported in Table 10 and Figures 6-8. The basic thermal energy storage properties of PCMs are unchanged.

4. CONCLUSIONS

1. None of Great Lakes fire retardants are soluble in LLN and NP15 waxes.
2. Horizontal and vertical flame tests do not indicate any promise for Saytex 105.
3. Plasterboards with >10% and <20% of PCM retain their non-flammability characteristics.
4. The flammability increases with the volume or weight percent PCM retained by percolation, and is pronounced at PCM contents >20% wt.
5. Thus, plasterboards with reduced degrees of flammability can be made by varying the solvent/PCM ratio, to obtain <20% wt. PCM pickup in the percolation process.
6. Weight gain in percolation experiments is higher for 45A/BCL 462 combination than for 45A alone. This is expected due to the higher density of the solution containing the brominated fire retardant.
7. The wetting agents, stearic acid and butyl stearate do not increase PCM absorption by percolation into plasterboard.
8. Butyl stearate may qualify for a PCM but at a lower energy rating and higher cost than hydrocarbon PCMs. Additionally, hydrolysis of the ester to higher melting stearic acid may be anticipated in the basic environment of cementitious building materials (concrete, plaster, etc.).
9. Basic thermal energy storage properties of PCMs microencapsulated by Eurand America (using the "NCR" process) are not changed.

TABLE 10
DSC ANALYSIS OF MELT MIXED PCMs FOR
ENCAPSULATION AT EURAND AMERICA

Sample Identification and Composition	T _m (°C)	T _c (°C)	T _m -T _c (°C)	ΔH _f (cal/gm)	ΔH _c (cal/gm)	Extrapolated to 100%	
						ΔH _f (cal/gm)	ΔH _c (cal/gm)
NP-15/Butyl Stearate 90/10	7.5	-0.60	8.1	45.0	45.1	50.0	50.1
K-61/Butyl Stearate 90/10	28.0	19.4	8.6	45.9	45.5	51.0	50.6
45A/BCL 462/ Butyl Stearate 70/20/10	28.3	22.0	6.3	32.5	33.9	46.4	48.4
NP-15 100/0	9.7 -24.0	2.0 -28.0	7.7	47.6	47.9	47.6	47.9
K-61 100/0 July 1986, 5 gal. drum	26.4	20.2	6.2	47.5	46.4	47.5	46.4
45A 100/0	30.7	23.8	6.9	42.1	42.9	42.1	42.9
Butyl Stearate 100/0	23.3	17.4	5.9	35.7	35.8	35.7	35.8

Sample: NP-15/ BUTYL STEARATE 90/10
 Size: 4.48 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: RUN0975.02
 Operator: ED DYKE
 Run date: 09/17/88 09:18

Figure 6. DSC Analysis of NP-15/Butyl Stearate, 90/10, Sent to Eurand America for Microencapsulation.

Sample: 45A/ BUTYL STEARATE/ BCL 462
 Size: 4.36 mg
 Method: DSC-MELT
 Comment: 70/ 10/ 20 10C/MIN

DSC

File: RUN0977.01
 Operator: ED DYKE
 Run date: 09/18/86 08:58

Figure 7. DSC Analysis of 45A/Butyl Stearate/BCL 462,
 70/10/20, Sent to Eurand America for Microencapsulation.

Sample: K-61/ BUTYL STEARATE 90/10
 Size: 4.85 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: RUN0976.02
 Operator: ED DYKE
 Run date: 09/17/88 11:58

Figure 8. DSC Analysis of K-61/Butyl Stearate, 90/10, Sent to Eurand America for Microencapsulation.

5. IMMEDIATE FUTURE PLANS

1. To evaluate via DSC analysis the thermal energy storage properties of Witco 45A and K-61 containing 20% and 25% wt. of Ethyl Corp. fire retardant BCL 462.
2. Develop the experimental techniques and procedures to implement the USG laboratory process for preparing gypsum plasterboards.
3. Melt spraying hardened wax beads from 45A/Fortex, 80/20; 45A/Shell Wax 300, 80/20; 45A/Shell Wax 400, 80/20.
4. Evaluate the thermal energy storage properties of permeated and nonpermeated samples of crosslinked HDPE, PP and the PCM used (Paraffin 115) as submitted by Matsushita.
5. Analyze by DSC the HDPE samples imbibed with Witco 45A, which was made for demonstration during Matsushita visit and send copy to Matsushita.
6. Analyze by DSC the samples of plasterboards, percolated with Witco 45A that was made during Matsushita visit and send a copy of the data to Matsushita.
7. To determine the thermal energy storage properties of gamma irradiation crosslinked Marlex 6006 powder.
8. To evaluate the 45A PCM uptake in Marlex 6006 powder that has been irradiation crosslinked to total doses of 4, 5, 6, 7, and 8 m-rads in nitrogen.
9. To evaluate the effect of "annealing" on the thermal energy storage properties of paraffin PCMs.
10. To evaluate the stability of PCMs to repeated thermocycling between the temperatures 0-50°C.
11. Evaluate microencapsulation on neat NP-15, K-61 and 45A and the same PCM containing 25% wt. of BCL 462 fire retardant.

APPENDIX 1
PREPARATION OF PCM/FIRE RETARDANT COMPOSITION

Work Request: 860917-1
Performed by: Lucy Dang/Mary Galaska
Date: September 26, 1986

Procedure:

50g blends of Witco LLN and Saytex 105 were weighed into separate 100g beakers to contain 10, 15, 20, and 25% of the fire retardant. Each beaker was equipped with a magnetic stirrer and heated to 80°C. The compatibility of the blends was observed in the melt and during cooling. The soluble blends were reheated and poured onto a 1/2" metal strip with a cotton wick and subjected to a horizontal and vertical flame test.

NOTE: A new procedure for pouring the blends onto the metal strip was introduced in order to get a consistent amount of wax on the strip for each sample. 'Walls' were made of tape to keep the wax from overflowing. 5g of the blends was used to just cover the strip. The thickness was between 1-2/16". (10g made the layer too thick 2-3/16").

APPENDIX 2
PREPARATION OF 11" x 22" PCM SOAKED PLASTERBOARD
FOR FIRE RETARDANCE TEST AT USG

Work Request: 860926-15-16
Performed By: Mary Galaska/Lucy Dang
Date: October 7-8, 1986

Procedure:

Four samples of plasterboard 11" x 22" were cut and dried in a vacuum for 24 hours. A dish of drierite was used to absorb any moisture. The weights of each were recorded.

The large porcelain tray was filled with 5000g of 45A and heated to 80°C. A red dye was used to track the PCM pickup. Metal supports were placed in the bath so that the plasterboard sheet would not rest on the bottom. When the wax reached 80°C, the sheet was placed in the tray and pushed down so that it would not float. After 5 minutes the sheet was turned over. After another 5 minutes, the sheet was removed, cooled, and reweighed. One of the duplicate sheets was rinsed with Methylene Chloride. The Methylene Chloride was allowed to evaporate before weighing. The PCM pickup was calculated and recorded. The sheets have been retained for later fire tests.

The procedure was repeated using a solution of 45A/BCL 462 in a ratio of 75/25 at 80°C. This solution was retained for later tests.

APPENDIX 3
THE EFFECT OF STEARIC ACID AND BUTYL STEARATE
ON PERCOLATION OF 45A IN PLASTERBOARD

Work Request: 860820-2 to 7

Performed By: Mary Galaska

Date: September 8, 1986

Procedure:

Ten 2" x 2" squares of plasterboard were cut and weighed. Five separate 200g melt mixed blends were prepared containing 45A (100%), 45A/butyl stearate (95/5), 45A/butyl stearate (90/10), 45A/stearic acid (95/5), and 45A/stearic acid (90/10). The blends were heated to 80°C before duplicate samples were immersed in each bath. One sample of each bath was removed at 5 minutes and the second at 10 minutes. PCM pickup vs. time in the bath was calculated. DSC scans were run on each bath.

MONTHLY PROGRESS REPORT NO. 5
CONTRACT NO. DE-FG03-86SF16308
COVERING OCTOBER, 1986

1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research, on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends".

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

In the first process, the PCM's (alkyl hydrocarbons) can be added directly into the wet mix of cementitious materials at concentrations up to 5% wt (cement) and 10% wt (plaster). However, considerable reduction in the strength properties of the cement and/or lengthening of the setting time is encountered. In one modification of this process, the cementitious products can also be made waterproof.

In the second process, the PCM's are first mechanically dispersed into rubbers, such as natural rubber, and plastics, such as polyethylene, using Banbury mixer or roll mill, at concentrations greater than 50% wt. These PCM "concentrates" can potentially be used directly, in sheet form, as floor or wall tiles and may be especially useful for retrofit use in building where they could be adhered to existing walls and floors.

In the third process the PCM is imbibed into small pellets of HDPE by swelling at elevated temperatures. The resulting small hard pellets contain up to 80% wt PCM, and should be easy to incorporate into the wet mix of cementitious materials with minimum reduction in strength properties.

The rubber or HDPE pellets from the second and third process above can potentially be used as an effective low-cost pellet bed heat exchanger; to heat or cool the air, or liquid medium, in solar passive hybrid applications.

In the fourth process, the PCM in liquid form is percolated directly into the open space in porous building materials (cement, plaster bricks). This process also has the attendant advantage that the porous products are simultaneously waterproofed. The process has obvious potential applications in waterproofing cement for other applications as well (i.e., highway bridge decks).

As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3). The building material will not burn. However, in process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard

after ignition will continue to burn slowly until the PCM is exhausted.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will initiate extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

The present month's work consists of the following:

1. To evaluate via DSC Analysis the thermal energy storage characteristics of Witco 45A and K-61 containing 20% and 25% wt. of Ethyl Corp. fire retardant BCL-462.
2. To permeate NP-15 into crosslinked Marlex 6006 HDPE, determine the PCM pickup and thermal energy storage properties.
3. Evaluate the 45A PCM uptake in Marlex 6006 powder that has been irradiation crosslinked to total doses of 4, 5, 6, 7 and 8 m-rads in nitrogen.
4. Evaluate the effect of annealing on the thermal energy storage properties of paraffin PCMs.
5. Demonstration experiments for Matsushita personnel.

3. TECHNICAL DESCRIPTION OF CURRENT RESEARCH

3.1 To Evaluate Via DSC Analysis the Thermal Energy Storage Characteristics of Witco 45A and K-61 Containing 20% and 25% Wt. of Ethyl Corporation Fire Retardant BCL-462

Our August 1986 report describes the solubility of the Ethyl Corporation fire retardant BCL-462 in phase change materials. This opens up the possibility of simultaneous introduction of the fire retardant-PCM combinations into substrates, e.g. HDPE beads, plasterboards, etc. The purpose of the present investigation is to make sure that the thermal energy storage properties of the PCM remains unaltered by mixing with the fire retardant, BCL-462. Table 1 presents the data for Witco 45A and K-61 PCMs, with 20 and 25% (by wt.) concentrations of BCL-462. A small lowering of T_m and T_c is observed. However, the fire retardant does not seem to affect the crystallization pattern of the PCM and the extrapolated value of ΔH_f and ΔH_c approaches that of the pure material. Small deviation of the 100% extrapolated value from the ΔH_f and ΔH_c of pure PCMs probably represent slight nonuniformity in the samples. Figures 1 and 2 compare the DSC curves at 20 and 25% by wt. BCL-462 for both Witco 45A and K-61. The characteristic curves of the parent PCM are retained in both cases. Figure 3 shows the DSC curve for BCL-462.

3.2 To Permeate NP-15 Into Crosslinked Marlex 6006 HDPE, Determine the PCM Pickup and Thermal Energy Storage Properties

The PCM, NP-15, melts slightly above the melting point of ice (7°C) and is a prospective candidate for applications such as bridgedeck deicing, cold packing for transportation, etc. Although our earlier experiments have established that a large amount of other PCMs (80-90%) can be permeated into HDPE pellets for varied applications, this has not been confirmed with NP-15. The purpose of the present experiment was to obtain such data for NP-15 PCM. The procedure for swelling is described in Appendix 1. Table 2 presents the swelling data after washing the swollen samples with various solvents. About 80% NP-15 is retained in

TABLE 1
THERMAL ENERGY STORAGE CHARACTERISTICS OF
WITCO 45A AND K-61 CONTAINING 20% AND 25% WT. OF
ETHYL CORPORATION FIRE RETARDANT BCL-462

Sample Identification and Composition	T _m (°C)	T _c (°C)	T _m -T _c (°C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)	Extrapolated to 100%	
						ΔH_f (cal/gm)	ΔH_c (cal/gm)
Witco 45A, BCL-462 (55 gallon drum)	100/0	30.7	23.8	6.9	42.1	42.9	---
	80/20	27.8	22.3	5.5	34.8	36.7	45.9
	75/25	29.1	21.9	7.2	31.4	33.8	45.0
Witco K-61, BCL-462 Received July 1986	100/0	26.4	20.2	6.2	47.5	46.4	---
	80/20	24.3	17.2	7.1	36.4	37.9	47.3
	75/25	24.1	15.7	8.4	33.8	36.1	48.1
Saytex BCL-462	72.0	---	---	14.3	---	---	---

Sample: 45A/ BCL / 80/20
 Size: 4.08 mg
 Method: DSC-MELT
 Comment: 10°C/Min NEW BLEND

DSC

File: RUN103
 Operator: GAL...A
 Run date: 11/05/88 14:20

Sample: 45A/ BCL 462 75/25
 Size: 5.88 mg
 Method: DSC-MELT
 Comment: 10°C/Min NEW BLEND

DSC

File: RUN1039.02
 Operator: GALASKA
 Run date: 11/06/88 10:41

Figure 1. Thermal Energy Storage Properties of Witco 45A Containing 20 and 25% Concentration of BCL-462 Fire Retardant.

Sample: K-61/BCL 462 80/20
 Size: 4.28 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A:RUN1002.02
 Operator: LUCY/MARY
 Run date: 10/07/88 12:42

Sample: K-61/BCL 462 75/25
 Size: 5.28 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: RUN1003.02
 Operator: ED DYKE
 Run date: 10/08/88 09:42

Figure 2. Thermal Energy Storage Properties of Witco K-61 Containing 20 and 25% Concentration of BCL-462 Fire Retardant.

Sample: BCL 462
 Size: 4.51 mg
 Method: DSC-TG
 Comment: 10°C/Min

DSC

File: RUN1030.01
 Operator: GALASKA
 Run date: 11/04/88 15:42

Figure 3. DSC Melting Curve of BCL-462 Fire Retardant.

TABLE 2
 WASHING OF SWELLED MARLEX 6006 HDPE
 WITH DIFFERENT SOLVENTS

Composition of the Swelling Bath	% Weight PCM After Washing With				
	Ethanol	Methanol	Eth. + Meth. 50:50	MEK	Warm Water +0.1% Joy
NP-15: Santowhite Powder 99:1	83.1	84.8	83.2	81.6	85.9
NP-15: BCL-462: Santowhite Powder 74:25:1	76.8	81.7	84.9	82.7	--

HDPE after washing. The same experiment was also repeated with a sample containing 25% (by wt.) BCL-462 fire retardant. The fire retardant does not seem to affect the weight gain of PCM into the HDPE pellets, although part of the weight gain may be due to the fire retardant. Different solvent washes do not seem to materially alter the weight gain. Warm water/detergent (0.1% Joy) wash seems to give the highest retained weight, consistent with the lower solubility of the hydrocarbon PCM in this solvent. DSC analyses of these samples will be reported later.

3.3 Evaluate the 45A PCM Uptake in Marlex 6006 Powder That Has Been Irradiation Crosslinked to Total Doses of 4, 5, 6, 7 and 8 m-rads Nitrogen

Our final report for DE-AC03-82CE30755, March 1986, describes unsuccessful attempts to contain hydrocarbon PCM by swelling in very small particle size crosslinked HDPE powders. Swollen beads containing 80-90% PCM are, however, easily obtained with much larger crosslinked HDPE pellets. It was surmised at that time that 10 m-rad gamma radiation which was used, possibly crosslinked the powder too highly. In order to test this hypothesis additional powder samples were sent to Neutron Products to expose them to smaller dosages. Table 3 shows the DSC analyses for HDPE powders crosslinked by 4, 5, 6, 7 and 8 m-rad gamma rays. No substantial variation of T_m and T_c are observed. T_{m-c} is increased slightly, while ΔH_f and ΔH_c are apparently unchanged by crosslinking with 4-8 m-rad gamma irradiation. The very high ΔH_f and ΔH_c values of the uncrosslinked powder (~55 cal/gm) is unexpectedly high, and is being rechecked.

Appendix 2 describes the procedure for swelling the powders and subsequent washing. It is apparent that PCM content of 88-90%, determined by weight gain, are obtained by swelling. Table 4 presents the DSC analysis of these swelled powders. Although DSC data shows substantial amount of PCM in the powders (66-77%), the amount is lower than that indicated by weight gain. This is apparent in "extrapolated to 100%" values for ΔH_f and ΔH_c the last

TABLE 3
THERMAL ENERGY STORAGE PROPERTIES OF
MARLEX 6006 POWDER, CROSSLINKED TO
DIFFERENT GAMMA INTENSITY IN NITROGEN

Sample Identification and Composition	T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)
Marlex 6006 Powder Crosslinked at 8 m-rad Gamma	132.2	115.3	16.9	44.0	42.4
Marlex 6006 Powder Crosslinked at 7 m-rad Gamma	133.0	115.5	17.4	45.1	44.9
Marlex 6006 Powder Crosslinked at 6 m-rad Gamma	133.3	115.8	17.5	45.8	45.8
Marlex 6006 Powder Crosslinked at 5 m-rad Gamma	133.9	115.9	17.9	45.4	46.0
Marlex 6006 Powder Crosslinked at 4 m-rad Gamma	134.4	116.2	18.2	45.9	46.9
Marlex 6006 Powder Uncrosslinked	134.1	118.8	15.3	54.8	56.5

TABLE 4

DSC ANALYSIS OF MARLEX 6006 POWDER CROSSLINKED
TO DIFFERENT GAMMA RAY INTENSITY IN NITROGEN
AND SUBSEQUENTLY SWELLED IN 45A AT 150°C FOR TWO HOURS

Sample Identification and Composition		T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)	Extrapolated to 100%	
							ΔH_f (cal/gm)	ΔH_c (cal/gm)
4 m-rad Gamma	45A Wax	30.9	23.5	7.4	29.9	28.8	33.9	32.6
	HDPE Powder	110.0	97.6	12.4	5.4	5.2	46.2	44.5
5 m-rad Gamma	45A Wax	29.9	23.3	6.6	25.9	24.2	29.3	27.4
	HDPE Powder	109.4	97.4	11.0	6.0	5.2	51.4	44.5
6 m-rad Gamma	45A Wax	30.5	23.5	7.0	30.5	29.5	33.8	32.7
	HDPE Powder	108.6	96.5	12.1	4.5	4.6	45.6	46.7
7 m-rad Gamma	45A Wax	31.9	23.6	8.3	34.3	34.4	38.5	38.6
	HDPE Powder	109.8	96.3	13.4	4.6	4.5	41.9	41.0
8 m-rad Gamma	45A Wax	32.0	24.3	7.6	29.0	23.4	32.4	26.2
	HDPE Powder	109.7	96.5	13.2	5.0	5.0	47.2	47.2
Witco 45A Wax		30.7	23.8	6.9	42.1	42.9	42.1	42.9
Uncrosslinked Marlex 6006 Powder		134.1	118.8	15.3	54.8	56.5	---	---

column of Table 4. This may be due to the nonuniformity of swelling and the fact that DSC only deals with a minute fraction of the sample. However, the reason for the failure of the earlier experiments was due to the MEK washing, which removed all the PCM permeated at high temperature. This was resolved and reported in our August 1986 report. The DSC data in Table 4 which uses methanol for washing further confirms our earlier observation. Thus, we are able to contain substantial portions of the PCM in small particle size HDPE. These small particles are not expected to affect the mechanical properties of the cementitious building materials as adversely as the large size HDPE pellets. Interestingly, there is no orderly variation of swelling with intensity of crosslinking of the HDPE powder within the 4-8 m-rad gamma range studied.

Figure 4 shows the DSC graph of uncrosslinked Marlex 6006 powder. Figure 5 compares the DSC graphs of the swollen and the unswollen 8 m-rad crosslinked powders. Note the double peak for the swollen Marlex 6006 powder.

3.4 Evaluate the Effects of "Annealing" on the Thermal Energy Storage Properties of Paraffin PCMs

In measuring the thermal energy storage properties of semi-crystalline polymers by DSC, an annealing step is often recommended. This is to destroy the prehistory of the sample and make sure that the sample is fully crystallized before the subsequent melting transition is recorded. Although our past data indicated that this step is not necessary for the normal alkane PCMs, an experiment was designed to verify this with 99% pure octadecane. The procedure for annealing is described in Appendix 3.

The data in Table 5 and DSC curves in Figure 6 do not show any significant difference between the annealed and unannealed sample. This is ascribed to the very fast rate of crystallization for the n-alkane hydrocarbons, so that the crystallization is complete during the time allowed for cooling the sample at 10°C/min. The data reported earlier (August 1986 report) also

Sample: MARLEX POWDER (UNCROSSLINKED)

Size: 4.16 mg

Method: DSC-MELT

Comment: USED IN EPDM

DSC

File: RUN0887.01

Operator: ED DYKE

Run date: 07/28/86 11:20

Figure 4. DSC Analysis of Unswollen Marlex 6006 Powder.

Sample: MARLEX 6006 POWDER
 Size: 3.82 mg
 Method: DSC-MELT
 Comment: BAG #5- 8.04 MR 10C/MIN

DSC

File: RUN1013.03
 Operator: ED DYKE
 Run date: 10/15/88 09:59

Sample: 6006POWDER/8MRD/45A/SANTOWHITE
 Size: 5.44 mg
 Method: DSC-MELT
 Comment: SWELLED 2HR@150C 10C/MIN

DSC

File: RUN0985.02
 Operator: LUCY
 Run date: 09/25/88 14:31

Figure 5. DSC Analysis of Swollen and Unswollen Crosslinked Marlex 6006 Powders.

Sample: HUMPHREY, C18 99%
 Size: 4.87 mg
 Method: DSC-ANNEALING
 Comments: ANNEALING
 Sum scale
 as untreated

DSC

File: E:RUN1020.01
 Operator: ED DYKE
 Run date: 10/22/88 10:28

Sample: n-OCTADECANE 99%
 Size: 3.23 mg
 Method: DSC-MELT 2°C/MIN
 Comments: 2°C/MIN

DSC

File: A:RUN0759.02
 Operator: ED DYKE
 Run date: 08/10/88 08:57

Figure 6. DSC Curve of Annealed and Unannealed n-Octadecane.

showed no substantial variation of thermal energy storage when the heating rate is varied between 2 and 10°C/min.

3.5 Demonstration Experiments for Matsushita Personnel

During October 16-21, 1986, three technical and management personnel visited our laboratory to discuss a option-licensing arrangement, and to observe some laboratory demonstrations. Three experiments were carried out in their presence. These were:

- (a) Permeation of Witco 45A PCM into Marlex 6006 pellets that have been crosslinked by 10 m-rad gamma irradiation. The procedure is reported in Appendix 4.
- (b) DSC analyses of PCM-permeated, crosslinked Marlex 6006 HDPE pellets. The procedure is reported in Appendix 5 and the results in Table 6. Figure 7 shows the DSC analysis.
- (c) Percolation of Witco 45A PCM, and 45A/BCL-462 separately into 6" x 6" samples of commercial plasterboards. The procedure is described in Appendix 6. The 6" x 6" plasterboards were taken to Japan by Matsushita personnel. DSC analyses of the portion taken out of these boards will be reported later.

4. CONCLUSIONS

- 1. Soluble fire retardant BCL-462, does not have significant effect on thermal energy storage properties of Witco 45A and K-61 PCMs.
- 2. About 80-85% NP-15 is retained in swollen Marlex HDPE pellets after washing with different solvents. Retained PCM is highest in water/detergent (0.1% Joy) washing of permeated pellets.
- 3. Gamma ray irradiation dosages between 4-8 m-rad do not seem to have significant effect on swelling or thermal energy storage parameters of Marlex 6006 powder in Witco 45A PCM.
- 4. DSC analysis of the swollen Marlex 6006 powder shows somewhat less PCM in the powder than indicated by weight gain.
- 5. Annealing does not change the thermal energy storage properties of alkyl hydrocarbon PCMs.

TABLE 5
EFFECT OF ANNEALING ON THERMAL ENERGY STORAGE
PROPERTIES OF HUMPHREY 99% PURE OCTADECANE
AT 2°C/MIN. RATE OF TEMPERATURE CHANGE

Sample Identification and Composition	T _m (°C)	T _c (°C)	T _m -T _c (°C)	ΔH _f (cal/gm)	ΔH _c (cal/gm)
Humphrey Octadecane 99% Pure Unannealed	28.0	24.4	3.6	58.4	59.2
Humphrey Octadecane 99% Pure Annealed	29.0	24.7	4.3	56.6	56.7

TABLE 6
ANALYSIS OF MARLEX 6006, SWELLED 4 HRS.
AT 150°C IN WITCO 45A WAX TO DEMONSTRATE THE DSC
PROCEDURE TO MATSUSHITA PERSONNEL

Sample Identification and Composition	T _m (°C)	T _c (°C)	T _m -T _c (°C)	ΔH _f (cal/gm)	ΔH _c (cal/gm)	Extrapolated to 100%	
						ΔH _f (cal/gm)	ΔH _c (cal/gm)
Witco 45A Wax in Swelled HDPE* HDPE in Swelled Marlex 6006	30.8	22.7	8.1	35.9	38.7	44.0	47.4
	112.0	100.0	12.0	4.8	4.5	26.2	24.5

* Percent 45A by wt. was 81.66.

5. IMMEDIATE FUTURE PLANS

1. To determine the thermal energy storage properties of microencapsulated PCMs via DSC analysis.
2. Develop the experimental techniques and procedures to implement the USG laboratory process for preparing gypsum plasterboards.
3. Melt spraying hardened wax beads from 45A/Fortex, 80/20; 45A/Shell wax 300, 80/20; 45A/Shell wax 400, 80/20; and 45A/BCL-462, 80/20.
4. Evaluate the thermal energy storage properties of permeated and nonpermeated samples of crosslinked HDPE, PP and the PCM used (Paraffin 115) as submitted by Matsushita.
5. Analyze by DSC the HDPE samples imbibed with Witco 45A, which was made for demonstration during Matsushita visit.
6. Analyze by DSC the samples of plasterboards, percolated with 45A that were made during Matsushita visit.
7. To evaluate the stability of PCMs to repeated thermocycling between the temperatures of 0-50°C.
8. To prepare and evaluate the fire retardance of crosslinked HDPE pellets that were permeated with Humphrey C-18/BCL-462 solution in different ratios.

APPENDIX 1
PROCEDURE FOR SWELLING MARLEX 6006
PELLETS IN NP-15

Work Order: 861015-7 and 8
Performed By: Mary Galaska/Lucy Dang
Date: October 24, 1986

Procedure:

(1) 371.3 grams of NP-15 wax and 3.7g of Santowhite powder or (2) 370 grams of NP-15 wax, 125 grams of BCL-462 and 5 grams of Santowhite powder (NP-15/BCL-462/Santowhite powder = 74/25/1) were weighed into a glass beaker and heated to 150°C with constant stirring. 25g of Marlex 6006 pellets that have been crosslinked with 10 m-rad powder was poured into the wax and heated at 150°C for two hours. Five batches of Ethanol, Methanol, MEK, 50% of Methanol and 50% Ethanol, and tap water mixed with 0.1% Joy Soap were used to wash the samples. The samples were cooled, washed 3X in a beaker with excess of Ethanol, Methanol, MEK, Methanol mixed with Ethanol or tap water mixed with 0.1% Joy Soap (warmed to 50°C) and filtered through a buchner funnel with a filter paper. They were washed again in the funnel with more warm solvent. The samples were air dried in a hood overnight. The samples will be analyzed by DSC for thermal energy storage.

APPENDIX 2
PROCEDURE FOR SWELLING MARLEX 6006
POWDER WITH 45A

Work Order: 860821-35 thru 40
Performed By: Mary Galaska/Lucy Dang
Date: September 12, 1986

Procedure:

100 grams of Witco 45A wax and 1g of Santowhite powder were weighed into a glass beaker and heated to 150°C with constant stirring. 10g of ground irradiation crosslinked 4 m-rad powder was poured into the wax and heated to 150°C for 2 hours. The samples were cooled, washed in a beaker with excess methanol (warmed to 50°C and filtered through a Buchner funnel with a filter paper. They were washed again in the funnel with more warm methanol. The samples were air dried in a hood overnight. The sample will be analyzed by DSC for thermal energy storage.

4 mrad	Original wt. 10g Final wt. 85.59g % wt. gain = $\frac{85.59 - 10}{85.59} = 58.32\%$
5 mrad	Original wt. 10g Final wt. 85.62g % wt. gain = $\frac{85.62 - 10}{85.62} = 88.32\%$
6 mrad	Original wt. 10g Final wt. 101.46g % wt. gain = $\frac{101.46 - 10}{101.46} = 90.14\%$
7 mrad	Original wt. 10g Final wt. 91.16g % wt. gain = $\frac{91.16 - 10}{91.16} = 89.03\%$
8 mrad	Original wt. 10g Final wt. 94.46g % wt. gain = $\frac{94.46 - 10}{94.46} = 89.41\%$

APPENDIX 3
DSC METHOD OF ANNEALING

1. Heat 10°C/min. to 45°C
2. Cool 10°C/min. to 5°C
3. Hold isothermally at 5°C for 30 min.
4. Cool 10°C/min. to -20°C
5. Start data collection
6. Heat 2°C/min. to 45°C
7. Hold isothermally at 45°C for 5 min.
8. Cool 2°C/min. to -20°C
- 9 Repeat steps 1 through 8 two more times for a total of three runs.

APPENDIX 4
PROCEDURE FOR SWELLING MARLEX 6006 PELLETS
IN 45A DURING DEMONSTRATION TO MATSUSHITA,
OCTOBER 21, 1986

Work Request No.: 861021-3
Performed By: Mary Galaska/Lucy Dang
Date: October 21, 1986

Procedure: (The PCM/pellet ratio was increased to 14/1 so the pellets would have more room to stir.)

350g of 45A wax and 3.5g of Santowhite powder was weighed into a glass beaker and equipped with a magnetic stirrer. The beaker was placed in a hood and heated to 150°C. 25g of Marlex 6006 HDPE pellets (10 m-rad) was poured into the hot wax and stirred for 4 hours. Small samples (3-5 pellets) were taken at 0, 5 min., 15 min., 30 min., 1 hr., 2 hrs., 3 hrs., and 4 hrs. and washed three times with 50°C MEK and filtered. After 4 hours, all remaining pellets were strained from the bath and washed three times with 50°C MEK and filtered. All samples were allowed to dry in a hood overnight. DSC analysis will be run on each sample using the standard PCM method with a heating and cooling rate of 10°C/min.

DSC results will be reported when completed. Also a graph of PCM uptake vs. time will be reported when DSC results are complete.

APPENDIX 5
DSC ANALYSIS OF MARLEX 6006 PELLETS
FOR MATSUSHITA

Work Request No.: 861021-4
Performed By: Mary Galaska
Date: October 21, 1986

Procedure:

A Marlex 6006 HDPE pellet from a previous swelling experiment (4 hrs. @ 150°C in 45A) was selected and a DSC sample was cut from the center portion. A DSC analysis was run using the standard PCM method with a heating and cooling rate of 10°C/min.

APPENDIX 6
DEMONSTRATION OF PERMEATION OF PLASTERBOARD
IN 45A FOR MATSUSHITA

Work Request No.: 861021-1 and -2
Performed By: Mary Galaska
Date: October 21, 1986

Procedure:

Two 6" x 6" squares of plasterboard were cut and weighed. 1800g of 45A wax was weighed into a metal pan and 0.1% red dye was added. The pan was placed on a hot plate and heated to 80°C. Two metal strips were placed on the bottom of the pan to keep the plasterboard from resting on the bottom. One of the samples was immersed in the bath for 5 minutes on each side. After the 10 minute soak, the sample was removed and allowed to dry, then weighed to determine % PCM pickup. The amount of wax absorbed into the first sample was determined in order to calculate the amount of fire retardant BCL-462 to add to the bath to make a 75/25 ratio of 45A/BCL-462. 569g of BCL-462 was added to the bath and stirred until it was completely dissolved. The second sample was then immersed for 10 minutes (5 minutes on each side). After 10 minutes, the sample was removed from the bath, allowed to dry and weighed. Some of the plaster was scraped off for later DSC analysis. The samples were given to the visitors from Matsushita.

#1 45A
Initial wt. = 193.52g
Final wt. = 285.5g
% PCM wt. gain = 32.22%

#2 45A/BCL-462(75/25)
Initial wt. = 194.04g
Final wt. = 301.85g
% PCM wt. gain = 35.70%

MONTHLY PROGRESS REPORT NO. 6
CONTRACT NO. DE-FG03-86SF16308
COVERING NOVEMBER, 1986

1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research, on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends".

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

In the first process, the PCM's (alkyl hydrocarbons) can be added directly into the wet mix of cementitious materials at concentrations up to 5% wt (cement) and 10% wt (plaster). However, considerable reduction in the strength properties of the cement and/or lengthening of the setting time is encountered. In one modification of this process, the cementitious products can also be made waterproof.

In the second process, the PCM's are first mechanically dispersed into rubbers, such as natural rubber, and plastics, such as polyethylene, using Banbury mixer or roll mill, at concentrations greater than 50% wt. These PCM "concentrates" can potentially be used directly, in sheet form, as floor or wall tiles and may be especially useful for retrofit use in building where they could be adhered to existing walls and floors.

In the third process the PCM is imbibed into small pellets of HDPE by swelling at elevated temperatures. The resulting small hard pellets contain up to 80% wt PCM, and should be easy to incorporate into the wet mix of cementitious materials with minimum reduction in strength properties.

The rubber or HDPE pellets from the second and third process above can potentially be used as an effective low-cost pellet bed heat exchanger; to heat or cool the air, or liquid medium, in solar passive hybrid applications.

In the fourth process, the PCM in liquid form is percolated directly into the open space in porous building materials (cement, plaster bricks). This process also has the attendant advantage that the porous products are simultaneously waterproofed. The process has obvious potential applications in waterproofing cement for other applications as well (i.e., highway bridge decks).

As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3). The building material will not burn. However, in process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard

after ignition will continue to burn slowly until the PCM is exhausted.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will initiate extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

The present month's work consists of the following:

1. Studies on fire retardance of PCMs. The fire retardance studies include the following specific aspects:
 - (a) DSC analysis of Witco 45A/BCL-462 fire retardant at 75/25 ratio at 2° and 10°C per minute rate of temperature change.
 - (b) DSC analysis of thermal energy storage of fire retardant plasterboard. The plasterboard sheet (11" x 22") were percolated with a red-dyed solution of 45A and 45A/BCL-462.
 - (c) Evaluate the fire retardance of plasterboard specimens that have been percolated with different fire retardant combinations.

2. Studies on containment of phase change material. These include:

- (a) DSC analysis of five samples of PCM that were microencapsulated at Eurand America.
 - (b) DSC evaluation of permeated samples of crosslinked HDPE, polypropylene and starting paraffin 115, submitted by Matsushita.
 - (c) To examine ethanol as a solvent for washing the crosslinked polyethylene powder, permeated with Witco 45A PCM.
 - (d) Explore the possibility of incorporation of PCMs into Hypalon 48 by mill mixing.
3. DSC analysis of thermal energy storage properties of a C₃₆ hydrocarbon PCM.

3. TECHNICAL DESCRIPTION OF CURRENT RESEARCH

3.1 Studies on Fire Retardance of PCMs

The study on fire retardance of PCMs consists of the following aspects:

- (a) Identification of a fire retardant that is soluble in the PCM.
- (b) DSC analysis of the thermal energy storage parameters of the PCM/fire retardant (FR) combination.
- (c) Incorporation of the PCM/FR combination into different building materials.
- (d) DSC analysis of the incorporated PCM/FR.
- (e) Determine fire retardance of the composite.

Ethyl Corporation fire retardant BCL-462 was mentioned in our earlier reports to be soluble in hydrocarbon PCMs in all proportions. This fire retardant (FR) was therefore selected for further studies. The following aspects were covered this month.

3.1.1 DSC Analysis of Witco 45A/BCL-462 Fire Retardant at 75/25 Ratio at 2°C and 10°C Per Minute Rate of Temperature Change

Our August, 1986 report discloses the identification of Ethyl Corporation fire retardant, BCL-462, which is soluble in hydrocarbons PCMs in all proportions. Last month's (October, 1986) report shows that the thermal energy storage characteristics of Witco 45A and K-61 PCMs remain unaltered by the incorporation of BCL-462. The data presented in Table 1 and Figures 1 and 2 describe the effect of heating and cooling rate on the thermal energy storage parameters of 45A/BCL-462 (75:25) combination. The data (Table 1 and Figure 1) show a small decrease of ΔH_f , ΔH_c and T_m and an increase of T_c at 2°C/min. The same characteristic changes were observed for other PCMs and are mentioned in our August, 1986 report. Figure 2 shows the characteristic convergence of T_m and T_c , as reported for other PCMs (August, 1986). Our August, 1986 report also shows a linear relationship for T_m and T_c vs. rate of heating/cooling at several rates (2, 5, 10 and 20°C/min.) for all the PCMs. Therefore, a straight line drawn from only two data points in Figure 2 may be justified. Figure 2 shows very little difference (<1.5°C) of T_m and T_c at zero rate of heating, indicating very little supercooling. The ΔH_f and ΔH_c data show that the thermal energy storage potential of the Witco 45A PCM is unaffected by blending with the soluble fire retardant, BCL-462.

3.1.2 DSC Analysis of Thermal Energy Storage of Fire Retardant Plasterboard

Our September report describes the preparation of fire retardant phase change material that was red dyed and permeated into 11" x 22" sheets of plasterboard for later fire retardance testing by USG. The fire retardant composition consisted of Witco 45A/BCL-462 in the ratio of 75/25. In addition, one of the permeated 11" x 22" plasterboard sheets was rinsed with methylene chloride. Two 11" x 22" plasterboards, both permeated in 45A, but one rinsed with methylene chloride served as controls.

Table 2 shows the DSC analysis of these plasterboards. The 45A control and the fire retardant plasterboard (Samples A and C) both show calculated PCM from DSC comparable to their weight gain. For C, 75% of the weight gain is considered to be due to the PCM. The rest of the weight gain is due to the fire retardant. The other two samples (B and D) show a slight depletion of the PCM by rinsing with methylene chloride.

T_m and T_c are slightly lower for C and D, the samples that contain the fire retardant BCL-462. The shape of the curve (Figure 3) remains unaltered. However, the solid/solid transition for all percolated samples occurs at a lower temperature, as compared to Witco 45A by itself (7.4°C vs. 12°C). This conforms to our observation (August, 1986 report) that the solid/solid transition temperature is more susceptible to extraneous material than the melting peak temperature.

3.1.3 Evaluate the Fire Retardance of Plasterboard Specimens That Have Been Percolated With Different Fire Retardant Combinations

In these experiments four melted PCM or liquid baths of the following compositions were prepared: (a) 45A (100%); (b) 45A/BCL-462 (75/25); (c) methylene chloride/BCL-462 (50/50); and (d) methylene chloride (100%).

Four 2-inch square plasterboard samples were permeated in bath (a), two in (b), and one each in (c) and (d) for 10 minutes. After the samples were dried and weight gain calculated, three samples from bath (a) were again immersed, one each, in baths (b), (c) and (d) for another 10 minutes and dried and reweighed. Similarly, one sample from (b) was reimmersed in bath (c). The details of this method are presented in Appendix 1.

The results for the weight gains are presented in Table 3. No weight gain is observed for methylene chloride as would be expected. Since methylene chloride does not stay on, 39.8% weight gain observed for methylene chloride/BCL-462 (50:50), should be for BCL-462 alone. Slightly higher wt. gain (39.8%) than for Witco 45A (34.7% avg.) must be due to higher density of

the fire retardant. However, the relative weight gains are not proportional to the densities of 45A (0.8) and BCL-462 (2.27). This indicates that the fire retardant may not be able to get into the smaller pores that are easily accessible by 45A.

The second immersion does not seem to increase the weight gain after 48 hours, although some gain is observed immediately afterwards and after 24 hours drying in a dessicator. It is, nowever, possible that the surface properties of the samples are changed by the second immersion.

Table 4 describes the horizontal flame test pattern of the samples made in Table 3. The Sample #32 dipped in 45A, ignites easily, burns for almost 10 minutes producing black smoke and the flame travels through the sample. When a similar sample (#17) is dipped in bath B (45A/BCL-476, 75/25) no improvement of the above characteristics are observed. Evidently, the sites are already occupied and little, if any, BCL-462 sticks to the sample.

The Sample #19, soaked in 45A (bath A) and subsequently in bath C (methylene chloride/BCL-462, 50/50) shows some improvement in fire retardance in all categories reported in Table 4. Since the weight gain (Table 3) does not change by the second immersion, some 45A may have been removed by the methylene chloride solvent and replaced by the fire retardant BCL-462. However, the improvement is only superficial, since the second ignition of the same sample shows poor fire retardance.

The sample #68, which was first soaked in 45A and subsequently in methylene chloride shows the same characteristics as sample #32. This would, however, be expected, since methylene chloride is driven off by the drying step.

The Sample #15, which was soaked in bath B (45A/BCL-462, 75/25), shows improvement in all categories, as expected. However, the second time ignition is easier, probably due to the depletion of BCL-462. A similar sample #52, subsequently soaked in bath C (methylene chloride/BCL-462, 50:50) shows marked improvement in fire retardance. Again, the weight gain (Table 3)

does not increase. Therefore, this improvement must be due to depletion of 45A and its partial replacement by BCL-462. This postulation needs to be confirmed by DSC analysis.

Finally, samples #10 and #9 did not ignite. This would be expected from their bath composition.

3.2 Studies on Containment of Phase Change Material

We continued the work on containment of PCM in different substrate and evaluation of their thermal energy storage properties. This month's work includes the following further evaluation.

3.2.1 DSC Analysis of Five Samples of PCM That Were Microencapsulated at Eurand America

Our September, 1986 report includes a DSC analysis of the samples of PCMs that were melt mixed with butyl stearate and BCL-462 fire retardant (Table 10, September 1986 report). This month we have reproduced these data in Table 5, along with the DSC analyses of microencapsulated samples. The general procedure for microencapsulation is reproduced from the brochure of Eurand America in Appendix 2. Further details available in Patent literature (U.S. Patent No. 3,341,466, 12 September 1967, NCR Corporation).

If we compare the data for melt mixed blends containing 10% wt. butyl stearate with those of the reference neat PCM samples, it is evident that the calculated percent PCM (last column) exceeds the actual composition (Column 1) by about 5-7%. This is probably due to the contribution of butyl stearate which has a ΔH_f and ΔH_c of around 36 cal/g (Table 10, September 1986 report).

The microencapsulated samples of 45A and Humphrey Technical Grade octadecane shows ΔH_f and ΔH_c values which are between 75% to 85% of the pure material. The rest is presumed to be the polymeric wall layer from microencapsulation. Again, the blends containing butyl stearate retains a higher proportion of the theoretical ΔH_f and ΔH_c values (90-99%). Evidently, this is

due to the contribution from butyl stearate transitions, as was also observed in non-capsulated melt blends (Table 5).

Another feature of the encapsulated PCM, is slightly higher T_m and slightly lower T_c as compared to the pure material. This results in $(T_m - T_c)$ values of around 12°C, which is slightly higher than that of the pure material (5-7°C). Figures 4 to 8 show the DSC curves from these encapsulated materials.

3.2.2 DSC Evaluation of Permeated and Unpermeated Samples of Crosslinked HDPE, Polypropylene and Starting Paraffin 115, Submitted by Matsushita

As mentioned in our October, 1986 report, during October 16-21, 1986, three technical and management personnel from Matsushita, Japan visited our laboratory to discuss an option-licensing arrangement. They had brought in with them some samples of peroxide and silane crosslinked low and high density polyethylene as well as polypropylene. These were swelled for different times and temperatures in a paraffin hydrocarbon PCM, which they call "Paraffin 115".

Table 6 shows the data for DSC analysis of some of these samples and Figures 9-15, illustrates their DSC curves. Paraffin 115 has reasonable thermal energy storage capacity in the range of 48 cal/g. However, its relatively high T_m and T_c outside the normal comfort range makes it unsuitable for heating or cooling of residential and commercial buildings. Also, Figure 9 shows multiple solid/solid transition indicating noncompatible components. This is very much different from the Witco commercial hydrocarbons used by us. This may also explain their experience that part of the hydrocarbon is lost by oozing and by repeated thermocycling. The multiple solid/solid transitions are also evident in swelled samples in Figures 13 to 15.

The low density polyethylene sample which was swelled for 30 minutes at 151°C has a lower paraffin content, as calculated from DSC ΔH_f and ΔH_c , than that calculated from weight gain. The composition from weight gain and DSC for the other two samples, which was run 60 minutes and 120 minutes, agrees very

well. This is similar to our experience that lower swelling time tends to make the samples nonuniform. Also, the lowering of T_m and T_c for the swelled polymers as reported in Table 6 is similar to our experience. However, the lowering of T_m is much more (34°C) for polypropylene than for either HDPE (17°C) and LDPE (12°C). Unswelled and swelled polypropylene have also the $T_m - T_c$ of 43°C and 37°C, respectively. These values are much higher than any of the HDPE polymers studied by us.

3.2.3 To Examine Ethanol as a Solvent For Washing the Crosslinked Polyethylene Powder, Permeated with Witco 45A PCM

Containment of PCM in crosslinked polyethylene pellets, seems to be an option that has great promise. Although it works very well in HDPE pellets, we have not yet been quite successful in developing a full proof process with the small particle size HDPE powder. The problem seems to be that MEK, which is used as a solvent for pellets, is too good a solvent for normal hydrocarbon PCM and washes out a major portion of the swollen PCM. Several different solvents including water and methanol were attempted. These do not wash away the combined PCM but also leave enough at the surface to produce sticky particles. Thus the particles cling together and are not free flowing.

In the experiments described in Appendix 3. HDPE powders which are gamma irradiated to different intensities at the Neutron Products Lab, were swelled in 45A and the swelled powders washed in methanol. Attempts were then made to wash away the surface wax by extraction with ethanol, which is a better solvent. The results for the extraction (Table 7) show that a considerable portion of PCM is washed and is collected as soluble wax after filtration, making this procedure unsuitable.

The data in Table 7 show that the insoluble portion increases with the intensity of gamma irradiation from 4-6 mrad and then decreases at 7 and 8 mrad. The increase of insolubility with more crosslinking would be expected. The reason for the decrease at 7 and 8 mrad cannot be explained.

Table 8 shows the DSC analysis of the insoluble powders, extracted with ethanol. Again, the PCM contents of 7 and 8 mrad samples are rather low.

3.2.4 Explore the Possibility of Incorporation of PCMs Into Hypalon 48 by Mill Mixing

An attempt was made to incorporate Witco 45A and polyethylene glycol 600 into Hypalon 48 and Chemigum N600 (high nitrile NBR), respectively, by mill mixing. The PCMs were previously soaked into an inorganic fiber (calcium sodium metaphosphate) or oven dried Cab-O-Sil MS7D to facilitate incorporation. However, only a small portion of the PCM can be incorporated by mill mixing. The rolls become oily very early. The material and the polymer then slide past one another, instead of being incorporated. The roll mill incorporation idea was, therefore, abandoned. A Banbury mixer, used extensively in the rubber industry, was successfully employed in prior research for incorporating the PCMs into these rubbers; and will be further investigated in the future work.

3.3 DSC Analysis of Thermal Energy Storage Properties of a C₃₆ Hydrocarbon PCM

During our extensive work on "DSC Analysis of Crystalline Paraffinic Hydrocarbons for Thermal Energy Storage" (August, 1986 report), we asked for a sample of hexatriacontane (C₃₆H₇₄) which has just arrived. Table 9 and Figure 16 report the data and DSC curves, respectively. The T_m and T_c data fit into the curves drawn earlier correlating the melting and crystallization temperature with number of carbon atoms in the chain. Also, the heat of fusion of 64.1 calories/g has a perfect fit in the straight line correlating molar heat of fusion and number of carbon atoms in the paraffin chain. Interestingly, Figure 16 shows a transient liquid/liquid transition in both melting and crystallization curves in addition to the small solid/solid transition during melting. The existence of monoclinic, orthorhombic and hexagonal phases in C₃₆ hydrocarbon have been reported in literature from X-ray and nuclear magnetic resonance studies (Atkins, C.M.L. and Richardson,

M.J., Trans. Faraday Soc., 65 (559), 1749-63, 1969). The transient transition is due to extremely small free energy differences existing between the orthorhombic and monoclinic phases, which is often missed in many studies but is distinctly present in the DSC curves.

4. CONCLUSIONS

1. Witco 45A PCM with soluble fire retardant BCL-462 in 75/25 ratio should melt and freeze with very little supercooling at 0°C rate of heating.
2. The thermal energy storage potential of Witco 45A is unaffected by melt blending with the fire retardant BCL-462.
3. The relative weight gains for plasterboards, soaked in Witco 45A and BCL-462 in separate baths, are not proportional to their densities. This indicates that BCL-462 probably cannot gain access to smaller pores, easily accessible to 45A.
4. Plasterboards first soaked in melt blended 45A/BCL-462 (75/25) and then having a second percolation with methylene chloride/BCL-462 show the best fire retardant properties. Evidently, some 45A is washed away from the paper surface and is replaced by BCL-462 fire retardant.
5. Microencapsulated PCMs have slightly lower storage potential than melt mixed blends of the same composition, since a polymer wall layer is present in the microencapsulated PCM and not in the melt mixed blends. Also, $T_m - T_c$ is higher in the microencapsulated PCM than in the "neat" material.
6. Butyl stearate, if a part of the composition, adds to the thermal storage in addition to the hydrocarbon PCM present.
7. Crosslinked low density and high density polyethylene samples swelled with Paraffin 115 by Matsushita behaves the same way as crosslinked Marlex 6006 samples, swelled by Witco hydrocarbons PCMs with regard to T_m , T_c , ΔH_f and ΔH_c .
8. Crosslinked polypropylene swelled by Paraffin 115, show higher supercooling and a larger decrease in T_m of the polymer phase as compared to polyethylene.
9. Paraffin 115 has too high a T_m (50.6°C) and T_c (41.4°C) for use as phase change material for heating and cooling of residential and commercial buildings.

10. Hydrocarbon PCMs, swelled in calcium sodium metaphosphate fiber and Cab-O-Sil MS7D cannot be mill mixed into high nitrile and Hypalon 48 rubbers.
11. The thermal energy storage properties of hexatriacontane is consistent with those of other normal aliphatic hydrocarbons studied earlier.

5. IMMEDIATE FUTURE PLANS

1. To evaluate the stability of PCMs and PCM compositions to repeated thermocycling between -10 to 60°C.
2. Complete development of the experimental techniques and procedures to implement the USG laboratory process for preparing gypsum plasterboards.
3. Melt spraying hardened wax beads from 45A/Fortex, 80/20; 45A/Shellwax 300, 80/20; 45A/Shellwax 400, 80/20; and 45A/BCL-462, 80/20.
4. To prepare and evaluate the fire retardance of crosslinked HDPE pellets that were permeated with Humphrey C-18/BCL-462 solution in different ratios.
5. Percolate Humphrey C-18, and C-18/BCL-462 (75/25), into the 2" cubes of plaster; and determine the compressive strength and fire retardance of these specimens and comparable controls.
6. Determine the highest concentration of 45A PCM, percolated into plasterboard, that will not continue to burn after ignition.
7. Evaluate vacuum percolation of plasterboard and concrete (from a hollow building block) with NP-15 and 45A PCM.
8. Determine the thermal energy storage properties of NP-15 and water by DSC at a heating and cooling rate of 2°C/min.
9. To evaluate the thermal energy storage properties of PCMs 45A, 45A/BCL-462 (75/25), K-61, K-61/BCL-462 (75/25) and NP-15/BCL-462 (75/25) that were microencapsulated by Eurand-America.

APPENDIX 1
METHOD FOR PREPARING PLASTERBOARD SPECIMENS
THAT WERE PERCOLATED TWICE IN DIFFERENT BATHS

Eight 2-inch squares of plasterboard were cut and weighed. Four percolating baths were prepared. The first bath (A) contained 45A (100%) and was heated to 80°C. The second bath (B) contained 45A/BCL-462 (75/25) also heated to 80°C. The third (C) contained MeCl_2 /BCL-462 (50/50) heated to 40°C, and the fourth (D) contained MeCl_2 (100%) heated to 40°C. Four of the squares (#17, #32, #19, and #68) were placed in bath A for ten minutes (flipped at 5 min.). Two (#15 and #52) were placed in B for 10 min. (flipped at 5 min.). One (#10) was placed in C for 10 min. (flipped at 5 min.). The final sample (#9) was placed in bath D for 10 min. (flipped at 5 min.). When soaking was complete the samples were removed and immediately weighed for solution pickup. They were then placed in a desiccator and reweighed after 24 hours and 48 hours for solution retention.

Solutions B, C and D were reprepared and heated to their respective temperatures. One sample (#17) from bath A was placed in bath B for 10 min. (flipped 5 min.). Another bath A sample (#19) was placed in bath C for ten minutes (flipped at 5 min.). Finally, a third sample (#68) from bath A was placed in bath D for 10 min. (flipped at 5 min.). Then sample (#52) from bath B was immersed in bath C for 10 min. (flipped at 5 min.). Each sample was weighed immediately upon removal from a solution. The samples were then placed back into the desiccator and reweighed after 24 and 48 hours. The samples were then subjected to a horizontal flame test.

APPENDIX 2
DESCRIPTION OF MICROENCAPSULATION
AS PER EURAND AMERICA

The coacervation or phase separation processes (Figure 17) are capable of microencapsulating a large number of liquids, solids, solutions and dispersions of solids in liquids.

The batch type processes consist of three steps which are carried out with controlled physical mixing. Step One of the process involves the formation of three immiscible chemical phases: a liquid manufacturing vehicle, core material and the coating material (the coacervate). Step Two of the process consists of depositing the liquid polymer coating upon the core material. This is accomplished by controlled, physical mixing of the liquid coating material and the core material in the manufacturing vehicle and by chemical driving forces, such as sorption and spreading of the coating material at the core material-vehicle interface. Step Three of the process involves solidifying the coating, usually by thermal, crosslinking or dissolvent techniques, to form a self-sustaining microcapsule. If the microcapsules are to be used in powder form, subsequent drying operations such as spray, freeze, fluid bed, solvent or tray drying techniques are required.

APPENDIX 3
PROCEDURE FOR EXTRACTION OF CROSSLINKED
AND PERMEATED HDPE POWDER WITH ETHANOL

Work Order: 861014-7 thru -11

Performed By: Lucy Dang

Date: November 17, 1986

Procedure:

35 grams of the samples of crosslinked powder 4, 5, 6, 7 and 8 mrad that were permeated with Witco 45A and washed with methanol were weighed into separate glass beakers. 250 grams of methanol were added and heated on a hot plate to 50°C for two hours with constant stirring and ventilation. The samples were filtered through a buchner funnel with a filter paper. The insoluble powders were filtered off and air dried in a hood overnight. The solvent was allowed to evaporate. The insoluble powder was analyzed by the standard procedure of 10°C/min. by DSC for thermal energy storage.

TABLE 1
THERMAL ENERGY STORAGE CHARACTERISTICS OF WITCO 45A
CONTAINING 25 WT. % OF ETHYL CORPORATION FIRE RETARDANT
BCL-462 AT DIFFERENT RATE OF TEMPERATURE CHANGE

Sample Identification and Composition	T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)	Extrapolated to 100%	
						ΔH_f (cal/gm)	ΔH_c (cal/gm)
Witco 45A: BCL-462 75:25 10°C/min. rate	29.1	21.9	7.2	31.4	33.8	41.9	45.0
Witco 45A: BCL-462 75:25 2°C/min. rate	27.6	25.1	2.5	28.6	29.4	38.1	39.2
Witco 45A Wax 10°C/min. rate	30.7	23.8	6.9	42.1	42.9	42.1	42.9

TABLE 2
THERMAL ENERGY STORAGE PROPERTIES OF 11" x 22" PLASTERBOARD
SHEETS THAT HAVE BEEN PERCOLATED WITH A RED-DYED
SOLUTION OF WITCO 45A AND 45A/BCL-462

Sample Identification and Composition	T _m (°C)	T _c (°C)	T _m -T _c (°C)	ΔH _f (cal/gm)	ΔH _c (cal/gm)	% 45A Calc. by DSC	
A. Plasterboard percolated with 45A (wt. % 45A - 33.3)	30.2	21.6	8.6	13.4	13.3	31.8	31.0
B. Plasterboard percolated with 45A, washed with methylene chloride (wt. % 45A - 32.8)	31.7	20.3	11.4	12.3	12.2	29.2	28.4
C. Percolated with 45A/BCL- 462 = 75:25 (% wt. gain - 35.7)	28.3	20.6	7.7	10.7	11.8	25.8	27.5
D. Percolated with 45A/BCL- 462 = 75:25, then washed with methylene chloride (% wt. gain - 36.3)	27.7	19.7	8.0	10.1	10.2	24.0	23.8
E. Witco 45A	30.7	23.8	6.9	42.1	42.9	100.0	100.0

TABLE 3
WEIGHT GAIN OF PLASTERBOARDS THAT
WERE PERCOLATED IN MORE THAN ONE BATH

		<u>% Wt. Gain After 10 Min.</u>	<u>% Wt. Gain After 24 Hrs.</u>	<u>% Wt. Gain After 48 Hrs.</u>
<u>1st Soaking</u>				
The percolating bath contained:				
	<u>Samples Soaked</u>			
(A) 45A (100%)	#17	34.2	34.1	34.2
	#32	34.6	34.5	34.6
	#19	34.2	34.0	34.2
	#68	35.7	35.7	35.7
(B) 45A/BCL- 462(75/25)	#15	38.0	37.7	37.7
	#52	38.3	38.0	38.0
(C) MeCl ₂ /BCL- 462(50/50)	#10	55.8	40.0	39.8
(D) MeCl ₂ (100%)	#9	50.6	0	0.41
<u>2nd Soaking</u>				
#17 from (A) soaked in (B)		35.9	34.7	35.2
#19 from (A) soaked in (C)		38.4	40.3	34.6
#68 from (A) soaked in (D)		38.5	38.0	32.4
#52 from (B) soaked in (C)		41.4	42.4	37.4

$$\% \text{ wt. gain} = \frac{\text{Final Initial Wt.}}{\text{Final Wt.}} \times 100$$

TABLE 4
FLAME TEST OF PLASTERBOARD SAMPLES THAT
WERE PERCOLATED IN MORE THAN ONE BATH

Horizontal Flame Test Results

Sample Number	What Solution(s) Soaked In	Time to Ignition	Time to Extinguish	Flame Traveled	Smoke
32	Bath A (45A)	5 sec.	541 sec.	yes	Black
17	Baths A and B (45A & 45A/BCL-462)	4 sec.	543 sec.	yes	Black
19	Baths A and C (45A & MeCl ₂ /BCL-462)				
	1st time	5 sec.	12 sec.	yes	Black
	3 sec.		315 sec.	(over entire square then retreated to edges)	
68	Baths A and D (45A & MeCl ₂)	5 sec.	535 sec.	yes	Black
15	Bath B (45A/BCL-462)				
	1st time	15 sec.	244 sec.	no	Black & White
	2nd time	6 sec.	151 sec.		
52	Baths B and C (45A/BCL-462 & MeCl ₂ /BCL-462)				
	1st time	5 sec.	24 sec.	no	Black
	2nd time	3 sec.	5 sec.		
10	Bath C (MeCl ₂ /BCL-462)	DID NOT IGNITE			
9	Bath D (MeCl ₂)	DID NOT IGNITE			

TABLE 5
THERMAL ENERGY STORAGE PROPERTIES OF FIVE SAMPLES OF
MICROENCAPSULATED PCMs BY DSC ANALYSIS

Sample Identification and Composition	T _m (°C)	T _c (°C)	T _m -T _c (°C)	ΔH _f (cal/gm)	ΔH _c (cal/gm)	% PCM Calc. from DSC	
Microencapsulated Recrystallized 45A #JAS6986	33.1	20.5	12.6	36.1	36.2	85.7	84.4
Microencapsulated Humphrey Tech. Grade Octadecane #JAS6995	32.5	21.0	11.5	38.3	41.3	75.5	81.4
Microencapsulated 45A/ Butyl stearate/BCL-462 (70/10/20) #JAS6982	30.2	18.3	11.9	27.2	28.7	64.6	66.9
Microencapsulated K61/ Butyl stearate (90/10) #JAS6989	29.3	17.9	11.4	40.7	41.5	85.7	89.4
Microencapsulated NP-15 /Butyl stearate(90/10) #JAS6988	9.9 -25.9	-2.7 -32.2	12.6 6.3	34.2 3.3	35.9 3.1	78.8	81.4
Melt Mixed Blends							
Melt mixed 45A/Butyl stearate/BCL-462 (70/10/20) Before Microencapsulation	28.3	22.0	6.3	32.5	33.9	77.2	79.0
Melt mixed K-61/ Butyl stearate(90/10) Before Micro- encapsulation	28.0	19.4	8.6	45.9	45.5	96.6	98.1
Melt mixed NP-15/ Butyl stearate(90/10)	7.5	-0.6	8.1	45.0	45.1	94.5	94.2
Reference Samples							
Humphrey Tech. Grade Octadecane Reference Sample	27.1	21.2	5.9	50.7	50.7	100	100
Witco 45A Reference	30.7	23.8	6.9	42.1	42.9	100	100
K-61 Reference	26.4	20.2	6.2	47.5	46.4	100	100
Butyl Stearate	23.3	17.4	5.9	35.7	35.8	100	100
NP-15 Reference	9.7 -24.0	2.0 -28.0	7.7 4.0	47.6	47.9	100	100

TABLE 6
DSC ANALYSIS OF MATSUSHITA PHASE CHANGE MATERIALS

Sample Identification and Composition	T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)	% PCM in Pellet Calc. from DSC ΔH_f ΔH_c Data	
1. Paraffin 115	50.6	41.4	9.2	48.8	48.3	---	---
2. Crosslinked LDPE (Low density polyethylene) PE AKZO No. 1 Unswelled Pellet	106.1	88.7	17.4	28.0	25.2	---	---
3. Crosslinked HDPE (High density polyethylene) PE No. 5 HF 40X Unswelled Pellet	136.2	114.9	21.3	50.1	50.1	---	---
4. CPP (Crosslinked poly- propylene) PP No. 6 PM 80X Unswelled Pellet	161.3	118.6	42.7	20.9	21.9	---	---
5. Composite Pellet*							
• Paraffin 115	51.4	37.7	14.1	31.2	32.7	63.9	65.0
• PE AKZO No. 1	94.3	77.7	16.6	4.8	5.7	17.1	28.1
6. Composite Pellet**							
• Paraffin 115	49.6	39.4	10.2	32.0	31.4	65.6	65.0
• PE No. HF 40X	119.7	106.7	13.0	15.0	14.1	29.9	28.1
7. Composite Pellet***							
• Paraffin 115	49.2	40.3	8.9	41.5	41.2	85.0	85.3
• PP No. 6 PM 80X	127.3	90.5	36.8	3.7	3.4	17.7	15.5

* Imbibing 30 min. at 151°C, % PCM by wt. gain 76.3%
 ** Imbibing 120 min. at 153°C, % PCM by wt. gain 66.4%
 *** Imbibing 120 min. at 183°C, % PCM by wt. gain 84.8%

TABLE 7
EXTRACTION OF CROSSLINKED HDPE

<u>Gamma Ray Intensity</u>	<u>Percent Insolubles (powder)</u>	<u>Percent Soluble (wax)</u>	<u>Total</u>
4 Mrad	$\frac{16.00}{34.74} \times 100 = 46.05\%$	$\frac{18.59}{34.74} \times 100 = 53.51\%$	$= 99.6\%$
5 Mrad	$\frac{17.08}{34.85} \times 100 = 49.9\%$	$\frac{17.60}{34.85} \times 100 = 50.50\%$	$= 100.4\%$
6 Mrad	$\frac{19.89}{35.00} \times 100 = 56.82\%$	$\frac{14.90}{35} \times 100 = 42.57\%$	$= 99.4\%$
7 Mrad	$\frac{11.09}{35.00} \times 100 = 31.68\%$	$\frac{23.91}{35.00} \times 100 = 68.31\%$	$= 100\%$
8 Mrad	$\frac{8.98}{35.00} \times 100 = 25.66\%$	$\frac{25.83}{35.00} \times 100 = 73.80\%$	$= 99.5\%$

TABLE 8

DSC ANALYSIS OF ETHANOL INSOLUBLES IN
MARLEX 6006 POWDER IRRADIATION TO DIFFERENT
- GAMMA RAY INTENSITY AND SWELLED IN 45A

Sample Identification and Composition		T _m (°C)	T _c (°C)	T _m -T _c (°C)	ΔH _f (cal/gm)	ΔH _c (cal/gm)	% Calculated from Control	
Marlex 6006 4 Mrad Gamma in Nitrogen	45A	32.2	23.7	8.5	30.9	31.5	73.4	73.4
	HDPE	114.7	99.7	15.0	14.4	11.4	---	---
Marlex 6006 5 Mrad Gamma in Nitrogen	45A	31.7	24.7	7.0	31.2	31.8	74.1	74.1
	HDPE	112.6	100.1	12.5	12.3	12.0	---	---
Marlex 6006 6 Mrad Gamma in Nitrogen	45A	32.8	26.1	6.7	36.2	34.8	86.0	81.1
	HDPE	110.3	98.4	11.9	9.0	7.8	---	---
Marlex 6006 7 Mrad Gamma in Nitrogen	45A	31.7	21.8	9.9	18.2	17.9	43.2	41.7
	HDPE	119.6	103.9	15.7	25.3	22.4	---	---
Marlex 6006 8 Mrad Gamma in Nitrogen	45A	33.3	24.5	8.8	21.5	21.0	51.1	50.1
	HDPE	117.3	103.1	10.2	21.4	21.5	---	---
Control - Uncrosslinked Nonswollen	45A	30.7	23.8	6.9	42.1	42.9	---	---
	HDPE	135.2	118.0	17.2	54.3	54.2	---	---

TABLE 9
DSC ANALYSIS OF HEXATRIACONTANE

Sample: Hexatriacontane C₃₆ - 99%

Run No.: 1064

File Name: Run 1064.01

Run No.	T _m (°C)	T _c (°C)	T _m -T _c (°C)	Heat of Fusion		Heat of Recryst.	
				(J/g)	(cal/g)	(J/g)	(cal/g)
1	78.37	69.30	9.07	267.9	64.01	250.4	59.83
2	78.23	69.22	9.01	268.8	64.23	251.1	60.00
3	<u>78.27</u>	<u>69.25</u>	<u>9.02</u>	<u>268.5</u>	<u>64.16</u>	<u>250.8</u>	<u>59.93</u>
Avg.	78.29	69.26	9.03	268.4	64.13	250.8	59.92

Sample: 45A/ BCL 462 75/25
 Size: 4.24 mg
 Method: DSC-MELT
 Comment: HEATING RATE 2°C/MIN

DSC

File: RUN1043.01
 Operator: ED DYKE
 Run date: 11/12/86 11.17

Figure 1. DSC Analysis of Thermal Energy Storage of 75 Wt. Percent Melt Blended Witco 45A/BCL-462 at 2°C/Minute.

Figure 2. Effect of Rate of Temperature Change Versus Melting and Crystallization Temperature of Melt Mixed Witco 45A/BCL-462 (75:25).

Sample: PLASTERBOARD #4
 Size: 3.89 mg
 Method: DSC-10°C/MIN
 Comment: PERCOLATED W/ 45A/ BCL 462

File: RUN1042.03
 Operator: ED DYKE
 Run date: 11/12/88 10:07

DSC

Figure 3. DSC Analysis of Thermal Energy Storage of Plasterboard That Was Percolated With Witco 45A/BCL-462 (75:25).

Sample: ENCAPSULATED RECRYSTAL. 45A *1
 Size: 5.24 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: RUN1008.03
 Operator: ED DYKE
 Run date: 10/09/86 12:23

General V1.0J DuPont 9900

Figure 4. DSC Analysis of Encapsulated Recrystallized Witco 45A
 #JAS6986.

Sample: ENCAPSULATED 45A #2
 Size: 4.88 mg
 Method: DSC-MELT
 Comment: 10C/NIN IN N2

DSC

File: RUN1017.03
 Operator: TODD SILL
 Run date: 10/17/88 11:58

General V1.0J DuPont 9900

Figure 5. DSC Analysis of Encapsulated Recrystallized Humphrey Tech.
 Grade Octadecane #JAS6995.

Sample: ENCAPSULATED 45/BS/BCL 482 #3
 Size: 5.41 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: RUN1007.01
 Operator: MARY/LUCY
 Run date: 10/09/86 13:45

Figure 6. DSC Analysis of Encapsulated 45A/Butyl Stearate/BCL-462
 (90/10/20) #JAS6982.

Sample: ENCAPSULATED K-61/B.S.
 Size: 5.22 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

File: RUN1008.02
 Operator: MARY/LUCY
 Run date: 10/09/86 18:03

DSC

Figure 7. DSC Analysis of Encapsulated K-61/Butyl Stearate (90/10)
 #JAS6989.

Sample: ENCAPSULATED NP-15/B.S. #5
 Size: 4.18 mg
 Method: DSC-PCM
 Comment: 10°C/MIN

DSC

File: RUN1009.02
 Operator: GALASKA
 Run date: 10/24/88 10:14

General VI.0J DuPont 9900

Figure 8. DSC Analysis of Encapsulated NP15/Butyl Stearate (90/10)
 #JAS6988.

Sample: PARAFFIN 115
 Size: 4.68 mg
 Method: DSC-10C/MIN

DSC

File: RUN1028.02
 Operator: BACKSCHEIDER
 Run date: 11/04/86 08:27

Figure 9. DSC Analysis of Thermal Energy Storage Properties for "Paraffin 115".

Sample: P.E. AKZO No1
 Size: 3.93 mg
 Method: DSC-10C/MIN
 Comments: UNSWELLED

DSC

File: RUN1029.02
 Operator: GALASKA
 Run date: 11/04/86 13:24

General V1.0J DuPont 9900

Figure 10. DSC Analysis of Thermal Energy Storage Properties for AKZO
 No. 1, Low Density Polyethylene, Peroxide Crosslinked.

Sample: P.P. (NO. 6) PM80X
Size: 3.81 mg
Method: DSC-10C/MIN
Comment: UNSWELLED

DSC

File: RUN1027.02
Operator: ED DYKE
Run date: 11/03/88 11:58

Figure 11. DSC Analysis of Thermal Energy Storage Properties for PM80X Polypropylene, Crosslinked by Silane.

Sample: P.E. (NO 5) HF40X
 Size: 5.78 mg
 Method: DSC-10C/MIN
 Comment: 10°C/Min UNSWELLED

DSC

File: RUN1034.02
 Operator: GALASKA
 Run date: 11/06/88 14:41

Figure 12. DSC Analysis of Thermal Energy Storage Properties for High Density Polypropylene, Crosslinked by Silane.

Sample: P.E. (NO. 5) HF40X
 Size: 3.43 mg
 Method: DSC-10C/MIN
 Comment: IN PARAFFIN 115 120 min @ 153°C

DSC

File: RUN1023.02
 Operator: ED DYKE
 Run date: 10/29/86 10:09

Figure 13. DSC Analysis of Silane Crosslinked HDPE, Swelled in "Paraffin 115".

Sample: P.E. (NO. 1) AKZO
 Size: 5.21 mg
 Method: DSC-10C/MIN
 Comment: IN PARAFFIN 115 30 MIN @ 151°C

DSC

File: RUN1024.02
 Operator: ED DYKE
 Run date: 10/30/86 09:27

General V1.0J DuPont 9900

Figure 14. DSC Analysis of Peroxide Crosslinked LDPE, Swelled in "Paraffin 115".

Sample: P.P. (NO. 6) PM80X
 Size: 4.69 mg
 Method: DSC-10C/MIN
 Comment: SWELLED FOR 120 min AT 183°C

DSC

File: RUN1026.02
 Operator: ED DYKE
 Run date: 11/03/86 09:13

Figure 15. DSC Analysis of Silane Crosslinked Polypropylene, Swelled in "Paraffin 115".

Sample: HEXATRIACONTANE C38 98%
Size: 3.34 mg
Method: DSC-10°C/MIN

DSC

File: RUN1064.02
Operator: GALASLA
Run date: 11/25/88 09:43

General V1.0J DuPont 9900

Figure 16. DSC Analysis of Thermal Energy Storage of Hexatriacontane.

STEP 1, ESTABLISHMENT OF THREE-PHASE SYSTEM

STEP 2. DEPOSITION OF LIQUID-POLYMERIC COATING MATERIAL

STEP 3. SOLIDIFICATION OF COATING MATERIAL

Figure 17. Microencapsulation Process.

MONTHLY PROGRESS REPORT NO. 7
CONTRACT NO. DE-FG03-86SF16308
COVERING DECEMBER, 1986

1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends".

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

The four processes are as follows:

1. Direct incorporation of PCM into the wet mix of building materials.
2. Direct incorporation into rubber or plastics medium for floor and wall tiles,
3. Indirect incorporation by first swelling the PCM into crosslinked polyethylene pellets or powder, which are then incorporated into building materials,
4. Direct incorporation by percolating the melted PCM into the open space in porous building materials.

As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3), the building material will not burn. However, in process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard after ignition will continue to burn slowly until the PCM is exhausted.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This is a subject of major emphasis in this year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will initiate extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

The present month's work consists of the following:

1. Fire retardance of plasterboard percolated with different PCM/fire retardant combinations.
2. Duplicate the density of commercial plasterboards by varying the amount of foaming agent in the recipe.

3. TECHNICAL DESCRIPTION OF CURRENT RESEARCH

3.1 Fire Retardance of Plasterboard Specimens That Have Been Percolated with Different PCM/Fire Retardant Combinations

Work reported last month show a slightly higher weight gain for the plasterboard percolated with the soluble fire retardant BCL-462 than for the Witco 45A PCM. This is ascribed to the higher density (2.27) of BCL-462 vs. 45A (~0.78). However, the relative weight gain for BCL-462 is less than expected from relative densities, indicating that the size of the fire retardant may exclude it from entering the smaller pores. The current experiments using PCM's C-18 and butyl stearate that are described in Appendix 2 and 3 and reported in Tables 2 and 4 also support the above ideas. In addition, the following conclusions may be drawn from Tables 2 and 4.

1. 10 minutes soaking time causes slightly higher weight gain than 5 minutes. This is particularly true for BCL-462 compositions indicating that the rate of percolation is slower for BCL-462 than for the PCMs.
2. Once the pores are filled with the PCM, subsequent soak in either a PCM or BCL-462 fire retardant does not substantially increase the total weight, e.g. A_1 vs. A_1+C_1 ; A_2 vs. A_2+C_2 ; B_1 vs. B_1+C_2 ; B_2 vs. B_2+C_2 ; A_2 vs. A_2+D_2 .
3. The reverse process of soaking in the fire retardant first leads to higher overall weight gain, since the remaining unoccupied smaller pores can now be filled up with PCMs in a subsequent soak, e.g. D_1+A_1 vs. A_1+D_1 ; D_2+A_2 vs. A_2+D_2 ; H_2+E_2 vs. E_2+H_2 .
4. A single soak in a 50/50, PCM/BCL-462 bath has a higher weight gain than a separate soak in 100% PCM followed by a soak in BCL-462 for the same total time (C_2 vs. A_1+D_1 ;

G_2 vs. $E_1 + H_1$). However, for the reasons stated in (3) above, this is not true if the sequence is reversed (C_2 vs. $D_1 + A_1$; G_2 vs. $H_1 + E_1$). Even higher gain is observed when the soak periods are increased to 10 minutes as in $D_2 + A_2$ and $H_2 + E_2$. Further work would be necessary to determine the maximum weight gain that can be achieved by varying the combination and soak time.

5. There is no substantial difference between Humphrey C-18 PCM and butyl stearate as regards percolation characteristics into plasterboard.

Tables 3 and 5 describe flame tests for the C-18 and butyl stearate samples made as in Tables 2 and 4, respectively. The samples were clamped in horizontal position during the flame test.

The term (a) denotes the first ignition, and (b) the second ignition of the same sample. The following observations seem pertinent from the data.

1. Time to first ignition increases as the proportion of BCL-462 fire retardant in the soaking bath increases, as would be expected.
2. The second ignition generally takes a shorter time, possibly due to the depletion of the fire retardant.
3. It is remarkable that the samples C_1 and G_1 (soaked in 50/50, PCM/BCL-462) extinguish immediately and that C_2 extinguishes in 4 seconds.
4. The samples soaked in PCM first and subsequently soaked in fire retardant does not show as good fire retardant properties as those where the sequence of soaking is reversed, e.g. $A_1 + D_1$ vs. $D_1 + A_1$.
5. The results in Tables 3 (C-18) and 5 (butyl stearate) corroborate each other. However, the flame travelled slower with butyl stearate than with Humphrey C-18 PCM.

It will be necessary to analyze the samples by DSC in order to correlate the flammability characteristics with the amount of PCM in the samples. Also, further work would be necessary to see the effect of varying the time of immersion in different sequences, in order to be able to optimize the quantity and proportion of PCM and fire retardant in the plasterboard.

3.2 Duplicate the Density of Commercial Plasterboards by Varying the Amount of Foaming Agent in the Recipe

Preliminary work indicates that the PCM incorporated into the wet mix should be more resistant to fire than the one percolated with PCM after it is prepared. We therefore intend to modify the plasterboard composition by including varying proportions of PCM as well as soluble and insoluble fire retardants in the wet mix.

In order to evaluate the effect of phase change material (PCM) and fire retardant in the plasterboard recipe, it is necessary to first of all make a sample that duplicates the density and physical properties of a commercial plasterboard. The density of a commercial plasterboard is around 0.67, which is much lower than gypsum (density 2.32) from which it is made. This is due to the fact that around 80% of the volume of commercial plasterboard is due to occluded air bubbles, introduced during the process of manufacture. We, therefore, devised experiments to introduce different quantities of a foaming agent in order to duplicate the density and other properties of the commercial product as closely as possible.

Appendix 1 gives a description of the process used. The recipe includes Millifoam as a foaming agent to introduce air bubbles in the product. The quantity of Millifoam used in the first experiment (3.6g in 58 ml water) produced a product which is too low in density. Subsequently, experiments were devised with different lower percentages of Millifoam in order to raise density. The results are presented in Table 1. Figure 1 shows that density follows a linear relationship with the concentration of foaming agent. From Figure 1, the extrapolated percentage for a density of 0.67 should be around 56.3. However, the preliminary experiment carried out with this quantity (Expt. #8) did not bear out this expectation. Since the process described in Appendix 1 is susceptible to many other subjective variations, the experiment will be repeated in future to confirm the data as well as to get the necessary practice for exact repetition of the whole preparation process.

The work reported above is very important to establish the base starting point, which can then be modified to include other materials (PCM, fire retardant, etc.).

3. CONCLUSIONS

1. Rate of percolation of BCL-462 is slower than the C-18 and butyl stearate PCMs used.
2. The weight gain for BCL-462 is less than would be expected from its high density, although the overall weight gain is higher than for the PCM.
3. In order to incorporate large quantities of BCL-462, the plasterboard has to be soaked in this fire retardant first. The quantity can be adjusted by varying the time of immersion.
4. Time to ignition increases as the proportion of fire retardant in the soaking bath increases.
5. The samples soaked in fire retardant first show less flammability.
6. Density of plasterboards, prepared in the laboratory, increases as the proportion of millifoam in the recipe decreases. Densities that closely approach those of commercial plasterboard can now be made. Encapsulation of PCM-containing pellets into the wet mix of plaster is expected to reduce the potential fire hazard of alkyl hydrocarbon PCM in plasterboard.

4. IMMEDIATE FUTURE PLANS

Due to current years funds being expended at significantly higher than the linear rate, it is necessary to drastically curtail the technical effort on this project for the immediate future. Thereby we can insure that funds will be available to complete a few high priority projects that are already in progress, meet outstanding travel and other commitments, and prepare an Annual Report. Accordingly, unless funding limitations are overcome in the interim, our immediate Future Plans are to complete the two projects described below that are already in progress.

1. Complete experiments, at Diconix, to determine the effect of polar additives, and detergent, on the wetting and spreading of alkyl hydrocarbon PCM on a plaster surface.
2. Evaluate crosslinking of high density polyethylene with peroxides during extrusion processing at the Springborn Corporation in Windsor Locks, Conn. This extrusion processing has already been scheduled, and will be completed during the next month.

APPENDIX 1

W.O. #860812-12 to 15 To Match the Density of Commercial Plasterboards By Varying the Amount of Foaming Agents

1. Weigh out the following quantities into a stainless steel beaker and mix thoroughly.
 - 400 gm Stucco
 - 2.5 gm hammermilled paper fibers
 - 1.5 gm LC 211 starch
2. Put 350 ml of H₂O into the mixer bowl.
3. Put 1.2 gm Norlig into H₂O in the mixing bowl.
4. Put 1.5 gm HRA accelerator in a small paper cup.
5. Weigh the desired amount of Millifoam.
6. Measure out 58 ml of H₂O.

* A malted milk mixer was used to prepare foam using Hi speed.
A Hobart mixer with the whip was used to mix plaster.

Procedure:

<u>Time (sec.)</u>	<u>Action</u>
0	Start foam generation
50	Stop foam generation
50	Sprinkle HRP on top of dry ingredients and add to mixer bowl
55	Start mixing
60	Add foam to mixing bowl
85	Stop mixing
	Remove whip and lean
88	Pour plaster into three 2" cube molds
	Tamp with putty knife, leave excess on top and put a glass plate on top and force out excess plaster
130	Clean mixing bowl

- Allow cubes to cure for 6 min. in mold then remove
- Cure in oven for 30 min. at 150°C
- Cure in oven until dry at 50°C
- Weigh, measure samples and calculate density

APPENDIX 2

PROCEDURE FOR TREATING PLASTERBOARDS WITH DIFFERENT COMBINATIONS OF HUMPHREY C-18 PCM AND THE SOLUBLE FIRE RETARDANT BCL-462

Work Order: 861210-1 thru 18
Performed By: Beth Backscheider/Mary Galaska
Date: December 18 and 19, 1986

Procedure:

Eighteen 2" squares of plasterboard were cut and weighed. Four percolating baths containing (A) C-18 (100%), (B) C-18/BCL-462 (75/25), (C) C-18/BCL-462 (50/50), (D) BCL-462 (100%) were prepared and heated to 80°C. Four squares were selected and placed one to a bath and percolated for 5 min. (A1,B1,C1,D1). Four more squares were percolated in the baths for 10 min. (A2,B2,C2,D2). After removal from the bath, each square was allowed to cool, then weighed for solution pick-up.

Then one square was percolated in A for 5 min., then immediately in C for 5 min. Then this was repeated at 10 min. soaking times (A1+C1, A2+C2).

One square was soaked in bath B for 5 min., then immediately in C for 5 min. This was repeated at 10 minute soaking times (B1+C1, B2+C2).

One square was soaked in bath A for 5 min., then in bath D for 5 min. Then this was repeated for 10 min. each (A1+D1, A2+D2).

One square was soaked in bath D for 5 min., then in bath A for 5 min. This was repeated for a soaking time of 10 min. each bath (D1+A1, D2+A2).

One square was soaked in bath D for 5 min., then in bath B for 5 min. This was then repeated for a soaking time of 10 min. each bath (D1+B1, D2+B2).

All samples were cooled and weighed for calculation of PCM solution pickup. DSC samples were taken for future analysis on

selected samples. The samples were then subjected to a horizontal flame test.

APPENDIX 3

PROCEDURE FOR TREATING PLASTERBOARDS WITH DIFFERENT COMBINATIONS BUTYL STEARATE AND THE SOLUBLE FIRE RETARDANT, BCL-462

Method:

Eighteen 2" squares of plasterboard were cut and weighed. Four percolating baths: (E) BuSt (100%), (F) BuSt/BCL-462 (75/25), (G) BuSt/BCL-462 (50/50), and (H) BCL-462 (100%) were prepared and heated to 80°C. Four squares were selected and placed one to a bath. These squares were percolated for 5 min. (E1, F1, G1, H1). Four more squares were percolated in the baths for 10 min. (E2, F2, G2, H2). After removal from its bath each square was allowed to cool, and then it was weighed for solution pickup.

Then one square was percolated in E for 5 min. then in G for 5 min. One was soaked in E for 10 min. and G for 10 min. One was soaked in F for 5 min. and G for 5 min. One was percolated in F for 10 min. and G for 10 min. One was soaked in E for 5 min. and H for 5 min. Another was percolated in E for 10 min. and H for 10 min. One was soaked in H for 5 min. then in E for 5 min. One was soaked in H for 10 min. and E for 10 min. One was soaked in H for 5 min. and F for 5 min. Finally, one was soaked in H for 10 min. and F for 10 min. Each of these 10 samples was allowed to cool after percolating and was then weighed for solution pickup. A small sample of each square was taken for selected DSC tests. The squares were then subjected to a horizontal flame test.

Figure 1. Effect of Millifoam Quantity on Density of Plasterboards.

TABLE 1
EFFECT OF MILLIFOAM QUANTITY ON
DENSITY OF PLASTERBOARDS

Experiment Number	Millifoam % USG Recommended Quantity	Average Density (g/cm ³)
3	100	0.628
4	100	0.609
5	100	0.609
6	92	0.623
7	80	0.639
8	56.3	0.619

TABLE 2
PCM PICKUP DATA IN DIFFERENT COMBINATIONS
OF HUMPHREY C-28 PCM AND BCL-462
FIRE RETARDANT

1 sample was soaked in each solution
1 denotes a 5 min. percolating time
2 denotes a 10 min. percolating time.

Bath and Soak Time	Bath Composition	% Weight Gain $\left(\frac{\text{final}-\text{initial}}{\text{final}} \times 100\right)$
A1	C-18(100%)	31.08
B1	C-18/BCL-462 (75/25)	34.75
C1	C-18/BCL-462 (50/50)	38.94
D1	BCL-462 (100%)	36.58
A2	C-18 (100%)	32.57
B2	C-18/BCL-462 (75/25)	36.57
C2	C-18/BCL-462 (50/50)	40.63
D2	BCL-462 (100%)	42.18
A1 + C1	C-18(100%) + C-18/BCL-462 (50/50)	32.43
A2 + C2	C-18(100%) + C-18/BCL-462 (50/50)	34.73
B1 + C1	C-18/BCL-462 (75/25) + C-18/BCL-462 (50/50)	36.58
B2 + C2	C-18/BCL-462 (75/25) + C-18/BCL-462 (50/50)	37.86
A1 + D1	C-18(100%) + BCL-462 (100%)	36.23
A2 + D2	C-18(100%) + BCL-462 (100%)	35.54
D1 + A1	BCL-462 (100%) + C-18 (100%)	44.08
D2 + A2	BCL-462 (100%) + C-18 (100%)	48.68
D1 + B1	BCL-462 (100%) + C-18/BCL-462 (75/25)	43.92
D2 + B2	BCL-462 (100%) + C-18/BCL-462 (75/25)	48.99

TABLE 3
HORIZONTAL FLAME TEST FOR THE SAMPLES OF
PLASTERBOARDS SOAKED IN DIFFERENT
COMBINATIONS OF HUMPHREY C-18 AND BCL-462

Sample	Time to Ignition	Time to Extinguish	Smoke	Traveled
A1	a* 6 seconds b* 11 seconds	564 seconds 37 seconds	very little-black vigorous flame	Yes
B1	a 17 seconds b 5 seconds	120 seconds 72 seconds	alot - black	Yes
C1	a 35 seconds b 3 seconds	immediately immediately	alot - white	Yes
D1	a didn't ignite b didn't ignite	immediately immediately	---	No
A2	a 6 seconds b didn't ignite	702 seconds immediately	black vigorous flame	Yes
B2	a 12 seconds b 3 seconds	282 seconds 56 seconds	black	Yes
C2	a 10 seconds b 2 seconds	4 seconds 4 seconds	black	No
D2	a didn't ignite b didn't ignite	--- ---	white	No
A1 + C1	a 17 seconds b 6 seconds	585 seconds 12 seconds	black	Yes
A2 + C2	a 14 seconds b 8 seconds	557 seconds 12 seconds	black	Yes
B1 + C1	a 24 seconds b 4 seconds	172 seconds 46 seconds	black	Yes
B2 + C2	a 14 seconds b 7 seconds	203 seconds 339 seconds	black	Yes
A1 + D1	a didn't ignite in 60 sec. b 40 seconds	immediately 606 seconds	black	Yes
A2 + D2	a 56 seconds b 10 seconds	28 seconds 445 seconds	black	Yes

* a = first ignition; b = second ignition.

TABLE 3 (Concluded)
HORIZONTAL FLAME TEST FOR THE SAMPLES OF
PLASTERBOARDS SOAKED IN DIFFERENT
COMBINATIONS OF HUMPHREY C-18 AND BCL-462

Sample	Time to Ignition	Time to Extinguish	Smoke	Traveled
D1 + A1	a didn't ignite in 60 sec. b didn't ignite in 60 sec.	immediately immediately	burned well with the flame held on	No
D2 + A2	a 55 seconds b 12 seconds	112 seconds 2 seconds	black	Yes
D1 + B1	a didn't ignite b didn't ignite	immediately immediately	burned well with the flame held on	No
D2 + B2	a didn't ignite b didn't ignite	immediately immediately	burned well with the flame held on	No

TABLE 4
PCM PICK-UP DATA IN DIFFERENT
COMBINATIONS OF BUTYL STEARATE
AND BCL-462

1 sample was soaked in each solution
A1 denotes a 5 min. percolating time
A2 denotes a 10 min. percolating time

Bath and Soak Time		Bath Composition	$\% = \frac{\text{Final}-\text{Initial}}{\text{Final}} \times 100$ % Weight Gain
E1	5 min.	Butyl Stearate (100%)	33.0
F1	5 min.	BuSt/BCL-462 (75/25)	35.4
G1	5 min.	BuSt/BCL-462 (50/50)	39.0
H1	5 min.	BCL-462 (100%)	38.1
E2	10 min.	Butyl Stearate (100%)	32.3
F2	10 min.	BuSt/BCL-462 (75/25)	37.2
G2	10 min.	BuSt/BCL-462 (50/50)	41.1
H2	10 min.	BCL-462 (100%)	46.0
E1+G1	10 min. (5+5)	BuSt(100%) & BuSt/BCL-462 (50/50)	33.8
E2+G2	20 min (10+10)	BuSt(100%) & BuSt/BCL-462 (50/50)	32.6
F1+G1	10 min. (5+5)	BuSt/BCL-462 (75/25) and BuSt/BCL-462 (50/50)	38.2
F2+G2	20 min (10+10)	BuSt/BCL-462 (75/25) and BuSt/BCL-462 (50/50)	40.5
E1+H1	10 min. (5+5)	BuSt(100%) and BCL-462 (100%)	37.5
E1+H2	20 min (10+10)	BuSt(100%) and BCL-462 (100%)	40.7
H1+E1	10 min. (5+5)	BCL-462 (100%) & BuSt (100%)	43.2
H2+E2	20 min (10+10)	BCL-462 (100%) & BuSt (100%)	49.3
H1+F1	10 min. (5+5)	BCL-462 (100%) & BuSt/BCL-462 (75/25)	45.8
H2+F2	20 min (10+10)	BCL-462 (100%) & BuSt/BCL-462 (75/25)	49.0

TABLE 5
HORIZONTAL FLAME TEST RESULTS FOR THE PLASTERBOARD
SAMPLES SOAKED IN DIFFERENT COMBINATIONS OF
BUTYL STEARATE AND BCL-462

Sample	Time to Ignition	Time to Extinguish	Smoke	Traveled
E1	a* 3 seconds b* 4 seconds	413 seconds 66 seconds	white clear flame/white	slowly
F1	a 15 seconds b 4 seconds	10 seconds 17 seconds	white clear flame/white	no
G1	a 4 seconds	immediate extinguishment	black	no
H1	a didn't ignite b didn't ignite		black	
E2	a 3 seconds b 15 seconds	342 seconds 164 seconds	black (clear flame)	yes
F2	a 7 seconds b 4 seconds	3 seconds 30 seconds	black	no
G2	a 4 seconds b 3 seconds	extinguished immediately	black	
H2	a didn't ignite b didn't ignite		black	
E1+G1	a 11 seconds b 13 seconds	7 seconds 623 seconds	white/black	yes
E2+G2	a 12 seconds b 3 seconds	3 seconds 47 seconds	white	no
F1+G1	a 15 seconds b 3 seconds	4 seconds 2 seconds	black	no
F2+G2	a 15 seconds b 3 seconds	2 seconds 2 seconds	black	no
E1+H1	a 25 seconds b 3 seconds	did not 2 seconds	black/white (evaporating pick- up burned)	no
E2+H2	a 26 seconds b 4 seconds	2 seconds 2 seconds	black	no

* a = first ignition; b = second ignition.

TABLE 5 (Concluded)
HORIZONTAL FLAME TEST RESULTS FOR THE PLASTERBOARD
SAMPLES SOAKED IN DIFFERENT COMBINATIONS OF
BUTYL STEARATE AND BCL-462

Sample	Time to Ignition	Time to Extinguish	Smoke	Traveled
H1+E1	didn't ignite		black	
H2+E2	a 30 seconds b 7 seconds	extinguished immediately	black/white	no
H1+F1	a 19 seconds b 5 seconds	extinguished immediately	black/white	no
H2+F2	a 18 seconds b 10 seconds	extinguished immediately	black/white	no

MONTHLY PROGRESS REPORT NO. 8
CONTRACT NO DE-FG03-86SF16308
COVERING JANUARY, 1987

1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research, on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends".

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

The four processes are as follows:

1. Direct incorporation of PCM into the wet mix of building materials,
2. Direct incorporation into rubber or plastics medium for floor and wall tiles,
3. Indirect incorporation by first swelling the PCM into crosslinked polyethylene pellets or powder, which are then incorporated into building materials,
4. Direct incorporation by percolating the melted PCM into the open space in porous building materials.

As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3). The building material will not burn. However, in process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard after ignition will continue to burn slowly until the PCM is exhausted.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will initiate extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

The present month's work consists of the following:

1. Fire retardance characteristics of the 11" x 22" PCM treated plasterboards.
2. Extrusion crosslinking and production of smaller diameter pellets of HDPE at Springborn Laboratories in Enfield, Connecticut.
3. Rate of wetting, spreading and penetration of NP-15 on cast plaster specimen using contact angle instrument.

3. TECHNICAL DESCRIPTION OF CURRENT RESEARCH

3.1 Fire Retardance Characteristics of the 11" x 22" PCM Treated Plasterboards

Our September 1986 report describes the preparation of four 11" x 22" plasterboards that were soaked in Witco 45A PCM and 45A/BCL-462 (75/25) fire retardant combination. The samples were intended for fire retardance test as per ASTM E119 at USG Laboratories. However, it was decided to repeat the laboratory screening tests for these large panels before sending for outside testing. Accordingly, 3" x 5" sample slabs were cut from these pieces. The samples were clamped in a flat, horizontal position with the cut edges forming the vertical sides and lit with the flame of a match. The results are presented in Table 1. The difference between sample numbers 2 and 3 are that #2 was rinsed with methylene chloride after the soaking experiment to remove 45A wax from the paper surface. It may be observed that the BCL-462 treated samples 2 and 3 show marked improvement over #1 in all respects. However, when the same samples were held in an inclined position and lit by a match, there were no visible differences among the samples. All of them burnt readily, the flame that started at the edges by the match propagated readily and travelled throughout the board. Also, the flame travelled better with the vent out than when it was on, the latter being the normal practice.

TABLE 1
HORIZONTAL FLAME TEST OF PCM TREATED PLASTERBOARDS

Work Order: 870126-1 & 2

Supplement to Work Order: 860926-15 & 16

	<u>Sample</u>	<u>Time to Ignite</u>	<u>Time to Extinguish</u>	<u>Flame Traveled</u>	<u>Smoke</u>
1.	(45A)	6	didn't stop in 3 min.	yes	black
2.	(45A/BCL-462),	11	50	no	black
	75/25, MeCl	8	33	no	black
	rinse	19	68	no	black
		9			
3.	(45A/BCL-462),	9	79	no	black
	75/25	9	74	no	black

Although the above results are disappointing, our later experiments with PCM/fire retardant combinations (described in December 1986 report) show that a much larger quantity of fire retardant/PCM combination can be incorporated into the plasterboard by soaking successively into BCL-462 and then into the PCM bath. A weight gain of 49% PCM/fire retardant can be obtained by this method as compared to 35% when the plasterboard is soaked in 75/25, PCM/BCL-462 as is the case with the samples described. A much better fire retardance is expected with these samples containing a higher amount of flame retarding agent. Also, better fire retardance is expected when the synergistic flame proofing chemical antimony oxide is included in the plasterboard recipe.

Previous attempts to percolate combinations of the standard commercial grade of antimony oxide and the soluble fire retardant (BCL-462) simultaneously with the PCM were not successful, since the comparatively large antimony oxide particles were "screened out" at the surfaces of the plasterboard. However, we have recently obtained, from Laurel Industries, samples of submicron particle size antimony oxide, that has >90% of its particles smaller than 1 micron. We believe that the synergistic combination of submicron particle size antimony oxide/BCL-462/PCM can probably be percolated directly into the small pores of the plasterboard. If successful, this will provide self-extinguishing plasterboard compositions at much lower concentrations than when BCL-462 is used alone (as described above).

These experiments will be scheduled as soon as possible.

3.2 Extrusion Crosslinking and Production of Smaller Diameter Pellets of HDPE at Springborn Laboratories in Enfield, Connecticut

As mentioned in earlier Progress Reports, a long standing objective of our research on HDPE pellets, as containers for room temperature hydrocarbon PCM, has been as follows:

- Produce pellets smaller than the 1/8" size that are commercially available. When the 1/8" pellets are subsequently swollen (permeated with alkyl hydrocarbon PCM, the pellets become undesirably large for incorporation into the wet mix

of plasterboard and concrete. Obviously, crosslinked pellets of significantly smaller initial size will result in permeated pellets of proportionately smaller size. These can be more readily incorporated into the wet mix, and detract less from physical properties and fire retardance, of the plasterboard and concrete.

- To investigate the possibility of simultaneous incorporation of antimony oxide during the extrusion/crosslinking process. Antimony oxide containing HDPE pellets should provide fire retardant compositions, after the pellets are subsequently permeated with a solution of alkyl hydrocarbon phase change material and a soluble halogenated fire retardant.
- To develop a low cost process for producing crosslinked HDPE pellets via extrusion crosslinking with small concentrations of peroxides; and using a lower cost process intermediate HDPE powder.

All of these objectives were preliminarily investigated in a series of experiments performed at Springborn Laboratories, in Enfield, Connecticut, January 28 and 29, 1987. Springborn Laboratories was selected because of the availability there of small single and twin screw extruders, pelletizing cutters, blenders, etc. During the first day, January 28, experiments were done that clearly established that their Brabender 1-5/8" twin screw extruder was not suitable for making small strands (that could be cut into small pellets). The intermeshing screws did not effectively remove the entrapped air between powder particles, and the air bubbles caused frequent breakage in the extruded strands. Consequently, the experiments were shifted to their 3/4" diameter Brabender single screw extruder, having an L/D of 24/1, and a compression ratio of 4/1. Extrusion temperatures were set at 400°F on the cylinder, and 380°F on the die, with a screw speed of 60 rpm, a sojourn time in the extruder of two minutes (sufficient time to achieve peroxide crosslinking at 400°F) and an output of 3 pounds per hour. A small amount of zinc stearate lubricant (0.25 or 0.50%) was used throughout.

The following three series of experiments were carried out:

1. Experiment Number 870128-1

This experiment was run as a "control", using Marlex 6006 powder without any crosslinking agent, to determine the smallest

size pellets that could be produced on this equipment. A strand size of 1/32" diameter was readily produced. However, pellet length could not be made less than 1/8" because of a mechanical link between the pelletizer feed rolls and the cutter. Separating the mechanical drive of the feed rolls and cutter should enable cubic pellets of 3/32" to be readily obtained. It was the opinion of Springborn personnel that pellets as small as 1/64" could also be obtained by the modification noted above.

These experimental results were important in indicating that it should be possible to produce the desired smaller pellets by an economic extrusion process capable of scale-up to production.

2. Experiment Number 870129-1 Through 4

In this series of four experiments, successively smaller concentrations of dicumyl peroxide crosslinking agent (0.35, 0.30, 0.25, and 0.20%) were investigated. In each sample, the HDPE powder, zinc stearate lubricant and dicumyl peroxide were uniformly mixed in a Henshel blender. To obtain a more uniform distribution, the peroxide was diluted with 0.25% of mineral oil, prior to adding to mix.

Small diameter strands of about 1/32" were obtained as readily as with the uncrosslinked control. A "wavy" strand indicative of crosslinking was obtained at all the four peroxide concentrations, including the lowest (0.2% wt.). Crosslinking was confirmed by a thermal form stability test of previously established validity. Extruded pellets were placed on Teflon coated metal plate heated to 200°C. Retention of pellet shape and form was taken as confirmation of crosslinking. Uncrosslinked control pellets flowed quickly into a flattened disc, in this same test.

It appears that even 0.2% of dicumyl peroxide may be higher than necessary to obtain the required degree of crosslinking and thermal form stability. Further experiments are planned at Springborn, to evaluate still lower dicumyl peroxide concentrations of 0.15 and 0.10%.

3. Experiment Number 870129-5

This was a single experiment designed to evaluate the feasibility of incorporating 30 phr of antimony oxide (a synergistic fire retardant) into the HDPE simultaneously with extrusion peroxide/crosslinking. A level of 0.2% of dicumyl peroxide (extended with an equal quantity of mineral oil), plus 0.5% zinc stearate lubricant was dry blended into the HDPE powder and extruded under the same conditions as for the prior experiments.

Small wavy strands of about 1/32" diameter were readily obtained, and the pellets exhibited excellent thermal form stability. There was no detectable effect on extrusion rate or quality. The antimony oxide did not appear to retard the crosslinking, and may have promoted it. As in the case of samples 870129-1 through 4 above, 0.2% of peroxide may be more than is necessary to obtain the required crosslinking and thermal form stability.

The amount of antimony oxide in this sample (30 phr) should be sufficient to provide a self-extinguishing formulation, when these pellets are subsequently permeated with a combination of alkyl hydrocarbon PCM plus a soluble fire retardant.

We plan to permeate all of the samples prepared at Springborn with PCM alone and with the combination of PCM plus fire retardant. The flammability of the pellets alone will be determined. The pellets will then be incorporated into plaster-board and concrete and the product also tested for flammability.

If the projected fire retardance is obtained in the plaster-board and concrete specimen, this will constitute a big step forward toward our program goals for the current fiscal year ending May 31, 1987.

3.3 Rate of Wetting, Spreading and Penetration of NP-15 on Cast Plaster Specimen Using Contact Angle Instrument

The results obtained in experiments performed with Mr. James Short at Diconix Lab in Dayton, are as follows:

1. Studied rate of wetting, spreading and penetration of NP-15 on cast plaster specimen. Used their contact angle instrument, Wild 352873, that dispenses a single drop (from a hollow needle/syringe) onto the plaster surface and continuously records results on VCR tape. Then used slow motion playback and counted the time as "beats". A beat is <1.0 slow motion seconds.
2. Samples tested as follows:
 - NP-15 (100%)
(13, 13, 13, 13) avg. 13.0
 - NP-15/butyl stearate (80/20)
(17, 18, 18, 15, 15) avg. 16.6
 - NP-15/Joy (99.9/0.1)
(15, 13, 13, 13, 13, 13) avg. 13.3
 - Butyl stearate (100%)
(50, 41, 31) avg. 40.6
 - Tap water (100%)
(4, 5, 6) avg. 5.0
3. Conclusions:
 - NP-15 without additives wets and penetrates plaster rapidly
 - Additives (Joy, butyl stearate) do not improve rate of penetration
 - Butyl stearate (100%) goes in slower than NP-15 probably due to higher viscosity
 - Tap water wets and penetrates fastest of all tested combinations.
4. We have tape on hand and can get quantitative time data for a cost now being estimated.

4. CONCLUSIONS

1. A higher concentration (more than 75/25) of BCL-462 would be necessary to impart reasonable flame retardance to plasterboards.
2. Making of small chemically crosslinked HDPE pellets by extrusion seems to be an inexpensive alternative to radiation crosslinking. Moreover, pellet size can be controlled to smaller size, necessary for maintaining properties in filled polyethylene.
3. Wetting agents appear to offer no improvement in wetting and penetration NP-15 in plasterboards.

MONTHLY PROGRESS REPORT NO. 9
CONTRACT NO. DE-FG03-86SF16308
COVERING FEBRUARY, 1987

1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research, on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends".

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

The four processes are as follows:

1. Direct incorporation of PCM into the wet mix of building materials,
2. Direct incorporation into rubber or plastics medium for floor and wall tiles,
3. Indirect incorporation by first swelling the PCM into crosslinked polyethylene pellets or powder, which are then incorporated into building materials,
4. Direct incorporation by percolating the melted PCM into the open space in porous building materials.

As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3), the building material will not burn. However, in process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard after ignition will continue to burn slowly until the PCM is exhausted.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will initiate extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. TECHNICAL DESCRIPTION OF CURRENT RESEARCH

Due to current years funds being expended at significantly higher than the linear rate, it was necessary to drastically curtail the technical effort on this project for the month of February. Thereby we could insure that funds would be available to complete a few high priority projects that are already in progress, meet outstanding travel and other commitments, and prepare an Annual Report. Accordingly, limited work was carried out during this month. However, we will continue working at a speed consistent with our funds for the remaining period from the middle of March, 1987 and at a much greater speed when the expected new grant is implemented. .

3. IMMEDIATE FUTURE PLANS

1. Solubility studies of Ferro's Bromoklor 50 and Bromoklor 70 fire retardants in C₁₈ PCM.
2. Evaluate Nyacol Colloidal antimony oxide samples HA-9 and HA-15E, as fire retardants in PCM percolated plasterboards.
3. Prepare extrusion/peroxide crosslinked Marlex 6006, with 0.50% and 0.75% concentration of dicumyl peroxide; and to determine the permeation characteristics of the crosslinked pellets by swelling in Humphrey Technical Grade C-18.

MONTHLY PROGRESS REPORT NO. 10
CONTRACT NO. DE-FG03-86SF16308
COVERING MARCH, 1987

1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research, on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends".

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

The four processes are as follows:

1. Direct incorporation of PCM into the wet mix of building materials,
2. Direct incorporation into rubber or plastics medium for floor and wall tiles,
3. Indirect incorporation by first swelling the PCM into crosslinked polyethylene pellets or powder, which are then incorporated into building materials,
4. Direct incorporation by percolating the melted PCM into the open space in porous building materials.

As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3). The building material will not burn. However, in process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard after ignition will continue to burn slowly until the PCM is exhausted.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will initiate extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

The present month's work consists of the following:

1. Further search for fire retardants that are soluble in PCM.
2. Containment of PCM in extrusion crosslinked HDPE.

3. TECHNICAL DESCRIPTION OF CURRENT RESEARCH

3.1 Further Search for Fire Retardants That Are Soluble in PCM

3.1.1 Bromoklor 50 and Bromoklor 70

In order to percolate the phase change material (PCM) and fire retardant combination (PCM-FR) into already made plasterboards, one of the primary requirements of the fire retardant is that it should be soluble in PCM. One fire retardant that satisfies this requirement is Ethyl's Saytex BCL 462. Our earlier reports, starting from September, 1986, covers the work done with this fire retardant.

In our search for an alternative, we obtained two samples of Bromoklor 50 and Bromoklor 70, manufactured by Ferro Corporation. Bromoklors are halogenated aliphatic liquids containing both bromine and chlorine. Typical properties of these flame retardants are as follows:

<u>Typical Properties</u>	<u>Bromoklor 50</u>	<u>Bromoklor 70</u>
% Bromine	30	35
% Chlorine	20	35
Sp. Gravity @ 25°C	1.38	1.65
Viscosity, CPS @ 25°C	270	5000
Gardner Color	3	5

Data obtained to determine the solubility of these FR's in C18 PCMs are reported in Table 1 and the experimental method is reported in Appendix 1. Table 1 shows that Bromoklor 50 is soluble in all ratios in octadecane, both at room temperature

TABLE 1

TO DETERMINE THE SOLUBILITY OF BROMOKLOR 50 AND BROMOKLOR 70
IN HUMPHREY TECHNICAL GRADE C18 PCM
AT 25°C AND 80°C

<u>Date</u>	<u>Sample</u>	<u>Weight(g)</u>		<u>Temp. (°C)</u>	<u>Time</u>	<u>Observations</u>
3/23	870313-1	C-18	7.50	80°C	1 hr.	Soluble at 80°C. No phase separation when cooled.
		B-50	2.50			
3/23	870313-2	C-18	7.50	80°C	1 hr.	Soluble at 80°C. Some phase separation on cooling.
		B-70	2.50			
3/24	870313-3	C-18	5.0	80°C	1 hr.	Soluble at 80°C. No phase separation when cooled.
		B-50	5.0			
3/24	870313-4	C-18	5.0	80°C	1 hr.	Soluble at 80°C. Phase separation on cooling-2 layers.
		B-70	5.0			
3/26	870313-5	C-18	7.50	R.T.	1 hr.	Soluble at R.T. after 1 hr.
		B-50	2.50	25°C	(stirring)	stirring. No phase separation.
3/26	870313-6	C-18	7.50	25°C	1 hr.	No soluble - some B70 seems to stick in bottom.
		B-70	2.50		(stirring)	
3/26	870313-7	C-18	5.0	25°C	1 hr.	Soluble at R.T. Stays in solution.
		B-50	5.0		(stirring)	
3/26	870313-8	C-18	5.0	25°C	1 hr.	No soluble - B70 stuck on bottom.
		B-70	5.0		(stirring)	

and at 80°C. Bromoklor 70 is soluble at 80°C, but phase separation takes place on cooling. Further work is under progress.

3.1.2 Nyacol Colloidal Antimony Oxide (HA-9) and HA-15E as Fire Retardants

It is a common knowledge that the halogenated organic fire retardant is much more efficient in the presence of antimony oxide. The two work as a synergistic combination. However, antimony oxide, which is prepared for use as a pigment, can only be incorporated into plasterboards during its manufacture. Nyacol Products Inc. offers colloidal size antimony oxides, which are already treated with fire retardants. Two such products are Nyacol HA-9 and Nyacol HA-15PE. The chemical compositions, as supplied by the manufacturer, are as follows:

<u>Material</u>	<u>Percent</u>	<u>Trade Name</u>
Antimony Pentoxide (Sb_2O_5)	14	HA-9
Pentabromodiphenyl oxide	65	
Surface Modifier	4.5	
Specific Gravity	2.0	
Antimony Oxide (Sb_2O_5)	14	HA-15PE
Bromochlorinated Paraffin	65	
Surface Modifier	4.55	
Specific Gravity	1.5	

These products, because of their small particle size, may get into the pores of plasterboards by percolation. In order to test this, attempts were made to suspend these, in 12.5% and 25% concentration in octadecane. The first experiment with hotplate and magnetic stirrer showed about one-third of HA-9 precipitated at the bottom of the beaker. It was conceived that vigorous stirring would be necessary to suspend this colloid size antimony oxide particle. Accordingly, Waring blender and ultimately a malt mixer were used in attempts to suspend this compound. So far, we have not been successful in achieving this, although a larger proportion is suspended with the Waring blender. The experiment is described in Appendix 2. Further work to

achieve complete dispersion of HA-9 as well as similar work with HA-15PE is under progress.

3.2 Containment of PCM in Extrusion Crosslinked HDPE

It would be much cheaper to chemically crosslink HDPE in a hot extruder than by gamma radiation, as was done in our earlier work. Also, an extruder is cheaper and more commonly available in polymer laboratories than a gamma ray generator. Experiments were therefore designed to crosslink the following samples at Springborn Laboratory, Connecticut by extrusion at barrel and die temperatures of 400°F and a sojourn time of approx. 2 minutes.

<u>Sample No.</u>	<u>Peroxide Concentration (DiCup R)</u>
870129-1	0.35%
870129-2	0.30%
870129-3	0.25%
870129-4	0.20%
870129-5	0.20% + 30 phr antimony oxide
870226-1	0.10%
870226-2	0.15%
870226-3	0.10% + 30 phr antimony oxide
870226-4	0.15% + 30 phr antimony oxide

Attempts were made to permeate these samples with octadecane. The experimental procedure and the data are reported in Appendix 3 and Table 2, respectively.

Table 2 shows that HDPE goes into solution in octadecane, instead of staying as swelled pellets. The dissolving of extrusion/peroxide crosslinked HDPE pellets (instead of swelling as with irradiation crosslinked product), clearly indicates that the necessary and sufficient level of crosslinking was not achieved in these experiments. This result was totally unexpected; since, in prior DOE research, we have several times prepared swellable/insoluble HDPE pellets by this process. Additionally, within this contract year (reference November 1986 Progress Report) we have tested extrusion/peroxide crosslinked

TABLE 2

PERMEATION OF CHEMICALLY CROSSLINKED
HDPE IN OCTADECANE

<u>Date</u>	<u>Sample</u>	<u>Wt. (g)</u>	<u>Temp.</u>	<u>Time</u>	<u>Wash</u>	<u>Observations</u>
3/17	870129-1 C-18/BCL-462	10.04	150°C	2 hr.	MEK	Samples totally dissolved
3/17	870129-2 C-18/BCL-462	10.00	150°C	2 hr.	MEK	Samples dissolved
3/18	870129-2	10.02	150°C	2 hr.	MEK	Lumpy powder 26.82g
3/19	870129-2	10.03	140°C	1 hr.	50/50 MEK/MeOH	Finer powder 23.63g
3/19	870129-2	Heated pellets for 1 hr. @ 140°C to further crosslink				
3/20	870129-1	10.00	150°C	30 min.	MEK	Strained pellets washed 2x MEK - lost wt. 3.36g

Experiment Record

Results: Swelling of the pellets in C-18 was attempted at 150°C for 2 hrs., 140°C for 1 hr. and 150°C for 30 minutes. The experiment did not prove to be successful. The pellets dissolved in the C-18 even at the 30 min. swell time. Washing with a 50/50 mixture of MEK/MeOH gave a slightly finer powder. Heating the pellets for 1 hr. at 140°C did not seem to make a difference in the melt temperature.

HDPE pellets prepared elsewhere, and obtained good swellable/insoluble pellets.

In view of the economic attractiveness of this process, further experiments are planned (e.g. higher temperatures, longer soujourn times)-in order to increase the crosslinking to the desired level.

4. CONCLUSIONS

1. A new fire retardant, Bromoklor 50, is soluble in octadecane and is a potential candidate for fire retardant in permeation and percolation experiments.
2. Chemically crosslinked HDPE is a potential candidate for containment of PCM, but needs further exploration.

5. IMMEDIATE FUTURE PLANS

1. Pursue percolation experiments with Bromoklor 50 and Bromoklor 70 fire retardants.
2. Investigate the cause for solubility of Springborn made chemically crosslinked samples of HDPE.
3. Pursue experiments for in-situ incorporation of fire retardants in plasterboards.
4. Make preparations for thermocycling experiments.

APPENDIX 1

To determine the solubility of Ferro's Bromoklor 50 and Bromoklor 70 in Humphrey Tech. Grade Cl8 at 25°C and 80°C.

Procedure:

1. Weigh samples containing a total of 10 grams of material.
The compositions are as follows:

870313-1 - Cl8/Bromoklor 50 (7.5/2.5)	} Mixed at 80°C
870313-2 - Cl8/Bromoklor 70 (7.5/2.5)	
870313-3 - Cl8/Bromoklor 50 (5.0/5.0)	
870313-4 - Cl8/Bromoklor 70 (5.0/5.0)	
870313-5 - Cl8/Bromoklor 50 (7.5/2.5)	} Mixed at 25°C
870313-6 - Cl8/Bromoklor 70 (7.5/2.5)	
870313-7 - Cl8/Bromoklor 50 (5.0/5.0)	
870313-8 - Cl8/Bromoklor 70 (5.0/5.0)	
2. Samples 1 thru 4
 - (a) heat on a hot plate w/stirbar to 80°C and hold for 1 hr.
 - (b) observe to determine if a solution was obtained
 - (c) allow samples to cool and stand overnight
 - (d) observe to determine if a solution was obtained or if the phases separated.
3. Samples 5 thru 8
 - (a) heat on a hot plate w/stirbar to 25°C and hold for 1 hr.
 - (b) observe to determine if a solution was obtained
 - (c) allow samples to cool and stand overnight
 - (d) observe to determine if a solution was obtained or if the phases separated.

APPENDIX 2

Suspension of colloidal antimony oxide in Octadecane by Waring blender.

Procedure:

1. The top section of the Waring blender was put in the oven at 60°C.
2. 150 gm of C18 weighed into a tared beaker and placed in the oven at 60°C.
3. 50 gm of HA-9 was weighed into a tared beaker and placed in the oven at 60°C.
4. The samples were kept in the oven for 1 hr. 15 min.
5. The warm blender top section was put in the base.
6. The C18 and HA-9 removed from the oven and the latter added to C18 in the warm blender top with slow stirring.
7. The speed was increased as much as was allowed without splashing and mixed for 5 minutes.
8. The C18/HA-9 was poured into a hot beaker.
9. It was noticed that some HA-9 was present at the bottom of the blender.
10. The blender was weighed, cleaned, and reweighed to determine amount HA-9 not in solution (12.1 gm).
11. The experiment was stopped and the C18/HA-9 solution retained.

Total lost 13.9 gm

APPENDIX 3

Permeation of chemically crosslinked HDPE with technical grade octadecane.

Procedure:

1. Weigh 10 grams of Marlex pellets on the Mettler balance.
2. Weigh 150 grams of PCM into a beaker Humphrey Techgrade C18 (5 gallon can).
3. Melt PCM on a hot plate with a stir bar and heat to the desired temperature for swelling.
4. Slowly add Marlex pellets to the hot PCM and readjust the temperature to the desired temperature.
5. Swell with stirring for the required time (1 or 2 hrs.).
6. When time is up, strain the Marlex from the wax and wash the Marlex with warmed solvent (Mek or MeOH/Mek mixture).
7. Allow Marlex to dry and weigh for PCM pickup.

MONTHLY PROGRESS REPORT NO. 11
CONTRACT NO. DE-FG03-86SF16308
COVERING APRIL, 1987

1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research, on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends".

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The four processes are as follows:

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As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3), the building material will not burn. However, in process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard after ignition will continue to burn slowly until the PCM is exhausted.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will initiate extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

1. Further work on dispersion of fire retardant systems in C-18 hydrocarbon for percolation into plasterboard.
2. Further investigation on the extrusion/peroxide crosslinking of Marlex 6006.
3. Differential scanning calorimetry of distilled water.
4. Thermocycling of samples containing phase change material (PCM).

3. TECHNICAL DESCRIPTION OF CURRENT RESEARCH

3.1 Further Work on Dispersion of Fire Retardant Systems in C-18 Hydrocarbon for Percolation Into Plasterboard

3.1.1 Dispersion of Bromoklor 50 and Submicron Size (Colloidal) Antimony Oxide in C-18 PCM

Last month's report describes two Ferro Corporation fire retardants--Bromoklor 50 and Bromoklor 70. Bromoklor 50 was found to be soluble in C-18 hydrocarbon up to 50/50 ratio. Attempts were made this month to make a stable suspension of 70/20/10, C-18/Bromoklor 50/antimony oxide in order to obtain a synergistic combination of fire retardants (Bromoklor 50/antimony oxide) in C-18 PCM.

Two hundred (200) grams of a mixture of 70/20/10, C-18/Bromoklor 50/antimony oxide, with 2 percent stearic acid added to improve dispersion, were mixed in a waring blender at high speed for 5 minutes. The temperature rose from room temperature to 76°C. As soon as the stirring stopped the antimony oxide started to settle. The mixture was placed in a beaker, heated to 80°C and a 2" x 2" plasterboard sample was percolated for 10 minutes into this mixture. The weight percent of PCM/flame retardant in the plasterboard was 39%, after the experiment. The weight gain is in the same range as with C-18/Bromoklor 50 by itself. Evidently, very little antimony oxide, if any, could gain access to the pores of the plasterboard. The results for the flammability test are reported in Table 1.

TABLE 1
FLAMMABILITY TESTS WITH PCM/FIRE RETARDANT
COMBINATIONS

<u>Sample</u>	<u>Ignition Time (min.)</u>	<u>Exting. After (min.)</u>	<u>Second Ignition (min.)</u>	<u>Second Extinction (min.)</u>	<u>Travel</u>	<u>Smoke</u>
1. Bromoklor 50/ C-18, 30/70 Spread on aluminum bar	Didn't ignite	---	---	---	---	---
2. HA-15PE/C-18 30/70, Spread on aluminum bar	Didn't ignite	---	---	---	---	---
3. Plasterboard soaked in C-18/BK50/ Sb ₂ O ₃ , 70/20/10	7	444	---	---	yes	Vigorous flame w/ black smoke
4. Plasterboard soaked in C-18/HA15PE, 70/30	9	126	12	113	yes	Light flame - white smoke

CONCLUSION: Neither of the plasterboard samples show flame retardance.

3.1.2 Further Work on Nyacol Colloidal Antimony Oxide (HA15 PE) as Fire Retardant

Last month's report mentions Nyacol HA-9 and Nyacol HA-15PE, which are essentially colloidal antimony oxide containing 65% by wt. halogenated organic compounds. These products combine the synergistic action of antimony oxide and halogenated compounds as flame retardant.

Unsuccessful attempts to suspend HA-9 in C-18 hydrocarbons were described in the last report. Similar experiments were carried out this month with HA-15PE and C-18 hydrocarbon (30/70) using a waring blender. The temperature rose from room temperature to 75°C during the experiment. Although a large proportion of the fire retardant remains in suspension, a small portion settles as soon as the stirring is stopped. A (2" x 2") plasterboard soaked into this suspension for 10 minutes at 80°C had a 59% weight increase, corresponding to 37% PCM/fire retardant in plasterboard. Again, this weight gain can be accounted for by the PCM/fire retardant combination, showing no access of antimony oxide into the pores of plasterboard.

The results for flammability tests with the plasterboard samples are shown in Table 1. Neither of the plasterboard samples show flame retardance. Experiments with alternative methods of introducing fire retardants into plasterboard are in progress. During the course of research on fire retarding of PCM (in building materials) we have investigated several different approaches with varying degrees of success as follows.

1. Reducing the Amount of PCM Percolated Into the Plasterboard to Below the "Wicking" Level

This approach still looks very promising and requires only that we reduce the PCM content to 25% weight or lower.

2. Encapsulation of Small Crosslinked Pellets of HDPE, Containing Permeated PCM Into the Wet Mix

This approach still looks promising since few of the small pellets would be at the surface. Further it should also be possible to fire retard these HDPE pellets and this is currently being investigated.

3. Incorporating FR Chemicals Simultaneously with PCM During Percolation

Although only negative results were obtained in the approaches reported above, much more encouraging results were obtained recently by percolating a dispersion of Firol PCF in technical grade PCM. The complete results will be reported next month.

4. Incorporating PCM and Fire Retardants Into the "Wet Mix" of Plasterboard

Lastly, we believe that if the fire retardant components, with or without the PCM, are incorporated into the plasterboard at the wet mix stage, an effectively fire retarded plasterboard should be obtained.

3.2 Further Investigation on the Extrusion/Peroxide Crosslinking of Marlex 6006

Further to our report for the last month, samples of Marlex 6006, dicumyl peroxide and antimony oxide were sent to Springborn Laboratory for extrusion crosslinking of Marlex 6006 with 0.35 phr peroxide. These samples will be used for permeation studies with C-18 PCM.

3.3 Differential Scanning Calorimetry of Distilled Water

In our October 1985 report, we presented data for DSC analysis of water at 10°C/min. rate of heating. The data showed smaller values of ΔH_f and ΔH_c than expected (80 cal/g). We repeated the same experiment at much lower rates of heating (2°C/min. and 0.1°C/min.). The data are summarized in Table 2 and the DSC curves are presented in Figures 1 through 4.

TABLE 2
ANALYSIS OF THERMAL ENERGY STORAGE
OF WATER BY DSC

<u>Sample Identification and Composition</u>	<u>T_m (°C)</u>	<u>T_c (°C)</u>	<u>T_m-T_c (°C)</u>	<u>ΔH_f (cal/gm)</u>	<u>ΔH_c (cal/gm)</u>
October, 1985 Deionized Water 10°C/min.	2.3	-11.5	13.8	73.8	63.7
May, 1987 Distilled Water 2°C/min.	2.0	-11.5	13.6	84.3	73.9
May, 1987 Distilled Water 0.1°C/min.	-0.68	-12.1	13.0	80.5	63.7

Sample: DISTILLED WATER
 Size: 8.90 mg
 Method: DSC- 2°C/MIN
 Comments: 2°C/MIN

File: RUN1159.07
 Operator: GALASKA
 Run date: 05/05/87 10:38

DSC

Figure 1. DSC Analysis of Thermal Energy Storage of Distilled Water at 2°C/Min. Rate of Heating.

Sample: DISTILLED WATER
 Size: 8.50 mg
 Method: DSC-0.1°C/MIN
 Comments: 0.1°C/MIN

DSC

File: RUN1165.03
 Operator: GALASKA
 Run date: 05/13/87 17:08

Figure 2. DSC Analysis of Thermal Energy Storage of Distilled Water at 1°C/Min. Rate of Heating.

Sample: DISTILLED WATER
 Size: 11.80 mg
 Method: DSC-0.1°C/MIN
 Comment: 0.1°C/MIN

File: RUN1165.02
 Operator: GALASKA
 Run date: 05/13/87 07:02

DSC

Figure 3. Amplified Scale for the DSC Analysis of the Melting of Distilled Water at 0.1°C/Min. Rate of Heating.

Sample: DISTILLED WATER
 Size: 9.50 mg
 Method: DSC-0.1°C/MIN
 Comment: 0.1°C/MIN

DSC

File: RUN1165.03
 Operator: GALASKA
 Run date: 05/13/87 17.08

Figure 4. Amplified Scale for the DSC Analysis of the Freezing of Distilled Water at 0.1°C/Min. Rate of Heating.

Table 2 shows the ΔH_f values are much closer to the theoretical values of 80 cal/g at very slow rate of heating. However, ΔH_c is still far below the theoretical value. This is due to the large supercooling, which makes the rate of freezing (exothermic heat) so fast that it causes an unbalance in the rate of heating. This unbalance shows up as discontinuity in the temperature plot (dashed curve) of Figures 1, 3 and 4. This probably causes an error in ΔH_c values obtained from these curves.

Another interesting observation is that the amount of supercooling does not change by the rate of heating. Therefore, T_c values remain unaffected. T_m values change only slightly and approaches the theoretical value of 0°C at 0.1°C/min. rate of heating.

3.4 Thermocycling of Samples Containing Phase Change Material

Thirty-three (33) samples of different PCM, PCM/fire retardant combinations and PCMs contained in LDPE, HDPE, Polypropylene, cement and plasterboards have been collected. A small portion of each have been sampled in a small bottle. Thermocycling will be started in the near future.

4. CONCLUSIONS

1. Permeation of colloidal size antimony oxide insoluble fire retardant combination does not show promise as a practical option to flame retard plasterboard.
2. The method of permeating soluble flame retardant/PCM combinations, described in December 1986 report, seems to be a feasible alternative.
3. In-situ incorporation of fire retardant into plasterboard is another alternative, which will be attempted in the future.

5. IMMEDIATE FUTURE PLANS

1. Permeation of peroxide crosslinked HDPE samples, with C-18 PCM.
2. In-situ incorporation of fire retardant/PCM into plasterboard.
3. Thermocycling experiments.

MONTHLY PROGRESS REPORT NO. 12
CONTRACT NO. DE-FG03-86SF16308
COVERING MAY, 1987

1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research, on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends".

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

The four processes are as follows:

1. Direct incorporation of PCM into the wet mix of building materials,
2. Direct incorporation into rubber or plastics medium for floor and wall tiles,
3. Indirect incorporation by first swelling the PCM into crosslinked polyethylene pellets or powder, which are then incorporated into building materials,
4. Direct incorporation by percolating the melted PCM into the open space in porous building materials.

As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3). The building material will not burn. However, in process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard after ignition will continue to burn slowly until the PCM is exhausted.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will initiate extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

The present month's work consists of the following:

1. Thermal energy storage properties of phase change materials at different heating and cooling rates.
2. Thermal energy storage properties of Humphrey technical grade octadecane at different heating and cooling rates.
3. Effect of heating and cooling rates on thermal energy storage properties of butyl stearate.
4. Evaluate permeation of butyl stearate into crosslinked Marlex 6006 pellets.
5. Evaluate percolation of butyl stearate into platerboard.

3. TECHNICAL DESCRIPTION OF CURRENT RESEARCH

3.1 Thermal Energy Storage Properties of Humphrey Technical Grade Octadecane at Different Heating and Cooling Rates

Humphrey technical grade octadecane is one of the candidate phase change materials (PCM) that we have been studying in building materials for solar passive heating and cooling of residential and commercial buildings. It melts and freezes at around the comfortable temperature of 75°F, has a high latent heat accompanying change of state and is commercially available. It would, therefore, be interesting to study the effect of heating and cooling rates on thermal energy storage properties of this PCM. Particularly interesting would be the effect of very slow (0.1°C/min.) heating and cooling rates which would simulate very closely the conditions of actual use.

Table 1 and Figure 1 summarize the data for thermal energy storage properties by differential scanning calorimetry (DSC) at higher rates (2-20°C/min., August, 1986 report), along with the very slow rate (0.1°C/min.) data obtained recently. As reported earlier (August, 1986 report), T_m and T_c get closer together as the rate of heating/cooling decreases. These temperatures are very close together at 0.1°C/min. rate ($T_m - T_c \sim 1.5$) and are

TABLE 1
THERMAL ENERGY STORAGE PROPERTIES OF HUMPHREY
TECHNICAL GRADE OCTADECANE AT DIFFERENT
HEATING AND COOLING RATES

Sample Identification and Composition	T _m (°C)	T _c (°C)	T _m -T _c (°C)	ΔH _f (cal/gm)	ΔH _c (cal/gm)
n-Octadecane 20°C/min.	30.2	18.6	11.5	52.4	51.0
n-Octadecane 10°C/min.	28.0	19.5	8.5	52.9	52.6
n-Octadecane 5°C/min.	27.1	21.2	5.9	50.7	50.7
n-Octadecane 2°C/min.	26.2	22.5	3.7	49.0	48.9
n-Octadecane 0.1°C/min.	25.2	23.7	1.5	43.7	44.9
<u>Secondary Transition</u>					
n-Octadecane 20°C/min.	--	13.7			
n-Octadecane 10°C/min.	--	15.0			
n-Octadecane 5°C/min.	--	16.8			
n-Octadecane 2°C/min.	--	17.7			
n-Octadecane 0.1°C/min.	--	20.2			

indistinguishable from the extrapolated temperatures obtained from Figure 1.

Pure n-octadecane shows only one transition both during melting and freezing (August, 1986 report) with a ΔH_f and ΔH_m of 59 calories per gram. The Humphrey technical grade octadecane also shows a single transition during melting but it shows an additional transition at a lower temperature during freezing. Its T_m , T_c , ΔH_f and ΔH_c are also somewhat lower, indicating the presence of other component hydrocarbons. Figure 1 includes the plot of secondary transition temperature (T'_c) vs. rate of temperature change. A linear relationship holds up to 2°C rate of cooling. Unlike the main transitions, the secondary transition temperature departs from linear relationship at very slow rate of cooling (0.1°C/min.).

Figure 2 shows the DSC curve for Humphrey technical grade octadecane at 0.1°C per minute rate of heating and cooling. The secondary transition during freezing is very sharp at this slow rate.

Table 1 shows that ΔH_f and ΔH_c values decrease as the rate of heating or cooling decreases. However, a comparatively sharp decrease is observed at slow rate of temperature change (0.1°C/min.). The reason for this is not apparent and in view of other data (butyl/stearate) where no decrease is observed, may be an anomaly. Because of the large amount of time needed for the slow heating and cooling rate the experiment was not repeated.

3.2 Effect of Heating and Cooling Rates on Thermal Energy Storage Properties of Butyl Stearate

Butyl stearate is another potential candidate for phase change material for solar passive heating and cooling of building materials for residential and commercial buildings. Table 2 and Figures 3 and 4 present the data obtained at 2 and 10°C per minute rate of heating and cooling. The same trends as described earlier for octadecane are also observed here. The extrapolated 0°C/min. rate show almost congruent melting and freezing. However, the

Figure 1. Effect of Rate of Temperature Change Vs. Melting and Crystallization Temperature of Technical Grade n-Octadecane.

Sample: C-18 TECH GRADE
 Size: 7.18 mg
 Method: DSC-0.1°C/MIN
 Comment: 0.1°C/MIN

File: RUN1182.01
 Operator: GALASKA
 Run date: 05/18/87 16:41

DSC

Figure 2. DSC Analysis of Thermal Energy Storage of Humphrey Technical Grade Octadecane at 0.1°C/Min. Rate of Heating or Cooling.

TABLE 2
THERMAL ENERGY STORAGE PROPERTIES OF
BUTYL STEARATE AT DIFFERENT HEATING
AND COOLING RATES

Sample Identification & Composition	T _m (°C)	T _c (°C)	T _m -T _c (°C)	ΔH _f (cal/gm)	ΔH _c (cal/gm)
Butyl Stearate 10°C/min.	23.3	17.4	5.9	35.7	35.8
Butyl Stearate 2°C/min.	21.9	19.5	2.3	36.0	38.0
Butyl Stearate 0°C/min. (extrapolated)	21.6	20.0	1.6	--	--
Butyl Stearate Secondary Transitions 10°C/min.	8.3	4.7	3.6		
Butyl Stearate Secondary Transitions 2°C/min.	6.9 10.6	5.8 9.3	1.1 1.3

Figure 3. Effect of Rate of Temperature Change Vs. Melting and Crystallization Temperature of Butyl Stearate.

Sample: BUTYL STEARATE
 Size: 3.95 mg
 Method: DSC-MELT
 Comment: HEATING RATE 10C/MIN

DSC

File: A:RUN0921.02
 Operator: MARY
 Run date: 08/25/88 10:58

Sample: BUTYL STEARATE
 Size: 3.95 mg
 Method: DSC-MELT
 Comment: HEATING RATE 2°C/MIN

DSC

File: A:RUN0920.02
 Operator: MARY
 Run date: 08/22/88 13:37

Figure 4. DSC Analysis of Thermal Energy Storage Properties of Butyl Stearate at Different Rates of Heating and Cooling.

rate of temperature change does not affect ΔH_f and ΔH_c as in the case of octadecane.

3.3 Evaluate Containment of Butyl Stearate in Building Materials

After recognizing the potential use of butyl stearate as PCM, it was important to investigate the possibility of its containment in building materials. This was investigated by the methods (3) and (4) mentioned in the "Background" and are described below.

3.3.1 Evaluate Containment of Butyl Stearate Into Crosslinked Marlex 6006 Pellets

The experimental procedure for permeation is described in Appendix 1. After permeation for 2 hrs. at 150°C and washing with warm MEK, the amount of butyl stearate determined from weight gain is 72.6%. The amount determined from DSC enthalpy (Table 3, Figure 5) of a single pellet is 67.2%. The lower figure from DSC measurement may be due to nonuniform permeation in different pellets. The amount permeated is in the same range as that of n-octadecane, under the same experimental condition. The DSC curves (Figure 5) shows that the energy storage potential of butyl stearate remains unaltered after permeation into crosslinked high density polyethylene pellets.

3.3.2 Evaluate Percolation of Butyl Stearate Into Plasterboard

The procedure for percolation was the same as with other PCM and is described in Appendix 1. The calculated amount of butyl stearate after percolation was 33.9% and 31%, respectively, by weight gain (percent of total weight) and DSC method. The data are comparable and are in the same range as other phase change materials studied. Also, Figure 6 shows that the energy storage potential of butyl stearate after percolation into plasterboard remains unaltered. Flammability test of the percolated board shows that it is easily flammable.

TABLE 3
THERMAL ENERGY STORAGE PROPERTIES OF
BUTYL STEARATE AT DIFFERENT HEATING
AND COOLING RATES

Sample Identification & Composition	T _m (°C)	T _c (°C)	T _m -T _c (°C)	ΔH _f (cal/gm)	ΔH _c (cal/gm)	Extrapolated at 100% ΔH _f (cal/gm)	ΔH _c (cal/gm)
*Swelled Marlex 6006 Pellets							
Butyl Stearate	21.4	16.8	4.6	24.0	24.7	33.1	34.0
Marlex 6006	115.5	107.7	7.8	9.2	8.7	33.6	31.8
**Plasterboard Swelled in Butyl Stearate							
Butyl Stearate	21.4	18.0	3.4	11.4	12.1	33.6	35.7
Butyl Stearate (Neat)							
Butyl Stearate	21.9	19.5	2.3	36.0	38.0		

*Percent Butyl Stearate by wt. ~72.6%; by DSC 67.2%.

**Percent Butyl Stearate by wt. ~33.9%; by DSC 31%.

Sample: MARLEX 10Mrad/BUTYL STEARATE
 Size: 4.70 mg
 Method: DSC-10 °C/MIN
 Comment: 10 °C/MIN

File: RUN1180.02
 Operator: GALASKA
 Run date: 05/15/87 12:04

DSC

Figure 5. DSC Analysis of Thermal Energy Storage of Butyl Stearate Permeated in Crosslinked (10 Mrad) Marlex 6006.

Figure 6. DSC Analysis of Thermal Energy Storage of Butyl Stearate Percolated in USG Plasterboard.

4. CONCLUSIONS

1. Humphrey technical grade n-octadecane melts and freezes congruently when subjected to extremely slow rate of heating/cooling (0.1°C), simulating slow atmospheric variations in temperature.
2. Butyl stearate is a potential back-up candidate for phase change material.
3. Butyl stearate can be incorporated in building materials by permeation into crosslinked high density polyethylene (indirectly); and by percolation in plasterboard (directly).

5. IMMEDIATE FUTURE PLANS

1. Further investigation of the extrusion/peroxide crosslinking of Marlex 6006.
2. Evaluate the fire retardance of plasterboard percolated with mixtures of C₁₈ PCM and commercial fire retarding agents.
3. Thermocycling of PCMs, PCM permeated into HDPE, and PCM contained in different building materials.

APPENDIX 1

PROCEDURES FOR PERMEATION AND PERCOLATION OF BUTYL STEARATE

Work Request: 870514-1 and -2
Date: May 14 & 15, 1987
Performed By: Mary Galaska

Procedure:

- A. Pellet permeation: 100g of butyl stearate was heated to 150°C with constant stirring. 5g of Marlex 6006 10 Mrad pellets were added and permeated for 2 hours at 150°C. The pellets were strained out, cooled, and washed 3x with 50°C MEK. They were then allowed to dry in a hood overnight.
- DSC: The center section of a pellet was weighed and a standard DSC analysis was run at 2°C/min.
- B. Plasterboard percolation: A dried and weighed 2" x 2" square of plasterboard was soaked for 10 min. in a bath of butyl stearate at 80°C. The sample was cooled and reweighed for PCM pickup. Then it was sampled for DSC analysis at a heating and cooling rate of 2°C/min.

MONTHLY PROGRESS REPORT NO. 13
CONTRACT NO. DE-FG03-86SF16308
COVERING JUNE, 1987

1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research, on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends".

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

The four processes are as follows:

1. Direct incorporation of PCM into the wet mix of building materials,
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As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3), the building material will not burn. However, in process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard after ignition will continue to burn slowly until the PCM is exhausted.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will initiate extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

The present month's work consists of the following:

1. Further investigation of the extrusion/peroxide crosslinking of Marlex 6006.
2. Effect of temperature on the pickup of Humphrey Technical Grade C-18 PCM in plasterboard.
3. Evaluate the fire retardance of plasterboard percolated with mixtures of C-18 PCM and commercial fire retarding agents.
4. DSC analysis of plasterboard, percolated with C-18 PCM/fire retardant combination.
5. Thermocycling of phase change materials (PCM).

3. TECHNICAL DESCRIPTION OF CURRENT RESEARCH

3.1 Further Investigation of the Extrusion/Peroxide Crosslinking of Marlex 6006

Marlex 6006 (Phillips high density polyethylene) requires some crosslinking in order to remain form-stable (prevent dissolving) in hydrocarbon phase change material. The cheapest way to introduce these crosslinks would be to use a suitable peroxide and extrude the polymer-peroxide combination at high temperature. The extrudate can be passed through a pelletizer to obtain pellets of different sizes. The process would be much cheaper than gamma ray irradiation used in our earlier work. In addition, extruders are more readily available and the pellets of predetermined sizes can be obtained.

Our March, 1987 report described a preliminary study of extrusion/peroxide crosslinking. However, these samples were not crosslinked enough and the pellets disintegrated in hot PCM. This month five more samples were sent to Springborn Laboratories for extrusion-crosslinking. The composition, processing conditions and the swelling data are reported in Table 1. The swelling procedure is described in Appendix 1.

TABLE 1
EXTRUSION CROSSLINKING OF MARLEX 6006 PELLETS AND POWDER
BY DICUMYL PEROXIDE AT SPRINGBORN LABORATORIES

Sample Number	Composition	Extrusion Temperature	% Swelled (Weight Gain/Total Weight)
870504-1	Marlex 6006 Pellets - 1000g Luperox 500R (Dicumyl Peroxide 99%) - 3.5g	400°F	The sample was recovered as powder 70.7
870504-2	Marlex 6006 Pellets - 1000g Luperox 500R (Dicumyl Peroxide 99%) - 3.5g	500°F	The sample was recovered as powder 68.3
870504-3	Marlex 6006 Powder - 1000g; Luperox 500R - 3.5g	500°F	The sample was recovered as powder 67.2
870504-4	Marlex 6006 Powder - 1000g; Luperox 500R - 3.5g	Extrude & pelletize the HDPE at 400°F. Then re-extrude these pellets plus 0.35% dicumyl peroxide at 500°F.	The sample was recovered as powder 66.9
870504-5	Marlex 6006 Powder - 1000g; Luperox 500R - 3.5g; Antimony Oxide - 300g	Extrude & pelletize the HDPE at 400°F. Then re-extrude the pellets + 0.35% dicumyl peroxide + 30 phr antimony oxide at 500°F.	The sample was recovered as powder 66.8 (on total) 86.7 (on polymer)

All the samples were recovered as powder indicating that crosslinking is not enough to prevent the pellets from disintegrating in hot PCM. Further experiments are planned with higher amounts of peroxide, longer extruder residence time, and postcuring, to further study the effects of extrusion variables.

Interestingly, these powders may be a useful, lower cost alternative to putting pellets into building materials. Because of smaller particle size they may have less effect on the mechanical properties of plaster, concrete, etc.

3.2 Determine the Effect of Temperature on the Pickup of Humphrey C-18 Technical Grade PCM, in Plasterboard

The fourth method of PCM incorporation, described in the "Background", uses melted PCM to soak into plasterboard. One of the process parameters that was not studied yet is the effect of temperature on PCM pickup. Our recent study closes this gap. The data are reported in Table 2.

Table 2 shows that above the melting point (30°C), the temperature has very little effect. Slightly lower pickup at 125°C may be due to dehydration of plaster. PCM pickup is complete at 5 minutes and further exposure up to 10 minutes has no effect. This finding eliminates the need for high temperature (e.g. 80°C) for percolating PCM that melt near room temperature, and thus reduces process cost.

3.3 Evaluate the Fire Retardance of Plasterboard Percolated in Mixtures of C-18 PCM and Commercial Fire Extinguishing Agent

In earlier work on fire retardance of PCM treated plasterboard, we endeavored to select a flame retardant that is soluble in the PCM, so that it can permeate into the mass of the plaster along with the PCM. Recent work shows, that although complete solubility of the fire retardant in PCM is desirable, it is not absolutely necessary. This is illustrated in the following work with Fyrol PCF (tri(B-chloroisopropyl) phosphate) in octadecane (C-18 PCM).

TABLE 2
EFFECT OF BATH TEMPERATURE ON
PICKUP OF HUMPHREY TECHNICAL GRADE C-18

Sample Number	Bath Temperature	Time	% PCM Pickup
870518-1	30°C	5 mins.	35.33
870518-2	30°C	10 mins.	32.58%
870518-3	50°C	5 mins.	31.94%
870518-4	50°C	10 mins.	32.39%
870518-5	80°C	5 mins.	31.60%
870518-6	80°C	10 mins.	31.02%
870518-7	100°C	5 mins.	30.90%
870518-8	100°C	10 mins.	32.18%
870518-9	125°C	5 mins.	28.97%
870518-10	125°C	10 mins.	27.48%

A suspension or solution of C-18 with Fyrol PCF and/or BCL-462 (soluble FR) was made in the following composition following the method described in Appendix 2.

- (1) C-18/Fyrol PCF (75/25)
- (2) C-18/Fyrol PCF/BCL-462 (75/15/10)
- (3) C-18/BCL-462/Santicizer 141* (75/15/10)

The first compound contains only the partially soluble Fyrol PCF fire retardant. The second has the insoluble Fyrol plus a soluble fire retardant (BCL-462). The third has a soluble fire retardant (BCL-462), along with fire retardant phosphate ester plasticizer.

The pickup of the above compositions in plasterboard is presented in Table 3. Around 5 percent higher weight gain than for C-18 only (Table 2) is observed for all the compositions. In the case of the first composition, DSC analysis at different locations of the plasterboard was undertaken to estimate the amounts of C-18 and Fyrol PCF that is percolated at different locations of the plasterboard. These data are presented in the next section.

Table 4 presents the flame test data of the percolated plasterboards. It is apparent that only the plasterboard percolated with 75/25, C-18/Fyrol PCF is flame retardant. It would not stay lit after the flame was removed and was self-extinguishing. This is an important advancement, since this shows that complete miscibility of the PCM and fire retardant is not an absolute requirement. Whether this is a characteristic for only specific types of fire retardants will be explored further in our future work.

3.4 DSC Analysis of Plasterboard, Percolated with C-18 PCM/Fire Retardant Composition

Table 5 shows the DSC analysis of the plasterboard sample, percolated with C-18/Fyrol PCF (75/25). Samples were taken from different locations of the plasterboard as described in Figure 1.

The first observation, to our surprise, is the large discrepancy between the percent C-18 by weight gain (37.8%), versus
*2-ethyl hexyl diphenyl phosphate - a flame retardant plasticizer from Monsanto.

TABLE 3
PERCOLATION OF C-18/FIRE RETARDANT
COMPOSITION IN PLASTERBOARD

Sample Number	Formulation	Initial Weight	Final Weight	% Weight Gain
870504-6	C-18/Fyrol PCF (75/25)	20.8524	33.5338	37.82
870504-7	C-18/Fyrol PCF/BCL-462 (75/15/10)	21.7803	34.0901	36.11
870504-8	C-18/BCL-462/Sant. 141 (75/15/10)	22.1959	34.6242	35.89

TABLE 4
FLAME TEST OF PLASTERBOARD CONTAINING
PERCOLATED C-18 PCM/FIRE RETARDANT COMPOSITION

Sample	First Ignition	Extinguish	Second Ignition	Extinguish	Travel	Smoke	Comments
870504-6 Plaster soaked in 75/25 C-18/ Fyrol PCF Wt. Soaked 37.8%	Wouldn't stay lit after flame was removed	Self- extin- guishing	---	---	no	white - alot	hood off
870504-7	15 secs.	371	---	---	yes-down one side other side	black ---	hood off ---
870504-8	5 secs.	440 sec.	---	---	yes-2 sides	black-alot	hood off

TABLE 5
DSC ANALYSIS OF SAMPLES FROM DIFFERENT
LOCATIONS OF PLASTERBOARD, PERCOLATED
WITH C-18/FYROL PCF (75/25)*

Sample Identification and Composition	T _m (°C)	T _c (°C)	T _m -T _c (°C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)	Extrapolated to 100%	
						ΔH_f (cal/gm)	ΔH_c (cal/gm)
Samples from the top of the paper cover, #6	26.2	20.1	6.1	3.7	3.5	9.8	9.3
Sample from the bottom of the paper cover, #9	27.1	20.1	7.0	3.0	3.1	7.9	8.2
Sample from under the top paper cover, #7	27.2	19.7	7.5	5.2	5.3	13.8	14.0
Sample from under the bottom paper cover, #8	26.0	20.5	5.5	0.84	0.93	2.2	2.5
Sample from outside the broken edge, #1	27.7	19.6	8.1	3.6	3.7	9.5	9.8
Sample from outside the broken edge, #5	28.0	19.1	8.9	3.4	3.8	9.0	10.1
Sample from inside mid portion, #2	25.9	20.5	5.4	1.3	1.4	3.4	3.7
Sample from inside mid-portion, #4	26.5	20.2	6.3	3.5	3.5	9.3	9.3
Sample from inside center of the sample, #3	25.9	19.4	6.5	0.66	0.72	1.7	1.9
Humphrey Technical Grade C-18 PCM	28.0	19.5	8.5	52.9	52.6	100	100

Figure 1. Sample Location for DSC Analysis of Plasterboard.

the maximum amount of C-18, calculated by DSC (9.8%). This leaves ~28% of the composition by weight to Fyrol PCF; and indicates that Fyrol PCF is percolated in preference to octadecane. This may be ascribed to the similar polarity of Fyrol PCF and the plasterboard.

Although there is some discrepancy in the DSC data, the results indicate progressively smaller amounts of octadecane from the top and bottom of the sample to the center. The sample at the center (#3) shows the smallest amount of octadecane by DSC (1.2%). This is also the sample which shows a separate endotherm (possibly for Fyrol PCF). DSC curves of the two samples showing the highest (#7) and lowest (#3) concentration of octadecane are shown in Figures 2 and 3.

Lower concentrations of Fyrol, and sequential percolation of PCM followed by Fyrol are planned for investigation in the following months.

3.5 Thermocycling of Phase Change Materials

One of the most important requirements of this project is to make sure that the PCM used in the building materials survives repeated cycles of freezing and cooling. The PCM permeated in HDPE; and that percolated into plasterboard and cement should not ooze out, and should also survive the thermal cycles without degradation of thermal energy storage properties.

In order to make sure that the above expectations are fulfilled, elaborate controlled thermocycling experiments have been planned. Thirty-five samples, consisting of neat PCM and PCM contained in HDPE pellets, plasterboard and concrete were selected and placed in sealed glass vials, capable of thermocycling between +60°C and -10°C temperatures. The 60°C high temperature was chosen to be above the melting point of all PCMs; and -10°C to be below the freezing points of all PCMs. Thermocycling will go up to 1000 cycles and will be completed on August 7, 1987. The samples selected in the beginning of thermocycling are presented in Table 6. Other samples were added at different stages of thermocycling. Samples are being visually observed at 5th, 50th,

Sample: 870504-6(C-18/FYROL PCF) #7
Size: 6.56 mg
Method: DSC-10°C/min
Comment: 10°C/min NIT

DSC

File: RUN1209.02
Operator: GALASKA
Run date: 06/10/87 09.10

Figure 2. DSC Analysis of Octadecane/Firol PCF, showing highest concentration of Octadecane.

Sample: 870504-6(C-18/FIROL PCF) #3
 Size: 3.79 mg
 Method: DSC-10°C/min
 Comment: 10°C/min NIT

DSC

File: RUN1205.02
 Operator: GALASKA
 Run date: 06/09/87 10:08

Figure 3. DSC Analysis of Octadecane/Firol PCF, showing lowest concentration of Octadecane.

TABLE 6
PCM COMPOSITIONS FOR THERMOCYCLING EVALUATIONS

Neat PCM	HDPE Pellets	Plasterboard	Concrete	Matsushita Samples
1 NP-15	7 NP-15	13 NP-15	19 NP-15	25 Paraffin 115
2 C-18T	8 C-18T	14 C-18T	20 C-18T	26 LDPE AKZO No. 1
3 K-61	9 K-61	15 K-61	21 K-61	27 HDPE HF40X No. 5
4 45-A	10 45-A	16 45-A	22 45-A	28 CPP PM80X No. 6
5 LLN	11 LLN	17 LLN	23 LLN	29 LDPE AKZO No. 1 + P-115 151°C + 30 min.
6 C-18T/BCL-462 (80/20)	12 C-18T/BCL-462 (80/20)	18 C-18T/BCL-462 (80/20)	24 C-18T/BCL-462 (80/20)	30 HDPE HF40X No. 5 + P-115 153°C + 120 min.
6.5 Butyl Stearate	12.5 Butyl Stearate	18.5 Butyl Stearate	24.5 Butyl Stearate	31 CPP PM80X No. 6 + P-115 183°C + 120 min.

100th, 200th, 500th, 800th, and 1000th cycle. DSC analysis will be carried out for selected samples.

4. CONCLUSIONS

1. None of the samples of peroxide/extrusion processed HDPE were sufficiently crosslinked to prevent dissolving in hot C-18 PCM. The powders obtained from low level crosslinked HDPE contains around 70% octadecane may be of interest as a hardened wax that may not degrade the physical properties of cement and plaster as much as the larger HDPE pellets.
2. Above the melting point of PCM, higher temperature, up to 100°C, has little effect on PCM up-take; and thus lower more economic percolation temperatures can be used.
3. Complete miscibility of PCM fire retardant is not an absolute requirement for flame resistance of percolated plasterboards.
4. DSC analysis indicates that the plasterboard percolated in octadecane/Fyrol PCF (75/25) absorbed more Fyrol PCF than octadecane.

5. IMMEDIATE FUTURE PLANS

1. Complete thermocycling and analyze the data.
2. Continue and complete thermocycling of large samples of PCM-percolated plasterboard and concrete.
3. Further study the gamma irradiation in nitrogen, of sheets, film, fabric and powder of CPP, HDPE and LDPE.
4. Thermal energy storage of flowerpot, cup, HDPE grocery bag, and LDPE dry cleaner's film, that have been crosslinked by gamma irradiation in N_2 , will be evaluated. Further evaluation of extrusion/peroxide crosslinking of HDPE at Springborn Laboratories using higher temperatures, longer extruder residence time, and post curing of the pellets.

APPENDIX 1
PROCEDURE FOR SWELLING EXTRUSION/PEROXIDE
CROSSLINKED HDPE PELLETS

Work Request: 870504-1 to -5

Performed by: Mary Galaska, Mike Beutel

Date Completed: June 9, 1987

Procedure:

10g of each batch of extruded pellets were evaluated for swelling in Tech grade C-18 for 2 hrs. at 150°C with constant stirring. All of the samples disintegrated but the powder was retained and washed 2x with warm MEK. The PCM pickup was calculated for each batch.

APPENDIX 2
PROCEDURE FOR PERCOLATION OF C-18 PCM/
FIRE RETARDANT COMBINATION

Work Request: 870504-7 thru -9

Date: May 15, 1987

Performed by: Mike Beutel

Procedure:

Three samples of 2" x 2" dry plasterboard were obtained and weighed. A solution of C-18 and Fyrol PCF (75/25) was made in a beaker and brought to 80°C. Since the Fyrol PCF was insoluble in the C-18, the solution was stirred constantly using a magnetic stirrer. This was done to maintain a good suspension. One sample of plasterboard was placed in the solution. It was supported above the stirrer by a wire stand. The plasterboard was percolated for 10 minutes at 80°C. After the 10 minutes, the sample was removed and allowed to air dry. The sample was weighed again and the pickup and the PCM/fire retardant mixture was calculated.

The same procedure was followed for the other two plasterboard samples. One was percolated in a C-18/Fyrol PCF/BCL-462 (75/15/10) mixture. The other was percolated in a C-18/BCL-462/Santicizer 141 (75/15/10) mixture.

MONTHLY PROGRESS REPORT NO. 14
CONTRACT NO. DE-FG03-86SF16308
COVERING JULY, 1987

1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research, on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends".

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

The four processes are as follows:

1. Direct incorporation of PCM into the wet mix of building materials,
2. Direct incorporation into rubber or plastics medium for floor and wall tiles,
3. Indirect incorporation by first swelling the PCM into crosslinked polyethylene pellets or powder, which are then incorporated into building materials,
4. Direct incorporation by percolating the melted PCM into the open space in porous building materials.

As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3), the building material will not burn. However, in process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard after ignition will continue to burn slowly until the PCM is exhausted. In process #2, where the alkylhydrocarbon is compounded into rubbers or plastics, the products will also burn unless fire retardant polymers, or additives, are used.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in the percolation process (No. 4). Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will initiate extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through

further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

The present month's work consists of the following:

1. Evaluate the stability of selected PCM compositions to thermocycling between the temperatures of -10 and 60°C.
2. Make a room temperature hardened composition of Humphrey Tech Grade C-18 with the specified hardening agents at 20 and 30% concentration.
3. Further study of the crosslinking by gamma irradiation in nitrogen, of sheets, film, fabric and powder of crystalline polypropylene, high density polyethylene and low density polyethylene.
4. Determine the total thermal energy storage of one square foot of plasterboard, percolated to 40% weight of C-18 PCM; and for one standard hollow core concrete block percolated to 5% weight PCM.

3. TECHNICAL DESCRIPTION OF CURRENT RESEARCH

3.1 Evaluate the Stability of Selected PCM Compositions to Thermocycling Between the Temperatures of -10 to 60°C

Thermocycling was carried out in an automatic oven capable of temperature control between -100°F and 350°F without humidity control (ambient humidity) and 40°F to 190°F with humidity control. The unit was custom made by Cincinnati Subzero and is shown in Figures 1-3. The temperature range (-10 to 60°C) chosen for the present experiment is within the range of the melting and freezing temperatures of the PCMs chosen.

A list of the PCMs chosen for thermocycling is given in Table 1. Thirty-five samples were chosen in the beginning. Others were added at different intervals as the thermocycling progressed. The samples were of five different categories (Table 1). They are:

Figure 1. Sample Rack Inside the Thermocycling Unit.

Figure 2. Temperature Control for the Thermocycling Unit.

Figure 3. General View of the Thermocycling Unit.

TABLE 1
PCM COMPOSITIONS FOR THERMOCYCLING EVALUATIONS

Neat PCM	HDPE Pellets	Plasterboard	Concrete	Matsushita Samples
1 NP-15	7 NP-15	13 NP-15	19 NP-15	25 Paraffin 115
2 C-18T	8 C-18T	14 C-18T	20 C-18T	26 LDPE AKZO No. 1
3 K-61	9 K-61	15 K-61	21 K-61	27 HDPE HF40X No. 5
4 45-A	10 45-A	16 45-A	22 45-A	28 CPP PM80X No. 6
5 LLN	11 LLN	17 LLN	23 LLN	29 LDPE AKZO No. 1 + P-115 151°C + 30 min
6 C-18T/BCL462 (80/20)	12 C-18T/BCL462 (80/20)	18 C-18T/BCL462 (80/20)	24 C-18T/BCL462 (80/20)	30 HDPE HF40X No. 5 + P-115 153°C + 120 min
6.5 Butyl Stearate	12.5 Butyl Stearate	18.5 Butyl Stearate	24.5 Butyl Stearate	31 CPP PM80X No. 6 + P-115 183°C + 120 min.

- (1) Neat PCM-seven PCMs, both single hydrocarbon (C-18) and commercial blends having different phase change temperatures (Column 1, Table 1).
- (2) High density polyethylene pellets which were crosslinked by gamma irradiation and swelled in different PCMs, mentioned in Column 2.
- (3) USG plasterboards that were percolated by the same PCMs.
- (4) Concrete samples percolated by the same PCMs.
- (5) Samples of paraffinic hydrocarbons and chemically crosslinked HDPE and crystalline polypropylene that were swelled in the paraffinic hydrocarbons (mentioned in the last column of Table 1).

Two grams each of the accurately weighed sample of PCM compositions were placed in a clean and dry 2 oz. bottle with cover. Because of higher density, 4g of the concrete sample was taken. These samples were drilled out of a flat specimen. A small amount, (0.1g) of sample for DSC was taken out from each bottle at intervals of 5th, 100th, 200th, 500th, 800th and 1000th thermocycles. Samples were visually observed for oozing, discoloration, etc. at each interval and at the end of thermocycling.

Table 2 reports the visual observation. It may be observed that several of the commercial paraffins hydrocarbon PCMs (K-61, 45A, LLN) show some degree of sticking and oozing in HDPE pellets as the thermocycling progresses. However, #8 (Humphrey Technical C-18) and NP-15, show a little sticking and no oozing. A large amount of oozing is observed for the samples 29, 30 and 31 which are the chemically crosslinked HDPE, LDPE and CPP polymer pellets supplied by Matshushita that were permeated by P-115, a commercial blend of hydrocarbons. The observation corroborates Matshushita's disclosure that oozing is a major problem with their pellets. Whether this is due to the nature of the polymer, the chemical crosslinking method (vinyl triethoxy silane), or the nature of the commercial hydrocarbon blends used, is not known. Although some oozing is observed from the gamma irradiated and subsequently permeated pellets made by us, the degree of oozing is insignificant compared to the Matshushita samples.

TABLE 2
VISUAL OBSERVATION FOR
INITIAL THERMOCYCLING SAMPLES

Number	100 Cycles	200 Cycles	500 Cycles	800 Cycles	1000 Cycles
1	N.C.	N.C.	N.C.	N.C.	N.C.
2	N.C.	N.C.	N.C.	N.C.	N.C.
3	N.C.	N.C.	N.C.	N.C.	N.C.
4	N.C.	N.C.	N.C.	N.C.	N.C.
5	N.C.	N.C.	N.C.	N.C.	N.C.
6	N.C.	N.C.	N.C.	N.C.	N.C.
6.5	N.C.	N.C.	N.C.	N.C.	N.C.
7	N.C.	N.C.	N.C.	N.C.	N.C.
8	Slt. stick/ No ooze	Slt. stick	Sticking	Sticking	Sticking
9	Some oozing	Some oozing	Some oozing	Some oozing	Some oozing
10	Slt. stick	Sticking	Very little oozing	Ltl. oozing	Some oozing
11	Slt. stick	Sticking	Sticking	Very little oozing	Very little oozing
12	N.C.	N.C.	Slt. stick	Slt. stick	Slt. stick
12.5	Very little oozing	Very little oozing	Very little oozing	Very little oozing	Very little oozing
13	N.C.	N.C.	N.C.	N.C.	N.C.
14	N.C.	N.C.	N.C.	N.C.	N.C.
15	N.C.	N.C.	N.C.	N.C.	N.C.
16	N.C.	N.C.	N.C.	N.C.	N.C.
17	N.C.	N.C.	N.C.	Very slt. oozing	Very little oozing
18	N.C.	N.C.	N.C.	N.C.	N.C.
18.5	N.C.	N.C.	N.C.	N.C.	N.C.
19	Some evap. /conden.	→			
20	Some evap. /conden.	→			
21	Ltl. evap.	Some evap. /conden.	→		

TABLE 2 (Concluded)
VISUAL OBSERVATION FOR
INITIAL THERMOCYCLING SAMPLES

Number	100 Cycles	200 Cycles	500 Cycles	800 Cycles	1000 Cycles
22	N.C.	N.C.	N.C.	N.C.	N.C.
23	Some evap./ conden.				→
24	Some evap./ conden.				→
24.5	N.C.	N.C.	Very little evap./conden.		→
25	N.C.	N.C.	N.C.	N.C.	N.C.
26	N.C.	N.C.	N.C.	N.C.	N.C.
27	N.C.	N.C.	N.C.	N.C.	N.C.
28	N.C.	N.C.	N.C.	N.C.	N.C.
29	Very much oozing				→
30	Very much oozing				→
31	Very much oozing				→

The term "N.C." in the tables stands for "no change". It may be observed in Table 2 that the percolated samples of plasterboard and cement show little change. Even the worst case, sample #17, LLN permeated plasterboard, shows only slight oozing after 800 cycles. Some moisture evaporation on the side of the glass bottle was observed for the cement samples, but no change was observed when these samples were predried by keeping in a desiccator for 24 hours.

Table 3 shows the changes observed in large (2" x 2") samples of percolated plasterboard and cement (introduced later) after 300 and 500 cycles. Only the samples percolated under vacuum to soak the maximum amount of PCM, show some oozing and loss of weight after 300 cycles. The loss is 7.6 percent for the plasterboard and 1.3 percent for the cement after 300 cycles. No further loss is observed on continued thermocycling up to 500 cycles.

The above samples of cements and plasterboards were red dyed during percolation. Slight discoloration and swelling were observed in some of these samples, as recorded in Table 3.

DSC experiments were carried out for all the samples before thermocycling. The data will be reported when the experiments with samples after thermocycling are complete.

3.2 Make a Room Temperature Hardened Composition of Humphrey Tech Grade C-18 with the Specified Hardening Agents at 20% and 30% Concentration

We made some hardened wax in the past by melt blending hard and soft waxes and made pellets from them by dropping in ice cold water. The small pellets were then incorporated into cement cubes and tested for compressive strength. It was, however, observed that the pellets were still soft and slippery and caused severe deterioration of strength. The purpose of the present experiments was to make harder pellets by solution blending with higher melting waxes, and HDPE; and to obtain preliminary data as to their

TABLE 3
VISUAL OBSERVATION LARGE CEMENT
AND PLASTERBOARD THERMOCYCLING SAMPLES

Sample	300 Cycles	500 Cycles
5. (Plasterboard soaked at ambient + press.) 32.6% PCM	very little weight loss very little oozing uneven coloring by red dyed C-18(discoloration)	very little weight loss very little oozing uneven coloring by red dyed C-18(discoloration)
6. (Plasterboard soaked at vacuum) 40.6% PCM	very much weight loss very much oozing uneven coloring by red dyed C-18(discoloration)	small weight gain P.B. swelled & uneven discoloration
7. (Cement soaked at ambient press.) 3.1% PCM	very small weight gain no discoloration	small weight gain discoloration: redder on top than on bottom
8. (Cement soaked at vacuum) 5.6% PCM	very much weight loss very much oozing no discoloration	very small weight gain no discoloration

compatibility with technical grade C-18 hydrocarbon. The experimental procedure is reported in Appendix 1 and the observations are reported in Table 4.

It may be observed from the last column in Table 4 that the compositions that show promise are 20 and 30% of Polywax, stearic acid, Marlex 6006 powder, and Chlorowax 70S. Extruded or cold hardened pellets will be made from the selected wax/PCM blend in order to incorporate the PCM in plasterboard and cement compositions.

3.3 Further Study of Gamma Irradiation in Nitrogen of Sheets, Film, Fabric and Powder of Crystalline Polypropylene, High Density Polyethylene and Low Density Polyethylene

So far, our major effort to incorporate phase change material in plastics has been to swell gamma irradiated pellets in PCM above the melting temperature of the polymer. However, we do not know whether these swelled pellets can be processed in plastics machinery to produce strong enough films, sheets and fabrics for different commercial and household uses. An alternative approach would be to start from already fabricated form and crosslink and swell it in PCM. A number of samples, as described in Table 5, were therefore collected from local plastics dealers in order to send them to Neutron Products, Inc., Dickerson, Maryland, for crosslinking by gamma irradiation.

Before sending these materials for crosslinking it was necessary to anneal the samples at a temperature, which is about 8/9th of the melting temperature in Kelvin scale. The melting temperature was therefore determined by DSC and is reported in the last column of Table 5. Annealing of these samples is under progress.

3.4 Determine the Thermal Energy Storage of One Square Foot of Plasterboard, Percolated to 40% Weight of C-18 PCM; and For One Standard Hollow Core Concrete Block, Percolated to 5% Weight

The paraffinic hydrocarbons used as PCM, has rather high latent heat of fusion and crystallization, which makes them a good candidate for passive storage of solar energy. However, the

TABLE 4
HARD PELLETS FROM C-18

Sample No.	Hardener	Melt Temp. (°C)	Time for Hardener to Melt (minutes)	Additional Mixing Time (minutes)	Mixing Compatibility	Clarity	Phase Separation	Selected for Thermo-cycling
870622-1	20% Fortex	96	2	5	Good	Cloudy	No	No
870622-2	30% Fortex	95	5	5	Good	Cloudy	No	No
870622-3	20% Starwax	90	5	5	Good	Cloudy	No	No
870622-4	30% Starwax	90	6	5	Good	Cloudy	No	No
870622-5	20% Polywax 500	88	10	3	Good	Fairly Clear	No	Yes
870622-6	30% Polywax 500	89	9	3	Good	Fairly Clear	No	Yes
870622-7	20% Shell Wax X-300	70	9	2	Good	Clear	No	No
870622-8	30% Shell Wax X-300	70	10	2	Good	Clear	No	No
870622-9	20% Stearic Acid	65	--	20	Suspended particles in solution. Slowly settled when stirring stopped.	---	Yes Partial	Yes
870622-10	30% Stearic Acid	65	--	20	Suspended particles in solution. Slowly settled when stirring stopped.	---	Yes Partial	Yes

TABLE 4 (Concluded)

HARD PELLETS FROM C-18

Sample No.	Hardener	Melt Temp. (°C)	Time for Hardener to Melt (minutes)	Additional Mixing Time (minutes)	Mixing Compatibility	Clarity	Phase Separation	Selected for Thermo-cycling
870622-11	20% Marlex 6006 Powder	135	10	5	Good	Clear, Syrupy	No	Yes
870622-12	30% Marlex 6006 Powder	138	15	5	Good	Clear, Syrupy	No	Yes
870622-13	20% Crystalline Polypropylene	185	22	3	Good	Fairly Clear	No	No
870622-14	30% Crystalline Polypropylene							
870622-15	20% PEG-14000							
870622-16	30% PEG-14000	70	15	5	Poor, much of the PEG was on the bottom and not dispersed	---	Yes, much	Yes
870622-17	20% Chloro-wax 70-S	109	5	5	Good	Cloudy	No	Yes
870622-18	30% Chloro-wax 70-S	106	5	5	Good	Cloudy	No	Yes
870622-19	20% BCL-462	83	3	4	Good	Fairly Clear	No	No
870622-20	30% BCL-462	85	3	4	Good	Fairly Clear	No	No

TABLE 5

SAMPLES FOR NEUTRON PRODUCTS GAMMA IRRADIATION CROSSLINKING

Sample No.	No. of Pieces	Sizes	Description	Melting Point (°C)
I. IRRADIATE TO A TOTAL DOSE OF 10 M-RAD IN N_2				
870623-1	12	6" x 6" x 0.125"	Sheets, Crystalline Polypropylene	164.2
870623-2	12	6" x 6" x 0.030"	Sheets, Crystalline Polypropylene	164.2
870623-3	12	6" x 6" x 0.125"	Sheets, HDPE	129.3
870623-4	12	6" x 6" x 0.030"	Sheets, HDPE	132.9
870623-5	12	6" x 6" x 0.003"	Film, HDPE, Grocery Bag	128.7
870623-6	12	6" x 6" x 0.125"	Sheets, LDPE	110.9
870623-7	12	6" x 6" x 0.060"	Sheets, LDPE	111.0
870623-8	12	6" x 6" x 0.010"	Film, LDPE	108.3
870623-9	12	6" x 6" x 0.001"	Film, LDPE Dry Cleaners Garment Bag	99.3
870623-10	1	6" x 6" x ---	HDPE Fabric	147.3
II. IRRADIATE TO A TOTAL DOSE OF 20 M-RAD IN N_2				
870623-11	1	6" x 6" x ---	HDPE Fabric	147.3
870623-12	1	1000 grams	Marlex 6006 Powder	---
870623-13	1	1000 grams	Marlex 6006 Powder	---
870629-1	1	---	Flower Pot	133.8
870629-2	1	---	Cup - Thermoset, no m.p.	---
870629-3	1	---	HDPE Grocery Bag	128.7
870629-4	1	---	LDPE Dry	---

storage capacity, expressed in calories per gram has little meaning to the builders. The storage capacities of plasterboard and a hollow core concrete block, two most common commercial building materials, were therefore evaluated in BTU/sq. ft. Actual calculations are reported in Appendix 2. For a USG plasterboard (1/2") the storage capacity is 106.4 BTU/ft² and for the hollow core brick it is 2427 BTU/ft² (both expressed as the weight without drying). It is not surprising that the brick has so much more storage capacity. Although, the concrete block holds only 5% of the final weight as PCM, as compared to 40% for the plasterboard, its higher density and thickness accounts for its 20x greater storage (per ft.²) than plasterboard.

4. CONCLUSIONS

1. Thermocycling up to 1,000 cycles between -10°C and 60°C does not seem to visually affect the PCM treated HDPE pellets, plasterboards and cement concrete samples. HDPE pellets preheated with Humphrey Techgrad C-18, and Exxon C-15 PCM remain intact. Commercial blends used by us show some oozing in HDPE pellets during the first 100 cycles and then remains unchanged. Similar crosslinked HDPE pellets from Matshushita show considerable oozing.

Larger samples of plasterboard and cement (2" x 2") lose a small percentage of PCM weight during thermocycling to 500 cycles.

2. Several wax hardened compositions with C-18 hydrocarbon show promise as PCM for incorporation into the wet mix of cement and plasterboard. Similar composition with Chlorowax 70S promises to be fire retardant.
3. Thermal energy storage capacity of PCM, percolated to 5% wt. in cement, is much higher than in plasterboard percolated to 30% wt. The higher storage of the concrete blocks is attributable to their higher density and thickness (compared with plasterboard).

Immediate Future Work

1. Further investigation of percolation of C-18 PCM into National Gypsum plasterboards and ceramic tiles that were obtained recently.

2. Optimize temperature and time for postcuring the peroxide catalyzed and extruded HDPE samples.
3. Complete DSC analysis of the United States Gypsum plaster-board samples which were sequentially percolated with C-18 PCM and Fyrol PCF fire retardant.
4. Continue DSC analysis of the HDPE pellets, plasterboard and cement samples that had been thermocycled, for thermal energy storage properties.
5. Evaluate the fire retardance of HDPE hardened blends of C-18, containing selected fire retardant additives.

APPENDIX 1
PROCEDURE FOR MAKING HARDENED WAX

Request No. 870622-1 thru -20

Hardened mixtures of Humphrey C-18T were prepared by the following procedure. Fifty grams of C-18T was weighed and melted in a beaker while stirring with a magnet. Appropriate amounts of each hardener were weighed up so that 20% and 30% mixtures could be made. The wax was brought to a temperature approximately 5°C above the melting point of the hardener being used. The hardener was then added incrementally to the stirred wax. Apparent compatibility and clarity of the mixture was visually observed and noted. The mixture was then taken off the heater and allowed to cool to room temperature. Any phase separation upon cooling was noted. Hardness of the coded samples was checked to determine mixtures of promise.

APPENDIX 2

CALCULATIONS FOR WORK ORDER 870513-1, THERMAL ENERGY STORAGE CAPACITY OF PLASTERBOARD

To determine the total thermal energy storage of 1 sq. ft. of plasterboard (USG), percolated to 40% wt. of PCM (C-18).

	<u>Dry</u>	<u>Wet</u>
Adjusted wt. of 1 sq. ft. (1/2") USG PB	(4x196.93)g = 787.72g	(4x197.53)g = 790.12g
Total wt. of 1 sq. ft. USG PB percolated to 40% by wt. of C-18	$\frac{787.72}{0.60}$ = 1312.87g	$\frac{790.12}{0.60}$ = 1316.87g
Wt. of C-18 PCM in 1 sq. ft. of USG PB percolated to 40% by wt. of C-18	1312.87x4 = 525.15g	1316.87x6 = 526.75g
Thermal energy storage of C-18 from DSC	= 50.9 cal/g	
TES of 1 sq. ft. USG PB	$= 525.15 \times 50.9 \text{ cal/ft}^2$ $= 26730.03 \text{ cal/ft}^2$	
	or $= 26730.03 \times 0.0039683 \text{ BTU/ft}^2$ $= 106.07 \text{ BTU/ft}^2$	
For wet USG PB	$= 26811.58 \text{ cal/ft}^2$ $= 106.4 \text{ BTU/ft}^2$	

Calculations for Request No. 870513-1 and -2

870513-2 hollow core brick		
Weight of hollow core brick = 16900g		
Total wt. of hollow core brick after percolation to 5% by wt. of C-18 PCM	$= 16,900\text{g}/0.95$ $= 17,789.5\text{g/brick}$	
Wt. of C-18 PCM in one hollow core brick after percolation to 5% by wt. of C-18 PCM	$= 17,789.5\text{g} \times 0.05$ $= 8894.8\text{g C-18/brick}$	
C-18 PCM thermal energy storage	$= 52 \text{ cal/g}$	
∴ total thermal energy storage per brick	$= 8894.8 \times 52 \text{ cal/g}$ $= 462,527 \text{ cal/brick}$	

Converting to BTU $462,527 \text{ cal/brick} \times 0.0039683 \text{ BTU/cal}$
 $= 1835 \text{ BTU/brick}$

For 1 ft^2 of a wall made from hollow core bricks
percolated with 5% by wt. of C-18 PCM

Face area of one brick $= 0.625 \text{ ft.} \times 1.21 \text{ ft.}$
 $= 0.756 \text{ ft}^2/\text{brick}$

$$462,527 \text{ cal/brick} \times \frac{1 \text{ brick}}{0.756 \text{ ft}^2} = 611,808 \text{ cal/ft}^2$$

$$1835 \text{ BTU/brick} \times \frac{1 \text{ brick}}{0.756 \text{ ft}^2} = 2427 \text{ BTU/ft}^2$$

NOTE: This assumes a wall made of 100% brick, i.e. no mortar
to hold the bricks together and the PCM in inside
faces are also effective.

MONTHLY PROGRESS REPORT NO. 15
CONTRACT NO. DE-FG03-86SF16308
COVERING AUGUST, 1987

1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research, on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends".

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

The four processes are as follows:

1. Direct incorporation of PCM into the wet mix of building materials,
2. Direct incorporation into rubber or plastics medium for floor and wall tiles,
3. Indirect incorporation by first swelling the PCM into crosslinked polyethylene pellets or powder, which are then incorporated into building materials,
4. Direct incorporation by percolating the melted PCM into the open space in porous building materials.

As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3), the building material will not burn. However, in process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard after ignition will continue to burn slowly until the PCM is exhausted. In process 2, where the PCM is compounded into rubbers and plastics, the resulting composite will also burn; unless the polymer matrix is made fire retardant with effective additives.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will complete extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through

further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

The present month's work consists of the following:

1. Investigation of percolation of C-18 PCM into commercial plasterboards and tiles from National Gypsum.
2. Evaluate the fire retardancy of U.S. Gypsum plasterboards percolated with C-18 PCM and Fyrol PCF fire retardant.
3. Evaluate the fire retardancy of U.S. Gypsum plasterboards sequentially percolated with C-18 PCM and Fyrol CEF fire retardant.
4. Study the fire retardancy of U.S. Gypsum plasterboards percolated in 75/25 by wt. % of C-18 PCM/Phosgard C-22A.
5. Investigate the fire retardancy of HDPE hardened blends of C-18 containing selected fire retardant additives.
6. Study the effects of processing parameters and peroxide concentration on extrusion crosslinking of HDPE.

3. TECHNICAL DESCRIPTION OF CURRENT RESEARCH

3.1 Investigate the Percolation of C-18 PCM into Commercial Plasterboards and Tiles from National Gypsum

So far, we have studied the incorporation of C-18 PCM into plasterboards manufactured by United States Gypsum. To check the feasibility of our procedure for the incorporation of PCM into commercial products, we are investigating the percolation of C-18 PCM into the following National Gypsum products:

1. (a) Gold Bond plasterboards
(b) MR Gypsum plasterboards
2. Ceramic tiles
3. Brick tiles

3.1.1 Percolation of C-18 PCM into Plasterboards

Table 1 presents the data on the percolation of red-dyed C-18 PCM into National Gypsum products for 5 minutes and 10 minutes at 80°C. Slight improvement in the PCM pickup was observed in all samples when the percolation time was increased from 5 minutes to 10 minutes. As mentioned in our previous monthly report, the amount of PCM that can be incorporated into any sample depends on its density and porosity. This is reflected in the present results also. PCM pickup has increased with decrease in apparent density. Gold Bond plasterboard with an apparent density of 0.736 g/cc has picked up 27-28% of PCM, whereas MR Gypsum with an apparent density of 0.89 g/cc gained only 19-20% of PCM. The average of DSC data from different parts of the same sample corresponds to the amount of PCM pickup by weight gain. However, DSC data has indicated that the PCM pickup was not uniform throughout the sample. As shown in Figures 1a, 1b, and 1c in Gold Bond plasterboard and Figures 2a, 2b, and 2c in MR Gypsum plasterboard PCM pickup was less in the midway between the edge and center of the samples compared to either edge or center. It is possible that the pickup will be uniform on prolonged percolation time.

A thin frost-like layer of crystals was observed on both the National Gypsum plasterboards a few days after percolation with C-18 PCM. DSC analysis was made on the crystals scraped from the surface of plasterboard to check if the formation of crystals was due to the oozing of PCM out of the plasterboards. DSC thermograms for the crystals formed on Gold Bond plasterboard and MR Gypsum plasterboard are presented in Figures 3 and 4, respectively. Data indicates that the crystals correspond to the C-18 PCM. It is not clear, however, why some of the PCM tends to ooze out of National Gypsum but not from U.S. Gypsum plasterboards.

3.1.2 Percolation of C-18 PCM Into Ceramic Tiles

C-18 PCM percolated through only the coarse (bottom) surface of the ceramic tiles. As indicated by the red dye on the broken surface of PCM percolated ceramic tile, C-18 penetrated

TABLE 1
PERCOLATION OF C-18 PCM INTO NATIONAL GYPSUM
PLASTERBOARDS AND TILES

Sample	App. Density (g/cc)	Percolation Time (mins.)	PCM Uptake, %		TES of 1 Sq. Ft. Product (BTU/sq.ft.)	
			Wet	Dry	Wet	Dry
Gold Bond Plasterboard	0.736	5	27.23	27.48	60.85	61.40
Gold Bond Plasterboard	0.738	10	27.75	27.84	61.94	62.43
MR Gypsum Plasterboard	0.890	5	19.64	19.64	48.88	49.37
MR Gypsum Plasterboard	0.901	10	20.36	20.38	51.17	51.68
Ceramic Tile	1.817	5	5.04	5.04	11.34	11.34
Ceramic Tile	1.817	10	6.56	6.56	17.56	17.56
Ceramic Tile*	1.817	10	7.74	7.74	20.15	20.15
Ceramic Tile*	1.817	30	8.51	8.51	22.97	22.97
Brick Tile	2.330	5	0.095	0.095	---	---
Brick Tile	2.330	10	0.159	0.159	---	---

* Ceramic tile dried at 80°C for 4 hours before percolation.

Sample: GOLD BOND N.A. #1, CENTER
 Size: 5.82 mg
 Method: DSC-10°C/min, REPEAT 3
 Comment: 10°C/MIN, HIT, (870717-12-17)

DSC

File: RUN1361.02
 Operator: VEISSMAN
 Run date: 08/28/87 12:28

(a)

Sample: NAT'L GYP. GOLD BOND #1 MIDPOINT
 Size: 9.00 mg
 Method: DSC-10°C/min, REPEAT 3
 Comment: DSC 10°C/MIN, HIT, (870717-12-17)

DSC

File: RUN1413.02
 Operator: VEISSMAN
 Run date: 09/18/87 12:30

(b)

Sample: GOLD BOND N.A. #1, EDGE
 Size: 7.33 mg
 Method: DSC-10°C/min, REPEAT 3
 Comment: 10°C/MIN, HIT, (870717-12-17)

DSC

File: RUN1362.02
 Operator: VEISSMAN
 Run date: 08/27/87 07:27

(c)

Figure 1. DSC Analysis of Gold Bond Plasterboard; (a) Edge, (b) Mid-point Between Edge and Center, (c) Center.

Figure 2. DSC Analysis of MR Gypsum Plasterboard; (a) Edge, (b) Mid-point Between Edge and Center, and (c) Center.

Figure 4. DSC Analysis of the Frost-Like Crystals Formed on the Surface of MR Gypsum Plasterboard Percolated in C-18 PCM.

Figure 3. DSC Analysis of the Frost-Like Crystals Formed on the Surface of Gold Bond Plasterboard Percolated in C-18 PCM.

through 3-4 mm from bottom surface in 5 minutes. The PCM penetration improved to 5 mm when the percolation time was increased to 10 minutes. The PCM uptake by ceramic tiles was only 5.0% in 5 minutes and 6.6% in 10 minutes. To improve the PCM uptake, the ceramic tiles were preheated at 80°C for 4 hours and the hot samples were percolated with octadecane. The PCM uptake has improved to 7.7% and 8.5% by this method when percolation was conducted for 10 minutes and 30 minutes, respectively. The calculated thermal energy storage per square foot of the ceramic tile surface is significant (23 BTU maximum) but still only about 1/3 of the storage in the National Gypsum plasterboard. Further modification of the percolation process to improve the PCM uptake in National Gypsum plasterboard and ceramic tiles is in progress at this time. Experiments done at National Gypsum have shown that much higher levels of PCM pickup are possible in their plasterboard.

3.1.3 Percolation of C-18 PCM Into Brick Tiles

Of all the National Gypsum commercial products studied for the percolation of Octadecane, brick tiles absorbed the least. The PCM uptake, as shown in Table 1, was only 0.16%. The thermal energy storage properties for one square foot of each sample of these National Gypsum products are presented in Table 1.

3.2 Evaluate the Fire Retardance of USG Plasterboards Percolated With C-18 PCM and Fyrol PCF Fire Retardant

Efficiency of Fyrol PCF (Tri(β -chloro isopropyl)phosphate) as a fire retardant for USG plasterboards containing C-18 PCM was studied by two methods. Procedures for both the methods are given in Appendix 1 and 2. In the first method plasterboard samples were percolated in specified ratios of C-18 PCM and Fyrol PCF. Ratios of C-18 and Fyrol PCF used in this study and the corresponding total weight pickup of C-18 and PCF by the plasterboards are presented in Table 2. Total weight pickup of C-18 and Fyrol PCF mixtures was found to vary from 37 to 43%, depending on the C-18/PCF ratio. Flame tests conducted according to the procedure reported in Appendix 3 produced encouraging

TABLE 2
PERCOLATION OF USG PLASTERBOARD WITH
C-18 PCM AND FYROL PCF

<u>Sample</u>	<u>Composition of C-18/PCF</u>		<u>% Total Wt. Pickup (C-18 + PCF)</u>
	<u>C-18, %</u>	<u>PCF, %</u>	
870610-1A	75	25	42.9
870610-2A	77½	22½	39.3
870610-3A	80	20	38.6
870610-4A	82½	17½	36.9
870610-5A	85	15	37.3

results. Table 3 presents the results of flame tests on the plasterboards percolated with different ratios of C-18 PCM and Fyrol PCF mixtures. As expected, flame resistance of the plasterboards decreased with decreasing PCF concentrations in the mixture. Plasterboards percolated in C-18/PCF (75/25) mixture showed an ignition time of more than 2-1/2 minutes and was self-extinguishing almost immediately. It was found to be self-extinguishing even on the second ignition.

DSC analysis was undertaken to compute the individual concentrations of PCM and Fyrol PCF in the plasterboard. As shown in Table 4 plasterboard samples contained higher concentrations of flame retardant at the edge compared to the center of the sample. When Fyrol PCF concentration was higher in the mixture, as in C-18/PCF (75/25), Fyrol PCF was found to replace the Octadecane to a great extent even at the center of the sample. Plasterboard percolated in C-18/PCF (77-1/2 / 22-1/2) was fire resistant for almost 2 minutes. It retained about 20% wt. PCM as indicated by DSC. However, all the other samples contained lower concentrations of PCF and were resistant to fire for 50 seconds, 38 seconds, and 20 seconds depending on the concentration of Fyrol PCF in the plasterboard. In using C-18/PCF mixtures for percolation, the incompatibility of PCF with C-18 was a problem. Fyrol PCF was suspended in C-18 by mechanical stirring. The extent of percolation of C-18/PCF depended on the rate and type of stirring.

In order to control the leaching of PCM by PCF, the plasterboard samples were then percolated sequentially in PCM followed by Fyrol PCF for different times as shown in Table 5. Our objective in this study is to incorporate the desired amount of fire retardant additive and still retain maximum amount of PCM in the plasterboards.

One set of samples was weighed immediately after percolation with C-18 (before percolation with Fyrol PCF). The PCM pickup was computed and compared with DSC data to check the amount of Octadecane replaced by Fyrol PCF in this method. The results are

TABLE 3

FLAME TEST OF PLASTERBOARD CONTAINING
PERCOLATED C-18 PCM/FIRE RETARDANT FYROL PCF

<u>Sample</u>	<u>First Ignition</u>	<u>Extinguish</u>	<u>Second Ignition</u>	<u>Extinguish</u>	<u>Travel</u>	<u>Smoke</u>
870610-1 C-18/Fyrol PCF (75/25)	157 secs.	7 secs.	18 secs.	82 secs.	No	White
870610-2 C-18/Fyrol PCF (77½/22½)	110 secs.	70 secs.	12 secs.	---	No --(travels on second ignition)	White Black
870610-3 C-18/Fyrol PCF (80/20)	50 secs.	222 secs.	10 secs.	---	No --(travels on second ignition)	Black
870610-4 C-18/Fyrol PCF (82½/17½)	38 secs.	277 secs.	8 secs.	87 secs.	Yes	Black
870610-5 C-18/Fyrol PCF (85/15)	20 secs.	---	---	---	Yes	Black

TABLE 4

DSC ANALYSIS OF PLASTERBOARDS PERCOLATED
WITH C-18/FYROL PCF

Sample Identification and Composition	T _m (°C)	T _C (°C)	T _m -T _C (°C)	ΔH _f (cal/gm)	ΔH _C (cal/gm)	% PCM DSC Data	% Fyrol DSC Data
870610-1A Center Edge	26.94	19.05	7.89	5.68	5.88	11.2	31.7
	26.76	18.81	7.95	5.78	5.55	11.4	31.5
870610-2A Center Edge	27.01	17.97	9.04	12.91	13.37	25.4	13.9
	26.56	18.51	8.05	7.23	7.40	14.2	25.1
870610-3A Center Edge	28.70	15.64	13.06	15.34	15.50	30.2	8.4
	30.76	15.57	15.19	12.55	12.15	24.7	13.9
870610-4A Center Edge	27.72	16.78	10.95	14.95	14.68	29.4	7.5
	30.24	15.53	14.71	11.53	11.86	22.7	14.2
870610-5A Center Edge	27.31	16.40	10.91	15.13	15.17	29.8	7.5
	28.86	16.96	12.17	13.26	13.46	26.1	11.2

TABLE 5
 SEQUENTIAL PERCOLATION OF PLASTERBOARD
 IN C-18 PCM/FYROL PCF

<u>Sample</u>	<u>Percolation Time in</u>	
	<u>C-18</u>	<u>Fyrol PCF</u>
870814-6	1 minute	5 minutes
870814-7	2 minutes	5 minutes
870814-8	2½ minutes	5 minutes
870814-9	3 minutes	5 minutes
870814-10	4 minutes	5 minutes
870814-11	5 minutes	5 minutes

presented in Table 6. As evidenced by these results we have succeeded in limiting the replacement of PCM by Fyrol PCF.

Table 7 presents the results of flame tests on the sequentially percolated samples. All samples were found to have an ignition time of about 1 minute and were self-extinguishing. As indicated by the DSC data, plasterboard samples picked up approximately 25% PCM when they were percolated for 2 minutes or longer in C-18. These samples contained 9-11.6% of Fyrol PCF. Further, the flame retardant did not replace much of the PCM from the samples. When the plasterboard was percolated for one minute in C-18, it contained 20-22% PCM and about 18% of Fyrol PCF. DSC analysis also indicated that Fyrol PCF replaced more PCM at the edges and on the surface than at the center of the same sample. This preferential placement of the Fyrol PCF is favorable for the combination of fire retardance with retention of high thermal energy storage.

3.3 Evaluate the Fire Retardance of Plasterboards Percolated with C-18 PCM and Fyrol CEF

Experiments were conducted to evaluate the fire retardancy of plasterboards using another fire retardant product; namely, Fyrol CEF which is a Tri(β -chloro ethyl)phosphate. Plasterboards were percolated with C-18 PCM and Fyrol CEF for different times as specified in Table 8. The total weight pickup of C-18/CEF by the plasterboard was in the range of 36-39%. Plasterboards sequentially percolated in C-18 and Fyrol CEF were found to have an ignition time of at least one minute and all the samples were self-extinguishing as indicated in Table 9. DSC analysis of these samples is presented in Table 10. Samples contained about 20% PCM and 16-18% of Fyrol CEF except for one, which was percolated for one minute in C-18, contained 15% of PCM and 24% of Fyrol CEF. These samples were promising as fire resistant plasterboards and were self-extinguishing even in the second ignition. Plasterboards were also percolated with mixtures of C-18 PCM and Fyrol CEF and the DSC analysis is in progress.

TABLE 6
ANALYSIS OF PLASTERBOARDS SEQUENTIALLY
PERCOLATED WITH C-18/FYROL PCF

<u>Sample</u>	<u>Average ΔH_f, cal/g</u>	<u>% PCM Pickup</u>		<u>Total C- 18 + PCF Pickup</u>	<u>Fyrol PCF Pickup (Avg.)</u>
		<u>Gravimetric*</u>	<u>DSC Data</u>		
870717-6A	11.24	25.34	22.13	38.8	16.67
-6B	10.3	---	20.28	39.8	19.52 (18.1)
870717-7A	13.57	31.60	26.71	36.8	10.09
-7B	12.10	---	23.82	36.9	13.08 (11.6)
870717-8A	12.70	33.45	25.0	36.5	11.5
-8B	12.76	---	25.12	36.2	11.08 (11.3)
870717-9A	12.96	32.4	25.51	35.5	9.99
-9B	13.92	---	27.4	35.5	8.10 (9.1)
870717-10A	13.54	33.10	26.65	35.8	9.15
-10B	12.31	---	24.23	35.5	11.27 (10.2)
870717-11A	14.40	33.48	28.35	36.6	8.25
-11B	13.38	---	26.34	36.0	9.66 (9.0)

* One set of samples were weighed after percolation with PCM to compute the PCM uptake.

TABLE 7
FLAME TEST OF PLASTERBOARD CONTAINING
PERCOLATED C-18 PCM/FIRE RETARDANT FYROL PCF
(SEQUENTIAL PERCOLATION)

<u>Sample</u>	<u>First</u>		<u>Second</u>		<u>Extinguish</u>	<u>Extinguish</u>	<u>Travel</u>	<u>Smoke</u>
	<u>Ignition</u>		<u>Ignition</u>					
870717-6A -6B	65 sec.		8 sec.		107 sec.	82 sec.	no	White
	55 sec.		68 sec.		268 sec.	15 sec.	no	White
870717-7A -7B	63 sec.		12 sec.		247 sec.	---	no	Black
	70 sec.		8 sec.		170 sec.	89 sec.	no	Black
870717-8A -8B	77 sec.		18 sec.		220 sec.	107 sec.	no	Black
	55 sec.		7 sec.		215 sec.	97 sec.	no	Black
870717-9A -9B	70 sec.		3 sec.		190 sec.	130 sec.	no	Black
	45 sec.		14 sec.		180 sec.	100 sec.	no	Black
870717-10A -10B	80 sec.		---		---	---	no	Black
	52 sec.		---		273 sec.	---	no	Black
870717-11A -11B	49 sec.		---		---	---	yes	Black
	50 sec.		---		---	---	yes	Black

TABLE 8
 SEQUENTIAL PERCOLATION OF PLASTERBOARD
 IN C-18 PCM/FYROL CEF

Sample	Percolation Time in	
	C-18	Fyrol CEF
870814-8	1 minute	5 minutes
870814-9	2 minutes	5 minutes
870814-10	2½ minutes	5 minutes
870814-11	3 minutes	5 minutes
870814-12	4 minutes	5 minutes
870814-13	5 minutes	5 minutes

TABLE 9
FLAME TEST OF PLASTERBOARD CONTAINING
PERCOLATED C-18 PCM/FIRE RETARDANT FYROL CEF
(SEQUENTIAL PERCOLATION)

<u>Sample</u>	<u>First</u>		<u>Second</u>		<u>Travel</u>	<u>Smoke</u>
	<u>Ignition</u>	<u>Extinguish</u>	<u>Ignition</u>	<u>Extinguish</u>		
870814-8	135 secs.	15 secs.	16 secs.	100 secs.	no	white
870814-9	76 secs.	9 secs.	22 secs.	7 secs.	no	white
870814-10	81 secs.	19 secs.	15 secs.	185 secs.	no	white
870814-11	85 secs.	7 secs.	31 secs.	---	travel on second ignition	heavy white smoke
870814-12	57 secs.	63 secs.	19 secs.	196 secs.	travel on second ignition	heavy white smoke
870814-13	78 secs.	21 secs.	11 secs.	198 secs.	travels on second ignition	black

TABLE 10
ANALYSIS OF PLASTERBOARDS SEQUENTIALLY
PERCOLATED WITH C-18 PCM/FYROL CEF

	<u>Avg. ΔH_f (cal/g)</u>	<u>% PCM from DSC</u>	<u>Total Pickup</u>	<u>Fyrol CEF Pickup(%)</u>
870814-8	7.64	15.1	39.4	24.3
870814-9	9.86	19.4	37.3	17.9
870814-10	9.42	18.5	36.6	18.1
870814-11	10.20	20.1	36.8	16.7
870814-12	9.97	19.6	36.3	16.7
870814-13	10.32	20.3	36.3	16.0

3.4 Evaluate the Fire Retardance of Plasterboards Percolated in 75/25 by wt. % of C-18 PCM/Phosgard C-22A

Fire retardant property of USG plasterboards was also evaluated by percolating the samples in C-18 PCM and Phosgard C-22A (an organo phosphorous compound containing chlorine, marketed by Monsanto). C-18/phosgard 75/25 by wt. % was used for percolation of plasterboards. Phosgard is not miscible in C-18 and agitation played a key role in the percolation process. Flame test has shown that Phosgard 22A is useful in making a plasterboard fire resistant. Samples did not ignite for more than 1-1/2 minutes and were self-extinguishing. However, the DSC analysis has shown that the PCM content at the edges was only 3% which is significantly low.

3.5 Investigate the Fire Retardance of HDPE Hardened Blends of C-18 Containing Selected Fire Retardant Additives

Melt blends of C-18 PCM and HDPE containing selected fire retardant additives were made according to the following compositions:

<u>System 1</u>		<u>System 2</u>		<u>System 3</u>	
C-18	40.0g	C-18	40.0g	C-18	40.0g
HDPE	10.0g	HDPE	10.0g	HDPE	10.0g
Fyrol PCF	10.0g	BCL-462	6.66g	Chlorowax 70-S	6.66g
		Sb ₂ O ₃	3.34g	Sb ₂ O ₃	3.34g
<u>System 4</u>		<u>System 5</u>		<u>System 6</u>	
C-18	40.0g	C-18	40.0g	C-18	40.0g
HDPE	10.0g	HDPE	10.0g	HDPE	10.0g
Zerogen-11	10.0g	Zerogen-15	10.0g	Micrat 932	10.0g

Results of flame tests conducted on disc samples of these melt blends are presented in Table 11. None of the samples showed any improvement in flame retardance and so no further analysis was made. These results were unexpected in view of favorable fire retardance obtained some time ago in very similar compositions. Different compositions of melt blends are planned for future studies. This process is a potentially lower cost route to fire

TABLE 11
FLAME TESTS FOR HDPE HARDENED BLENDS
OF C-18 CONTAINING FLAME RETARDANT

<u>Sample #</u>	<u>Flame Retardant</u> <u>Type</u>	<u>Amount</u>	<u>Time</u> <u>to Ignite</u>	<u>Time to</u> <u>Extinguish</u>	<u>Nature of</u> <u>Smoke,</u> <u>Flame, etc.</u>
870720-1	Fyrol	10.0g	5 secs.	>300 secs.	Profuse burning, black smoke, dripping
870720-2	BCL 462: Sb ₂ O ₃ :	6.66g 3.34g	3 secs.	>300 secs.	
870720-3	Chlorowax 70S: Sb ₂ O ₃ :	6.66g 3.34g	2 secs.	>300 secs.	
870720-4	Zerogen-11:	10.0g	3 secs.	>300 secs.	
870720-5	Zerogen-15:	10.0g	3 secs.	>300 secs.	
870720-6	Micral-932:	10.0g	3 secs.	>300 secs.	

retarded pellets that can be incorporated directly into the wet mix of plasterboard and concrete.

3.6 Further Investigation on the Peroxide Catalyzed Extrusion Crosslinking of HDPE

Effects of peroxide (Dicumyl peroxide, DiCup R) concentration, extrusion temperature and extrusion RPM on the crosslinking of HDPE were studied using six different formulations. Table 12 presents the extrusion conditions, peroxide concentration, postcuring conditions and PCM pickup in percolation. HDPE samples extruded at 300°F were not crosslinked enough to directly percolate in C-18 PCM. They were completely or partially soluble in Octadecane during percolation. Increasing the extrusion temperature to 500°F resulted in insoluble (higher crosslinking) HDPE which picked up 44% PCM. On the other hand, increasing the peroxide concentration from 0.35% to 1.0% did not improve the crosslinking to the desired extent. Postcuring of HDPE samples extruded at 300°F was attempted at 320°F for 1 hour and at 302°F for 2 hours. After postcuring, HDPE extruded with 0.35% and 0.50% peroxide was still partially soluble. Postcured sample of HDPE extruded with 0.75% peroxide was insoluble and gained 45% PCM during percolation. Further increase in peroxide concentration was not of any significant advantage. HDPE extruded with 0.7% peroxide and 30 phr Sb_2O_3 were also found to be insoluble upon postcuring. Further efforts will be directed to achieve higher PCM uptake by improving the extent of crosslinking in HDPE.

4. CONCLUSIONS

1. Significant improvements were achieved in the fire retardance of plasterboards by incorporating fire retardant additives. Sequential percolation of plasterboard in PCM and fire retardant additives is useful in retaining the PCM. Among the various fire retardant additives used in this study, Fyrol CEF was found to be the best fire retardant for plasterboards containing C-18 PCM. This results is a very important milestone in our work toward an effective fire retardant system for plasterboards.

TABLE 12
PEROXIDE CATALYZED EXTRUSION CROSSLINKING OF HDPE

Sample	Extrusion Temp. RPM	DiCup R (%)	Thermal Curing Temp. Time	% PCM Pickup in Percolation	Observations
870609-1	300°F 60	0.35	--- ---	---	Soluble
			320°F 1 Hr.	---	Partially soluble
			302°F 2 Hrs.	---	Pellets molten in postcuring
870609-2	300°F 60	0.50	--- ---	---	Soluble
			320°F 1 Hr.	32	Pellets lost their size and shape
			302°F 2 Hrs.	---	Pellets molten in postcuring
870609-3	300°F 60	0.75	--- ---	---	Pellets imbibed in PCM
			320°F 1 Hr.	39	Pellets almost retained shape
			302°F 2 Hrs.	45	Pellets almost retained shape
870609-4	300°F 60	1.0	--- ---	18	Not soluble but lost shape
			320°F 1 Hr.	34	Pellets retained shape
			302°F 2 Hrs.	38	Pellets retained shape

TABLE 12 (Continued)
PEROXIDE CATALYZED EXTRUSION CROSSLINKING OF HDPE

<u>Sample</u>	<u>Extrusion</u> <u>Temp.</u>	<u>RPM</u>	<u>DiCup R</u> <u>(%)</u>	<u>Thermal Curing</u> <u>Temp.</u>	<u>Time</u>	<u>% PCM Pickup</u> <u>in Percolation</u>	<u>Observations</u>
870609-5	500°F	30	0.35	---	---	43.9	Almost retained shape
870609-6	280- 290°F	80	0.7 + Sb ₂ O ₃ 30 phr	---	---	9.3 43.2	Pellets imbibed in PCM Almost retained their shape

2. Percolation procedure established for U.S. Gypsum plasterboards could be extended for other commercial plasterboard products. But the extent of PCM pickup varies from one product to the other. Percolation procedure needs to be modified in case of tiles.
3. In the extrusion crosslinking of HDPE, 0.7% of Dicumyl peroxide was found to be optimum. Postcuring at 160°C was essential for improving the extent of crosslinking in HDPE.

Immediate Future Work

1. Complete the DSC analysis of United States Gypsum plasterboard samples percolated with mixtures of C-18 PCM/Fyrol CEF.
2. Make thermally form stable hardened PCM composites of C-18 and high molecular weight HDPE using different ratios of C-18 and HDPE.
3. Determine the thermal energy storage properties of Humphrey Tech Grade C-16 and permeate the C-16 into radiation crosslinked HDPE pellets.

APPENDIX 1
PROCEDURE FOR THE PERCOLATION OF USG
PLASTERBOARDS IN MIXTURES OF C-18 PCM
AND FYROL FLAME RETARDANT

Work Request Nos.: 870610-1 thru 5 and 870814-3 thru 7

Plasterboards were percolated in mixtures of C-18 PCM and fire retardant by the following method: C-18 PCM and fire retardant additive were weighed into 600 ml beakers according to the specified ratios. Total weight of the mixture in each composition was found to be about 200 gms. Each mixture was heated and maintained 80°C, while stirring the contents vigorously with a magnetic paddle. Two-inch by two-inch samples of weighed dry plasterboard were suspended in each mixture for 10 mins. at 80°C. Vigorous stirring of the mixture was maintained to suspend the fire retardant additive in C-18 PCM throughout the experiment. The plasterboard sample was taken out after percolation and weighed to determine the total weight pickup.

APPENDIX 2
PROCEDURE FOR THE SEQUENTIAL PERCOLATION OF USG
PLASTERBOARDS IN C-18 PCM AND FIRE RETARDANT

Work Request Nos.: 870717-6 thru 11 and 870814-8 thru 13

Plasterboards were sequentially percolated in C-18 PCM and fire retardant additive by the following method: C-18 PCM and fire retardant additive were taken in separate 600 ml beakers and heated to 80°C with constant stirring. Duplicate samples of dried and weighed 2" x 2" squares of USG plasterboards were used for sequential percolation. Each plasterboard was suspended in C-18 PCM for specified times at 80°C and then in the fire retardant for 5 minutes at 80°C. Samples were then weighed to determine the total PCM plus fire retardant pickup. In order to compute the PCM pickup, one set of samples (870717-6A thru 11A) were weighed immediately after percolating in C-18 PCM at 80°C and then percolated in the fire retardant additive for 5 minutes at 80°C.

APPENDIX 3
FLAME TEST FOR PLASTERBOARD SAMPLES PERCOLATED
IN C-18 PCM AND FIRE RETARDANT ADDITIVE

Flame tests for plasterboard samples percolated in
(1) mixtures of C-18 PCM and fire retardant additive, and
(2) sequentially percolated in C-18 PCM and fire retardant
additives were conducted by the following procedure:

The plasterboard sample was horizontally clamped in
a hood and ignited with a burner at the center of an edge.
A stopwatch was started simultaneously at the time of
introducing the flame to the sample. Flame was removed
from the sample at 3 secs., 5 secs., 10 secs., and so on,
for a short time, to check if the sample was ignited. At
the time of ignition, flame was taken away and the sample
was allowed to burn. Time of self-extinguishment was noted
and the type of flame, smoke and travel were observed.

If the sample was self-extinguishing in nature, the
above procedure was repeated for a second ignition.

CONTRACT NO. DE-FG03-86SF1
COVERING SEPTEMBER, 1987

1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research, on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends".

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

The four processes are as follows:

1. Direct incorporation of PCM into the wet mix of building materials,
2. Direct incorporation into rubber or plastics medium for floor and wall tiles,
3. Indirect incorporation by first swelling the PCM into crosslinked polyethylene pellets or powder, which are then incorporated into building materials,
4. Direct incorporation by percolating the melted PCM into the open space in porous building materials.

As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3), the building material will not burn. However, in process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard after ignition will continue to burn slowly until the PCM is exhausted. In process 2, where the PCM is compounded into rubbers and plastics, the resulting composite will also burn; unless the polymer matrix is made fire retardant with effective additives.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will complete extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through

further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

The present month's work consists of the following:

1. To determine the thermal energy storage properties of Humphrey Technical Grade hexadecane (C-16) and permeate the C-16 into radiation crosslinked HDPE pellets.
2. To evaluate Nyacol colloidal antimony pentoxide in combination with a brominated cyclic hydrocarbon as a fire retardant for C-18 PCM in US Gypsum plasterboards.
3. To evaluate the Humphrey technical grade C-18 used for the percolation of plasterboards at the National Gypsum Building Products Laboratory.

3. TECHNICAL DESCRIPTION OF CURRENT RESEARCH

Due to current year's funds being expended at significantly higher than the linear rate, it was necessary to drastically curtail the technical effort on this project for the month of September. Thereby, we could insure that funds would be available to complete a few higher priority projects that are already in progress, meet outstanding travel and other commitments. Accordingly, only limited work was carried out during this month. However, we will continue working at a rate consistent with our funds for the remaining contract period; and, at a higher rate when additional grant funds become available.

3.1 Determination of the Thermal Energy Storage Properties of Humphrey Technical Grade Hexadecane

Octadecane which melts at 28°C has thermal energy storage properties quite suitable for ambient temperature applications. Accordingly, our efforts have been concentrated in the incorporation of Humphrey Tech Grade C-18 PCM into plasterboards, tiles and crosslinked HDPE. Hexadecane, which melts at 10° lower than Octadecane, is a potential candidate for applications at slightly

lower temperatures (for example, in air conditioning systems). With this view, we have done DSC analysis of Humphrey technical grade C-16 and then studied its permeation into crosslinked HDPE pellets. Figure 1 shows the DSC analysis of technical grade C-16 at a heating and cooling rate of 10° per minute. Figure 2 shows DSC analysis at 2°C/min. rate of heating and cooling. T_m , T_c , ΔH_f and ΔH_c of the technical grade C-16 are slightly lower than the 99% pure hexadecane, as seen from Table 1. DSC analysis indicates that presence of other hydrocarbon components in the technical grade C-16.

3.2 Permeation of Technical Grade C-16 into Radiation Crosslinked HDPE Pellets

Experimental procedure for the permeation of C-16 into radiation crosslinked HDPE (Marlex 6006) is described in Appendix 1. After permeation of C-16 for 1 hr. at 150°C, the amount of C-16 permeated into crosslinked HDPE pellets is 77% as determined by weight gain. The amount of C-16 PCM permeated into HDPE pellets as determined by DSC analysis (Figure 3) is 82.5%. The amount of HDPE used for DSC scan is 5 mg (fraction of one pellet) and a slight amount of HDPE solubles extracted during permeation may be the reason for higher weight gain value by DSC analysis. As indicated in Figure 3 the thermal behavior of C-16 remained almost same after the permeation into crosslinked HDPE pellets. HDPE pellets, however, lost about 1% of C-16 by oozing at room temperature over a period of several days. HDPE pellets, at the percolation temperature of 150°C, are swollen to a great extent. In this configuration, the polymer chains are extended thereby increasing the free volume of the molecules. This results in maximum uptake of C-16 by HDPE molecules. When the pellets are cooled to room temperature the free volume of the molecules is reduced to certain extent resulting in the oozing of a slight amount of C-16. When the pellets were heated to 60°C for 4 hours, they showed very good thermal stability by retaining the shape and size. An additional 1.5% loss (a total of 2.5% loss) of C-16 was observed due to heating to 60°C. HDPE pellets still retained about 75% of C-16 PCM and did not ooze out any further C-16 at

Figure 1. DSC Analysis of Humphrey Tech Grade n-Hexadecane at 10°C/min.

Figure 2. DSC Analysis of Humphrey Tech Grade n-Hexadecane at 2°C/min.

TABLE 1
DSC ANALYSIS OF N-HEXADECANE AT A RATE
OF 10°/MIN. HEATING AND COOLING

Sample	T _m (°C)	T _c (°C)	T _m -T _c (°C)	Heat of Fusion (cal/g)	Heat of Recrystallization (cal/g)
n-Hexadecane 99% pure	21.1	12.2	8.9	56.5	56.5
n-Hexadecane Humphrey Tech Grade	18.5	9.8	8.7	45.1	44.4
n-Hexadecane Permeated Into x-linked HDPE	19.86	3.2	16.7	37.3	36.8

Sample: MARLEX W/C-16 870911-4
 Size: 5.03 mg
 Method: DSC-10°C/min
 Comment: 10 C/MIN, N2

File: RUN1481.01
 Operator: GALASKA
 Run date: 10/27/87 11:45

DSC

Figure 3. DSC Analysis of Radiation Crosslinked HDPE Pellets Permeated with n-Hexadecane.

room temperature after heat treatment. Further experiments will be designed to eliminate the slight oozing of C-16 from crosslinked HDPE pellets. "Annealing" of the permeated pellets in boiling water immediately after removal from the 150°C bath will be investigated; as well as permeating to slightly lower levels of PCM.

3.3 To Evaluate Colloidal Antimony Pentoxide in Combination with Saytex BCL-462 as a Fire Retardant for US Gypsum Plasterboards Percolated with C-18 PCM

In continuation of our efforts to suspend antimony oxide and a halogenated flame retardant in C-18, we have now successfully used a new colloidal antimony pentoxide (Nyacol ADP-480) and dibromo ethyldibromo cyclohexane (Saytex BCL-462) in C-18 PCM. In the past (refer to our technical progress report for March and April, 1987), we have attempted to achieve the synergistic combination of antimony trioxide and BCL-462 as flame retardant for plasterboards percolated with C-18 PCM. Flame retardancy in the plasterboards could not be achieved as our trials to suspend antimony trioxide were not successful. With the use of colloidal antimony pentoxide Nyacol ADP-480, which has a particle size of 0.03 microns, a stable suspension of Sb_2O_5 /BCL-462 in C-18 was obtained. A simple procedure to make the suspension is described in Appendix 2. US Gypsum plasterboard samples percolated in this suspension for 5 minutes and 10 minutes have shown excellent flame retardancy as presented in Table 2. DSC analysis of the percolated plasterboards is in progress and further results of this experiment will be reported in future reports.

3.4 To Evaluate the Humphrey Technical Grade C-18 Received from National Gypsum Building Products

Experiments conducted at National Gypsum Laboratory to percolate their plasterboards in C-18 PCM have resulted in higher PCM uptake and blooming of the PCM onto the plasterboard surface. Lower PCM uptake and reduced blooming was obtained in our laboratories. In order to make sure the C-18 PCM used by National Gypsum is similar to ours, one gallon sample was procured and analyzed. The DSC thermograms of C-18 PCM used by National Gypsum

TABLE 2
FLAME TEST OF PLASTERBOARD PERCOLATED IN A
SUSPENSION OF C-18 PCM/ETHYL BCL-462/
NYACOL ADP-480

Sample	Percolation Time (minutes)	Ignition Time* (seconds)	Extinguish Time (seconds)	Travel	Smoke
870910-1B	5	Does not ignite	---	no	white
870910-2B	10	Does not ignite	---	no	white

* Plasterboard tested for 5 minutes to ignite with a Bunsen burner.

as obtained and after recrystallization are shown in Figure 4. T_m , T_c , ΔH_f and ΔH_c values are tabulated against the values of C-18 used in our laboratory (Table 3). It is clear from these values that C-18 PCM used in National Gypsum Laboratory is significantly different from our sample. Inferior TES properties of the C-18 used in National Gypsum Laboratory indicate the presence of larger amounts of other hydrocarbon compounds. We believe the impurities in C-18 PCM used in National Gypsum Laboratory as well as the higher PCM uptake are the reasons for the discrepancies observed in the separate percolation experiments done in their laboratory and ours.

4. CONCLUSIONS

1. A fine suspension of antimony oxide in halogenated hydrocarbon in C-18 PCM was prepared to achieve fire retardancy in US Gypsum plasterboards. Plasterboard percolated in this suspension showed excellent fire retardancy. Further experiments to analyze products and optimize the parameters are in progress.
2. Hexadecane was analyzed for thermal energy storage properties and was successfully permeated into crosslinked HDPE pellets.
3. Discrepancies observed in the percolation experiments conducted at National Gypsum Laboratory were resolved by analyzing the PCM used.

Immediate Future Work

1. To evaluate Phoschek P-30 (a non-halogenated flame retardant) as a flame retardant for US Gypsum plasterboards percolated with C-18 PCM.
2. To complete the preparation and evaluation of thermally form stable hardened PCM composites of C-18 and high molecular weight HDPE.
3. Complete DSC analysis of US Gypsum plasterboards percolated with various fire retardant compounds. (This could not be done due to the breakdown of the DSC cell.)

Sample: C-18 FROM NAT'L GYPSUM
 Size: 4.12 mg
 Method: DSC-10°C/min, REPEAT 2
 Comment: 10°C/MIN, N2

DSC

File: RUN1434.01
 Operator: WEISSMAN
 Run date: 09/24/87 10:21

Sample: C-18 FROM NAT'L GYPSUM GOLDBOND
 Size: 8.86 mg
 Method: DSC-10°C/min, REPEAT 3
 Comment: DSC 10°C/MIN, N2, 870811-5A

DSC

File: RUN1418.01
 Operator: BACKSCHEIDER
 Run date: 09/17/87 15:43

Figure 4. DSC Analysis of C-18 PCM Used in National Gypsum Laboratory; (a) As-Obtained, (b) After Recrystallization.

TABLE 3
DSC ANALYSIS OF C-18 USED AT
NATIONAL GYPSUM LABORATORY

Sample	T _m (°C)	T _c (°C)	T _m -T _c (°C)	Heat of Fusion (cal/g)	Heat of Recrystallization (cal/g)
C-18 from National Gypsum (specimen sample)	28.5	16.1	12.4	41.6	42.5
C-18 from National Gypsum (1 gallon re- crystallized)	29.5	18.3	11.2	42.8	43.6
C-18 Humphrey Tech Grade (used in our lab)	28.0	19.5	8.5	52.8	52.6

APPENDIX 1
THERMAL FORM STABILITY OF C-16 PERCOLATED
CROSSLINKED HDPE

Procedure

500g of Humphrey Tech Grade n-Hexadecane was heated to 150°C in a beaker under constant stirring. Exactly 10.0g sample of crosslinked Marlex 6006 pellets irradiated at 10 μ Rad in N₂ was added to the beaker containing C-16. Permeation was carried out for 1 hr. at 150°C. HDPE pellets were removed after permeation and cooled to room temperature. Sample was then placed in an oven at 60°C for 4 hours to observe thermal form stability and possible oozing of C-16. Pellets oozed a slight amount of C-16 after permeation. Pellets retained their shape and size after heating at 60°C for 4 hours and did not ooze out C-16 thereafter.

Initial Weight of Pellets: 10.00g

Weight of Permeated Pellets: 42.55

C-16 PCM in Pellets Immediately After Permeation: 76.5%

C-16 PCM in Pellets After 3 Days at Room Temperature: 75.7%

C-16 PCM in Pellets After Heating at 60°C for 4 Hours: 74.4%

APPENDIX 2
PERCOLATION OF C-18 PCM/BCL-462/NYACOL ADP-480
INTO USG PLASTERBOARDS

Procedure:

Four 2" x 2" squares of USG plasterboard samples were cut and dried in a dessicator overnight. 500g of Humphrey tech grade C-18 was heated to 80°C under stirring. 110g of Ethyl BCL-462 followed by 55g of colloidal antimony pentoxide (Nyacol ADP-480) were added to C-18 PCM under constant stirring at 80°C. The suspension then obtained appeared stable. It was transferred to another beaker to observe any settled material. Very little material (about 1.0g) was observed at the bottom of the beaker. Weighed duplicate samples of USG plasterboards were then percolated for 5 minutes and 10 minutes. Samples were taken out of percolation bath, cooled and weighed.

MONTHLY PROGRESS REPORT NO. 17
CONTRACT NO. DE-FG03-86SF16308
COVERING OCTOBER, 1987

1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research, on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends".

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

The four processes are as follows:

1. Direct incorporation of PCM into the wet mix of building materials,
2. Direct incorporation into rubber or plastics medium for floor and wall tiles,
3. Indirect incorporation by first swelling the PCM into crosslinked polyethylene pellets or powder, which are then incorporated into building materials,
4. Direct incorporation by percolating the melted PCM into the open space in porous building materials.

As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3), the building material will not burn. However, in process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard after ignition will continue to burn slowly until the PCM is exhausted. In process 2, where the PCM is compounded into rubbers and plastics, the resulting composite will also burn; unless the polymer matrix is made fire retardant with effective additives.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will complete extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through

further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

The present month's work consists of the following:

1. To evaluate fire retardancy of USG plasterboards percolated with dispersions of C-18 and Phoschek P-30.
2. Evaluate fire retardancy of USG plasterboards percolated with mixtures of C-18 and Fyrol CEF.
3. DSC analysis of plasterboard percolated with a suspension of colloidal antimony pentoxide/BCL-462 in C-18 PCM.

3. TECHNICAL DESCRIPTION OF CURRENT RESEARCH

3.1 Percolation of Plasterboards with Dispersions of C-18 Containing 10% and 20% Weight of Phoschek P-30 for Fire Retardancy

Attempts were made to incorporate Phoschek P-30 (Monsanto), a non-halogenated fire retardant into US Gypsum plasterboards. Phoschek P-30, which is a polymeric ammonium phosphate, was dispersed in C-18 PCM. It was observed that Phoschek P-30 settles down almost immediately and a high speed sitring was essential to keep the fire retardant dispersed in C-18 PCM. Plasterboard samples percolated in C-18 containing 10% and 20% by weight of Phoschek P-30 were found to gain about 34%. As shown in Table 1, increasing the percolation time from 5 minutes to 10 minutes also did not change the total weight gain.

Flame tests conducted on all the samples did not show any self-extinguishing nature. No further analysis was conducted on these samples.

TABLE 1
PERCOLATION OF USG PLASTERBOARDS IN
C-18 PCM/PHOSCHEK P-30

<u>Sample Number</u>	<u>% of Phoschek</u>	<u>Percolation Time (mins.)</u>	<u>% Total Pickup</u>
871102-1A	10	5	34.7
-1B	10	5	33.5
871102-2A	10	10	33.9
-2B	10	10	34.3
871102-3A	20	5	33.3
-3B	20	5	33.6
871102-4A	20	10	34.4
-4B	20	10	34.2

3.2 Evaluate the Fire Retardance of Plasterboards Percolated with Mixtures of C-18 PCM and Fyrol CEF

In our previous studies (refer to our August progress report) we have found that excellent fire retardance in plasterboards could be achieved by incorporating C-18 PCM/Fyrol CEF via sequential percolation. Now, we studied the fire retardance of plasterboards percolated with mixtures of C-18 PCM and Fyrol CEF. Several compositions of C-18 PCM containing 5% to 25% by weight of Fyrol CEF were used for percolation. In all the compositions studied, Fyrol CEF was observed to be immiscible with the Octadecane. Vigorous stirring was essential to disperse Fyrol CEF in Octadecane.

DSC analysis of samples indicated that amount of PCM gained by the plasterboard varied from 9% to 23% as shown in Table 2. In general, high concentrations of Fyrol CEF in the percolation mixture decreased the amounts of PCM uptake in the plasterboards. For sample 870814-6, uniform stirring could not be maintained during percolation due to a mechanical problem. DSC analysis of this sample clearly indicates that Fyrol CEF was preferentially percolated into the plasterboard.

Flame tests as shown in Table 3, did not show any particular trend in fire retardancy. Samples 3, 6 and 7 were self-extinguishing, whereas Samples 4 and 5 burned continuously. This again confirms that controlling the composition of C-18/Fyrol CEF is difficult in this method of percolation. However, as reported earlier, composition of Fyrol in the plasterboard could be regulated in a sequential percolation process.

3.3 DSC Analysis of Plasterboard Percolated with a Suspension of Colloidal Antimony Pentoxide/BCL-462 in C-18 PCM

In our previous report we have described the percolation of plasterboards in a stable suspension of Nyacol antimony pentoxide ADP-480 with Saytex BCL-462 fire retardant in C-18 PCM. These samples have shown excellent fire retardancy and did not ignite for more than 5 minutes. DSC analysis of a sample percolated for 10 minutes in the suspension was carried out at three different

TABLE 2
DSC ANALYSIS OF PLASTERBOARDS PERCOLATED
IN MIXTURES OF C-18 PCM AND FYROL CEF

<u>Sample Number</u>	<u>T_m (°C)</u>	<u>T_c (°C)</u>	<u>T_m-T_c (°C)</u>	<u>Δ H_f (cal/gm)</u>	<u>% PCM DSC Data</u>	<u>% Fyrol CEF* DSC Data</u>
870814-3B	27.4	19.0	8.6	4.6	9.0	31.8
870814-4B	29.0	19.0	10.0	10.0	19.6	20.5
870814-5B	28.7	17.3	11.4	10.4	20.5	17.4
870814-6B	29.5	18.5	11.0	5.4	10.6	31.5
870814-7B	27.5	17.9	9.6	11.7	23.1	14.7

* % Fyrol CEF in plasterboard = Total % wt. gain - % PCM from DSC data.

TABLE 3
FIRE RETARDANCE OF PLASTERBOARDS PERCOLATED
IN MIXTURES OF C-18 PCM AND FYROL CEF

Sample Number	Composition C-18/CEF	C-18/CEF Uptake % (Dry)	Time in Seconds to Ignite Extinguish		Nature of Smoke, Flame, etc.
870814-3A	75/25	41.36	125 27	14 9	Dense white smoke, slow flame
870814-4A	80/20	39.92	72	---	Flame spread out profuse burning
870814-5A	85/15	37.32	33	---	Flame spread out profuse burning
870814-6A	90/10	40.63	145 10	10 7	Dense white smoke
870814-7A	95/5	35.88	39 18	47 225	Sooty flame, slow burning

points - center, edge and top surface of the plasterboard. A specimen sample at the top surface of the plasterboard (just below the paper) was taken for analysis to check the distribution of PCM throughout the bulk of the plasterboard. Results as presented in Table 4 indicate that the amount of PCM present in the center of the plasterboard was much less than at the surface or edge. This problem may be solved by increasing the percolation time. Further experiments will be designed to decrease the amount of Sb_2O_5 in suspension and also prolong the percolation process to enable the PCM to percolate into the bulk of plasterboards.

CONCLUSIONS

1. It was confirmed that a sequential percolation with C-18 PCM and Fyrol CEF would impart better fire retardancy in USG plasterboards compared to percolation in a mixture of C-18/Fyrol CEF.
2. Excellent fire retardancy in plasterboards was achieved using a suspension of colloidal antimony pentoxide with Saytex BCL-462 in C-18 PCM. However, analysis indicates that concentrations of PCM and fire retardant have to be optimized.
3. Experiments to incorporate Phoschek P-30 with C-18 PCM into plasterboards were not very successful.

Immediate Future Work:

1. Prepare and analyze thermally form stable hardened PCM composites of C-18 PCM and high molecular weight HDPE.
2. Prepare melt mixed blends of C-18 PCM and powder HDPE with/without fire retardant additives and extrude into thermally form stable pellets.

TABLE 4
DSC ANALYSIS OF PLASTERBOARD PERCOLATED
WITH Sb_2O_5 /BCL-462/C-18

<u>Sample Number</u>		<u>T_m (°C)</u>	<u>T_c (°C)</u>	<u>T_m-T_c (°C)</u>	<u>ΔH_f (cal/gm)</u>	<u>% PCM DSC Data</u>
870910-2A	edge	27.3	17.7	9.6	6.2	12.4
	center	26.6	17.6	9.0	1.7	3.5
	top	25.5	18.2	7.3	7.5	14.8

ANNUAL TOPICAL SUMMARY OF RESEARCHES ON:
"ADVANCED PHASE CHANGE MATERIALS FOR SOLAR
PASSIVE HEATING AND COOLING OF RESIDENTIAL BUILDINGS"

Grant No. DE-FG03-86SF16803

Prepared By:
Ival O. Salyer and Anil K. Sircar

PHASE I. CONTRACT PERIOD MAY 29, 1986 TO MAY 29, 1987

1. OBJECTIVES

- To find, test and develop low-cost effective phase change materials (PCMs), that melt and freeze sharply in the comfort temperature range of 73-77°F, for use in solar-passive heating and cooling of buildings.
- To define practical materials and processes for fire retarding plasterboard/PCM building products.
- Develop cost-effective methods for incorporating PCMs into building construction materials (concrete, plasterboard, etc.) which will lead to the commercial manufacture and sale of PCM-containing products, resulting in significant energy conservation.

2. WORK DONE DURING THE CURRENT YEAR BEGINNING MAY 29, 1986

Work during this period was curtailed during the fourth quarter of 1986 and the first quarter of 1987 due to a higher rate of spending during the first six months. Most of the work during the current fiscal year was directed to: (1) PCM materials development, (2) fire retard plasterboards, and (3) improve containment methods.

2.1 Phase Change Materials Development

2.1.1 Basic Studies of Pure Linear Alkyl Hydrocarbon

Extensive work with 99% pure n-hydrocarbons confirmed the earlier observations that "C-18" crystalline alkyl hydrocarbons PCMs are the most effective PCM systems available for solar passive heating and cooling of buildings.

The work also established the little or no super-cooling ($\sim 2^{\circ}\text{C}$) of these PCMs at the low rate of heating and cooling that may be expected during their actual usage. Selective blending of pure normal hydrocarbons showed that sharp transitions and minimum loss of latent heat are obtained in blends that have adjacent homologues as components with a normal distribution of carbon chains. This gives us an insight to select blends for intermediate temperature ranges as well as to check suitability of commercially available PCM materials.

Interestingly, odd carbon atom pure paraffins show a pronounced solid state transition at chains as short as C-9. This type of transition is encountered in even carbon chains of length C-22 and longer.

2.1.2 Evaluation of Humphrey Chemical Company Technical Grades of Linear Alkyl Hydrocarbons

The ultrapure alkyl hydrocarbon PCMs, evaluated above, are not obtained by refining of petroleum; but rather by polymerizing ethylene. The products obtained by this process consist of even numbered carbon atom PCM, which have little or no solid state secondary transition at carbon chain lengths of 16 to 22 carbon atoms. In preparing these PCM, the ethylene is polymerized by Chevron to an olefin that contains a terminal double bond. The olefin is subsequently hydrogenated, by Humphrey Chemical Company, to form saturated linear alkyl hydrocarbon PCM, that are sold without purification, as "Technical Grades". The technical grades are then fractionally distilled to make expensive products of 98-99% purity.

The Humphrey Technical Grades are available in chain lengths of 14-24 carbon atom lengths. Because of the absence of odd carbon chain length compositions, the technical grades tend to melt and freeze over a narrower range of temperature, and to have significantly higher heats of fusion and crystallization than the lower cost products from Petroleum Refining. For this reason we have conducted a thorough evaluation of the Humphrey Technical

Grade of PCM; since they may be cost effective despite their higher price.

DSC analysis showed that the Humphrey Technical Grade of C-18 has a melting temperature (T_m) and freezing temperature (T_f) near the comfort temperature range of 23°C (73°F); and stores and releases about 50 cal/gm during melting and freezing.

2.1.3 Cooperative Research with Witco Chemical Company to Develop Improved PCM, in the Temperature Range for Residential Heating and Cooling, from Petroleum Refining Operations

As pointed out in Paragraph 2.1.2 above, the "purer" alkyl hydrocarbons from ethylene polymerization are considerably more expensive than the corresponding by-products of normal petroleum refining. Accordingly, one of our projects of emphasis during the last year, was to collaborate with Witco Chemical Company to develop purer PCMs, in the C-16 to C-18 range, that are not now commercially available.

We participated with Witco in developing an effective process for commercial manufacture of K-61, a PCM that is a likely candidate to be used for solar heating and cooling of buildings, because of its transitions near the comfort range. DSC and gas chromatographic analyses of different fractions from distillation vs. solvent crystallization were carried out. It was observed that fractions from crystallization precipitates mostly the higher molecular weight linear hydrocarbons, leaving the lower (and branched) homologues in solution. This is reflected in higher heats of fusion and crystallization (46-48 cal/gm) as compared to the unfractionated products (35-44 cal/gm).

A 5-gallon supply from a larger lot of solvent fractionated K-61 (prepared by Chevron for Witco) was found to compare favorably, as regards thermal energy storage characteristics, with that of small laboratory samples of K-61 previously obtained from Witco. This is important in indicating that scale-up of the solvent fractionation process, for eventual commercial production, is feasible.

2.1.4 Evaluation of Fatty Acid Ester PCM for Solar Passive Application

In the event of a major crisis in the Mid-East, that curtailed the supply, and escalated the price of petroleum, a renewable indigeneous source, such as the fatty acid esters could become of interest. For this reason, as well as to obtain background data on research elsewhere (e.g. Canadian Mines and Resources), we have determined the chemical composition and thermal energy storage properties of a commercial grade of butyl stearate.

The chemical composition of the butyl stearate was determined by chromatographic analysis to be butyl stearate/butyl palmitate (67/33). The thermal energy storage properties were analyzed by DSC, at several rates of heating and cooling. The butyl stearate was found to melt and freeze near 20°C, and to store and release about 35 cal/gm.

This "impure" grade of butyl stearate is projected to sell in the United States for about \$0.70/lb. A purer grade obtained by distillation of the mixed esters is projected to sell for \$1.10/lb. The fatty acid esters could undergo hydrolysis in long term exposure in cementitious building materials, and they may also support mold growth. Thus, on the basis of overall cost/performance, the fatty acid esters, are less desirable than the alkyl hydrocarbon PCM, unless petroleum should suddenly become less available and less competitive in price.

2.1.5 Effect of Rate of Heating and Cooling on Thermal Energy Storage Properties as Determined by Differential Scanning Calorimeter (DSC)

As a matter of standard practice we have ordinarily run all our DSC analysis on thermal energy storage materials at 10°C/minute rate of heating and cooling. In practical end-use applications, the rates of heating and cooling would be considerably lower than this. At 10°C/minute rate of heating and cooling, we also note a significant difference in the melting temperature (T_m) and freezing temperature (T_f).

Accordingly, to obtain a better evaluation of these rate effects, we ran DSC measurements on the Humphrey Tech grade of C-18, and butyl stearate at 10, 5, 1, and 0.1°C/minute rate of heating and cooling. The results were interesting in showing that for both C-18 and butyl stearate the melting and freezing temperatures closely approach the same temperature at slower rates of heating and cooling (e.g. 1.0 and 0.1°C/minute). These results are of considerable practical importance since, in solar passive applications, the rate of change in temperature is not likely to exceed 0.1°C/minute (6°C/hour). Further, it indicates that with truly congruent melting and freezing, a single material, such as the Humphrey C-18 and butyl stearate, could be effective in both winter heating and summer cooling.

2.2 Fire Retardance of Solar Passive Building Materials Containing Alkyl Hydrocarbon PCM

Most of these experiments were directed at making plasterboards fire retardant. Chlorowax 70S and antimony oxide, the cheapest and most common fire retardants, are not soluble in hydrocarbon PCMs and so can not be used to fire retard plasterboard during incorporation of PCM by percolation. After examining a number of halogenated organic compounds from Ethyl Corporation and Great Lakes Corporation, Ethyl's BCL-462 (dibromoethyl-dibromocyclohexane) was found to be soluble with the hydrocarbon PCMs used by us, in all proportions. This was considered a breakthrough, since this has the potential of fire retarding plasterboards simultaneously with percolation of the PCM. Some plasterboard samples, percolated with 45A/BCL-462 in the ratio of 75/25 showed improved fire retardance in laboratory experiments.

In parallel experiments, it was considered that it may be possible to fire retard plasterboards by lowering the amount of PCM absorption, by using PCM diluted in a solvent, as the imbibing medium. Accordingly, samples with varying PCM content from 2 to 23% by weight were prepared by percolation of PCM in heptane and methylene chloride. The samples containing up to 6% PCM does not ignite in 10 seconds, and the sample with 18% PCM extinguishes in

5 seconds. This is also a very encouraging development, since plasterboards with significant thermal energy storage and reduced flammability can be made by varying the solvent/PCM ratio to reduce the PCM content.

Experiments were also carried out to fire retard plasterboard by (1) in-situ incorporation of insoluble (and cheaper) fire retardants during manufacturing process, and (2) during percolation experiments.

In order to introduce fire retardants by the in-situ process, it was necessary to duplicate the commercial process to prepare low density plasterboards. Preliminary experiments show that it is possible to match the density of commercial plasterboards by adjusting the amount of foaming agent. Further experiments are planned with the fire retardants in-situ when additional funds are available.

In follow-up experiments with the soluble fire retardant BCL-462, it was found that up to 49% Witco 45A/BCL-462 combination can be incorporated in plasterboards by sequential percolation in PCM and BCL-462. By varying the duration and order of immersion, different ratios of these components can be incorporated in plasterboard. A number of these combinations show potential for improved fire retardance.

In very recent experiments, we found that solubility of the fire retardant in the PCM is not a requirement, if the sequential percolation method referred to above is used.

From the Dow Chemical Company, we have obtained two phosphate ester fire retardant compounds; FYROL CPF (tri chloro isopropyl phosphate), and FYROL CEF (tri chloro ethyl phosphate). Neither of these compounds are soluble in alkyl hydrocarbon PCM. In sequential percolation experiments, we found that we could control the PCM uptake by varying the PCM and FYROL percolation time. Best results were obtained with the FYROL CEF in that we obtained excellent resistance to initial ignition, quick extinction after the flame was removed, and little smoke or fumes emitted.

In the following contract period, we will continue and expand our investigation of this very promising approach to fire retardant plasterboard that contains useful concentrations of alkyl hydrocarbon PCM as well. We also plan experiments on combinations of a soluble fire retardant with a submicron antimony pentoxide.

2.3 Further Developments on Containment Methods

In further studies on permeation, it was possible to swell about 90% K-61 PCM and about 81% NP-15 in Marlex 6006 (10 mrad). NP-15 melts and freezes below room temperature and can be potentially useful for cool storage and breeze deck deicing.

In the above experiments with NP-15 and HDPE pellets, it was observed that washing with poorer solvents (MEK > ethanol > methanol) increases the ultimate weight gain of swelled pellets. This indicates that washing removes the swelled wax from the top layer of the pellets. This has been confirmed by DSC experiments from different layers of the swelled pellets.

The above observation about the removal of swelled wax by washing with MEK is of minor consequence for the pellets, but it has a major impact for the HDPE powders. We would like to imbibe HDPE powders with PCM, since the small particle size of the powder would be less detrimental to the strength of the building materials. However, earlier work showed no weight gain for HDPE powder swelled in Witco 45A at 150°C for two hours and washed with MEK. Follow-up work during this period with methanol rinsing showed about 80% weight gain for 45A imbibed with Marlex 6006 powder. Only minor effect of the level of gamma irradiation between 4 to 8 mrad was noted, on imbibed weight, or DSC determination of PCM (provided the samples are washed with methanol). This conclusively proves that because of the smaller size, a good solvent like MEK washes away most of the imbibed PCM in powders.

The work was also directed to alternatives to the containment methods already described. One of the methods attempted

is microencapsulation. Preliminary data show good encapsulation and thermal energy storage.

The second method attempted is crosslinking of HDPE by chemical methods (e.g. peroxide and vinyl triethoxy silane). Some samples of LDPE, HDPE and polypropylene prepared by one or the other of these methods, and subsequently swelled in paraffinic hydrocarbon, have been tested by us for thermal energy storage and were found to contain up to 85% hydrocarbon, an amount comparable to crosslinking by gamma irradiation.

Prior work shows that potentially the peroxide method, will be cheaper than gamma irradiation. Accordingly, a series of samples were recently made by extrusion crosslinking with dicumyl peroxide, at different concentration levels, at Springborn Laboratories. Some of these also contain antimony pentoxide, to simultaneously fire retard the pellets (after they are subsequently permeated with PCM/BCL-462 solution). Pellet sizes can also be adjusted to obtain smaller sizes. Further work on swelling of these pellets, analysis of thermal energy storage, and subsequent incorporation into building materials is under way.

2.4 Stability of PCM to Repeated Cycles of Melting and Freezing

One of the most important criteria of PCM for use in Solar Passive heating and cooling of buildings, is the ability to undergo many repeated cycles (e.g. 1000X) of melting and freezing, without degradation of thermal energy storage properties. To test the stability of the alkyl hydrocarbon PCM to such thermocycling, samples of the PCM, PCM in HDPE pellets, and PCM in building materials, were placed in small glass vials in an automated oven, and cycled between -20 and +80°C for 1000 cycles.

This experiment was in progress when this report was written, and was not be completed during the contract period ending May 29, 1987. The preliminary results to date have been very encouraging in that no apparent degradation has been observed to date.

MONTHLY PROGRESS REPORT NO. 18
CONTRACT NO. DE-FG03-86SF16308
COVERING NOVEMBER, 1987

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Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

The four processes are as follows:

1. Direct incorporation of PCM into the wet mix of building materials,
2. Direct incorporation into rubber or plastics medium for floor and wall tiles,
3. Indirect incorporation by first swelling the PCM into crosslinked polyethylene pellets or powder, which are then incorporated into building materials,
4. Direct incorporation by percolating the melted PCM into the open space in porous building materials.

As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (Processes No. 1 and No. 3), the building material will not burn. In Process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard after ignition will continue to burn slowly until the PCM is exhausted. In Process No. 2, where the PCM is compounded into rubbers and plastics, the resulting composite will also burn; unless the polymer matrix is made fire retardant with effective additives. We have preliminarily addressed the flammability problem in this process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing.

There are difficulties in applying the above state-of-the-art fire retarding technology effectively in Process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated simultaneously. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will complete extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing

the results, through further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

In order to conserve remaining project funds, the current research is continuing at only a minimum level. The present month's work consisted of the following:

- To prepare and analyze thermally form stable hardened PCM composites of C-18 and high molecular weight HDPE.
- To prepare melt mixed blends of C-18 PCM and HDPE powder and extrude into thermally form stable pellets.

3. TECHNICAL DESCRIPTION OF CURRENT RESEARCH

3.1 Prepare and Evaluate Melt Mixed Composites of PCM and HDPE

In prior research on incorporating neat low melting hydrocarbon PCM's (Process No. 3), into the wet mix of concrete and plaster, we have consistently observed a decrease in strength properties of the cured products that was disproportionate to the volume of PCM present. We have attributed this undesirable effect to the lubricating action of the "oily" PCM in coating the surfaces of the components in concrete and plaster, and thereby preventing effective adhesion. In one approach to overcoming this problem, we have investigated hardening of low melting or liquid PCM, with minor amounts of higher melting paraffins, stearic acid, and Chlorowax 70-S, with only marginal success.

A separate and effective method of hardening the low melting PCM has been well developed by us in Process No. 3, wherein the PCM is permeated into small crosslinked pellets of HDPE at elevated temperature (eg 150°C). The crosslinked pellets can contain up to 80% wt. of liquid or low melting PCM (eg C-16, C-18); and are stable to repeated thermocycling, without any PCM running out (oozing). However, this process involves added costs for the crosslinking and permeating steps. We have therefore continued to evaluate less expensive potential routes to a

thermally form stable pellet that can be added to the wet mix of concrete and plaster without a prohibitive decrease in the strength properties of the cured products.

This month, experiments were conducted to prepare and evaluate melt mixed blends of PCM hardened with minor percentage of uncrosslinked HDPE. Composites of C-18 PCM with high molecular weight HDPE (Phillips Marlex EHN-6001) were prepared by manual mixing of the two components at 150°C. Composites containing 70, 75, and 80% weight of C-18 PCM (30, 25, and 20% weight HDPE) were mixed. The difficulty of manual mixing increased with the percentage of HDPE in the blend, due to increased viscosity. The composite blends were clear at the 150°C mixing temperature, thus indicating complete compatibility of the components. The composite blends were then poured into a flat-bottomed tray to form a sheet that was allowed to cool to room temperature. The sheets became opaque as the temperature went below the crystalline melting point of the HDPE, and were knife cut into rough granules. The procedure for preparing the melt blends is described in more detail in Appendix No. 1.

The melt mixed composites were tested for thermal form stability, and PCM oozing (running out), by heating for four hours at 60°C. The pellets were observed to retain their shape and form, and there was no evidence of oozing (both favorable results). The apparent hardness of the pellets decreased with increasing PCM content (70%>75%>80%). However, in contrast to the crosslinked HDPE pellets permeated with PCM (Process No. 3), all four of the melt-mixed blends showed an undesirable "pressure sensitivity". When strong manual pressure was applied to the blend pellets, some of the PCM could be squeezed out. This new process is so economically attractive however, that we plan to evaluate the incorporation of absorptive fillers (eg finely divided silica) to see if they can eliminate the pressure sensitivity.

DSC analysis on 4-6 mg samples of the blends was conducted, using a heating and cooling rate of 10°C/minute. A typical DSC

thermogram, shown in Figure 1, confirms the presence of the C-18 in the composite, with the indicated melting temperature near 25°C, as expected. However, calculation of the weight percent of PCM from the DSC ΔH_f and ΔH_c values showed the amount of PCM to be lower than predicted from the starting blend compositions. The difference between starting PCM content, and PCM from DSC analysis, was most pronounced in the sample containing the highest (30% wt.) HDPE. We believe this anomaly may be due to the small size of the DSC sample, and micro inhomogenieties in the blends; resulting from non-uniform mixing, or phase separation during cooling. This is being investigated by analyzing a number of samples from different portions of the composite.

3.2 Preparation of Melt Mixed blends of C-18 PCM/HDPE Powder, and Extrusion to Produce Small Thermally Form Stable Pellets

When the melt mixed C-18/HDPE blends are prepared, following the procedure outlined in 3.1 above, and the molten mix is poured into a flat bottomed tray and allowed to cool, a hard opaque sheet is formed that can be cut into rough granules, during the cooling or afterward. For easier incorporation into the wet mix of concrete and plaster, smaller uniform size pellets are needed.

Accordingly, it was decided to prepare a somewhat larger quantity of melt blended granules; extrude these into strands, and to then cut the strands into small uniform pellets.

Based on the results obtained in Section 3.1, a ratio of C-18 PCM/HDPE of 75/25 was chosen. Marlex 6006 powder was selected because it was believed that solution of the powder in the PCM would be quicker than with the EHN-6001 pellets. Other than for the change to use the 6006 Powder, the procedure was identical to that used in 3.1, and is described in detail in Appendix 2.

The extrusion was carried out in a HAAKE 1" diameter, electrically heated extruder, using two different screws (venting and non-venting) having a compression ratio of about 3, a length to diameter ratio of 25/1, a screw speed of 40 rpm, temperatures

Figure 1. DSC Thermogram of a Melt Mixed Blend of C-18 PCM/Marlex EHN-6001 HDPE (80/20).

of 190 and 140°C respectively, and a single opening circular strand die. Under these conditions, a small strand was successfully extruded and cut to form pellets of about 1/16" cross section. The pellets are apparently thermally form stable, do not exhibit any oozing; but are pressure sensitive like the starting granules.

More research is required to overcome the pressure sensitivity, as well as to develop optimum extrusion and cutting conditions. The optimized pellets will then be incorporated into the wet mix of building materials, and the physical properties of the products evaluated.

CONCLUSIONS

1. Thermally form stable composite granules containing 70, 75, and 80% wt. of C-18 PCM and 30, 25, and 20% wt. of high molecular weight Marlex EHN-6001 HDPE can be prepared by simple melt mixing of the components followed by cooling, and cutting. With the manual mixing method used, problems of inhomogeneity may be present. Further, the "pressure sensitivity" of the product granules remains to be overcome.
2. Melt mixed blends of C-18 PCM and Marlex 6006 HDPE powder (75/25) were also prepared, and the granules obtained extruded into small thermally form stable pellets. However, more research is required to optimize extrusion conditions; and to overcome the problems of inhomogeneity and pressure sensitivity.

IMMEDIATE FUTURE WORK

1. To determine the fire retardance of Melt mixed blends of C-18/HDPE containing various fire retardant agents.
2. Evaluate peroxide initiated crosslinking of HDPE pellets at various temperatures, including temperatures below the melting point of the HDPE.

APPENDIX 1
PREPARATION OF HARDENED PCM COMPOSITES

Part 1

40g of C-18 PCM was heated to 150°C and 10g (20% by weight) Marlex EHN-6001 high molecular weight HDPE was added in steps with vigorous manual stirring. Temperature was maintained at 150°C throughout. The solution was stirred manually until HDPE was uniformly distributed into C-18, which took about 30 minutes. It was then allowed to cool and was cut into rough granules with a putty knife. The relative difficulty of stirring and breaking were noted.

Part 2

The procedure was the same as in Part 1 except that 37.5g of C-18 and 12.5g (25% by weight) of Marlex EHN-6001 were used.

Part 3

The method of preparation remained the same as in Part 1, but 35g of C-18 and 15.0g (30% by weight) of Marlex EHN-6001 were used.

The rough cut granules from all three samples were heated at 60°C for 4 hours and observed for (1) any change in form; or, (2) oozing.

APPENDIX 2
PREPARATION AND EXTRUSION OF MELT MIXED
BLENDS OF C-18 PCM/HDPE

750g of C-18 PCM was weighed into a 2L metal beaker and heated to melt. While adding Marlex 6006 powder HDPE in increments of about 10g, temperature of the solution was raised to 150°C. Vigorous manual stirring of C-18/HDPE solution was maintained throughout the addition. Total amount of HDPE added to C-18 was 250g. The viscous solution obtained was poured into a warm metal tray and spread into a thin sheet. The solution of the blend solidified almost instantaneously. The blend was then cut into granules suitable for feeding to the extruder.

A Haake 1-inch extruder with a single strand die was used with a cooling water bath and cutter/take-off assembly attached. The extruder assembly was warmed for at least 30 minutes. Original HDPE pellets (Marlex 6006) were extruded first, as a trial run. Melt mixed blend of C-18/HDPE was then extruded with a venting screw at a temperature of 190°C and a screw speed of about 40 rpm. With a non-venting single stage screw, a lower temperature of 140°C was used. A cohesive strand obtained from the die exit was cooled with ice cold water and fed to a cutter via a take-off belt. With a belt speed of 8 ft/min. and cutter speed of 850-1050 RPM small pellets (1/16 inch dia.) of the melt mixed blends were obtained.

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1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research, on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends".

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and

the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

The four processes are as follows:

1. Direct incorporation of PCM into the wet mix of building materials,
2. Direct incorporation into rubber or plastics medium for floor and wall tiles,
3. Indirect incorporation by first swelling the PCM into crosslinked polyethylene pellets or powder, which are then incorporated into building materials,
4. Direct incorporation by percolating the melted PCM into the open space in porous building materials.

As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3), the building material will not burn. However, in process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard after ignition will continue to burn slowly until the PCM is exhausted. In process 2, where the PCM is compounded into rubbers and plastics, the resulting composite will also burn; unless the polymer matrix is made fire retardant with effective additives.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We

will complete extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

In order to conserve remaining project funds, the current research is continuing at a minimum level. The present month's work consisted of the following:

1. To prepare and evaluate additional fire retardant compositions of melt mixed blends of C-18 and uncrosslinked HDPE.
2. Evaluation of commercial fatty acid esters as possible alternates to the hydrocarbon PCMs.
3. Annealing and crosslinking of commercial polyethylene and polypropylene products.

3. TECHNICAL DESCRIPTION OF CURRENT RESEARCH

3.1 Prepare and Evaluate Additional Fire Retardant Compositions of Melt Mixed Blends of C-18 and Uncrosslinked HDPE

In recently completed research, we have prepared mechanically mixed melt blends of C-18 and uncrosslinked (thermoplastic) high density polyethylene (Marlex 6001 and 6006) wherein the HDPE pellets were dispersed at 20, 25, and 30% weight concentration in Humphrey Tech Grade C-18, at 150°C. The resulting viscous syrup was then poured into flat pans to cool; and knife-cut into crude pellets while still warm. These pellets are hard, and apparently thermally form stable at room temperature. However, with the application of vigorous manual pressure, some of the PCM can be squeezed out; and, this is obviously a severe limitation to this otherwise attractive process.

However, it is possible that the "pressure sensitivity" can be minimized or eliminated while simultaneously introducing fire resistance property by the incorporation of absorptive fire retardant fillers. Accordingly, this month, we have investigated the melt mixing of similar C-18 and Marlex 6001, that also contained various previously proven fire retardants. The primary fire retardants were: Phoschek P-30, Fyrol CEF, BCL-462, Bromochlor 70 and Chlorowax 70-S. In the last three fire retardant formulations, we have also incorporated some of the sub-micron particle size antimony pentoxide. The complete formulations are summarized in Table 1.

In the first series of experiments, all the components of the formulation were added simultaneously to melt and hand stirred at 150°C. Since considerable time was required to disperse the components in the viscous syrup, at 150°C, some pronounced darkening of the mixture, due to thermal decomposition of the fire retardants themselves was noted. Therefore, a second series of experiments was carried out in which the melt mix of the HDPE and C-18, was first prepared at 150°C, and the fire retardants added later at a lower temperature. By this means the thermal decomposition was avoided altogether.

The resulting products, after cooling, were tested to determine their fire retardance properties. Unfortunately, none of the blends prepared by the manual mixing process exhibited significant resistance to initial ignition, and continued to burn after ignition.

We plan to do further experiments to improve the fire retardance, by increasing the concentration of fire retardant additives, and changing the amounts of the antimony pentoxide. We will also attempt to improve the homogeneity of the melt mixes. With these modifications, we expect to obtain truly fire retardant products, by this simpler, lower cost process.

3.2 Evaluation of Commercial Fatty Acid Esters, As Possible Alternates to the Alkyl Hydrocarbon PCM

If for any reason the supply of petroleum should become inadequate, a renewable, indigeneous source of PCM, such as the fatty acid esters, could become of increased interest for solar passive applications. For this reason, we have completed this month the determination of the chemical composition and thermal energy storage properties of some commercial fatty acid esters sold under the trade name Thermotop. A knowledge of the chemical composition of the commercial samples would help us to understand and correlate the thermal energy storage data. It will also enable us to blend different esters to match or better the thermal energy storage properties of the commercial samples at a lower cost.

The chemical composition of the Thermotop 13, 15, and 20 were determined using chromatographic analysis supplemented by elemental analysis, saponification, infrared, and nuclear magnetic resonance (NMR). From these analyses it was determined that the chemical composition of these fatty acid esters is as follows:

- Thermotop 13 is butyl palmitate containing about 11% wt. impurities.
- Thermotop 15 is a very pure grade of butyl palmitate with 1.7% wt. impurities.
- Thermotop 20 is a mixed ester of butyl stearate/butyl palmitate (57/43), probably derived from palm oil.
- The "butyl stearate" we have been using at UDRI is also a mixed ester of butyl stearate/butyl palmitate (67/33) and is obtained from animal fats - which accounts for the higher percentage of stearic acid compared with Thermotop 20 (from palm oil).

We have done differential scanning calorimeter (DSC) analysis of the Thermotops at a heating and cooling rate of 10°C and 2°C/minute. The results are summarized in Table 2 along with similar data on the Humphrey Chemical Company Technical Grade of C-18 and C-16. The Thermotop 20 has a heat of fusion (ΔH_f) and crystallization (ΔH_c) of about 30 cal/gm

which is significantly below that of the alkyl hydrocarbon PCM C-18 and C-16.

The Thermotop 13 and 15 both have ΔH_f values up to 43 cal/gm, and ΔH_c of 26 cal/gm. This result was not expected. We do not have a complete explanation for this unusual behavior. We believe that it may be due to a solid state change in crystallinity that occurs when the melted sample is cooled down to -40°C , as is our standard practice in running DSC measurements. We have checked this theory by cycling the Thermotop 13 and 15 DSC sample between narrower temperature limits of 0 and 20°C , and find ΔH_f and ΔH_c values of about 20 and 25 cal/gm, respectively. The practical implications of this effect is that, after charging (melting), this PCM on crystallization will only release about 20 to 25 cal/gm, even if cooled to well below 0°C . This value is of course significantly lower than we obtain from even the less pure commercial alkyl hydrocarbon PCM (e.g., Witco 45-A, 43 cal/gm).

The Thermotop 20 does not show the anomaly of different heats of fusion and crystallization when cycled between -45°C and $+55^\circ\text{C}$.

DSC graphs of Thermotop 13, at $2^\circ\text{C}/\text{min}$. rate of heating and cooling, cycled between -40 and $+75^\circ\text{C}$, and 0 and 40°C , are attached as Figures 1 and 2, respectively. Figures 3 and 4 show DSC curves at $2^\circ\text{C}/\text{min}$. for Thermotop 15 cycled between -45°C and -5°C , respectively. Figure 5 shows the DSC graphs of Thermotop 20 cycled between -45°C and $+55^\circ\text{C}$ at a heating and cooling rate of $2^\circ\text{C}/\text{minute}$.

The Humphrey Tech Grade C-18 and C-16 are made by polymerizing ethylene to the corresponding α olefin (Chevron) and hydrogenating (Humphrey). These PCMs contain no odd number carbon atom species, and thus do not have a solid state secondary transition. As a result, they melt and freeze over a narrower temperature range.

Relative Merit of Fatty Acid Esters and Alkyl Hydrocarbon PCM

The fatty acids and esters have been investigated for several years in research sponsored by the Energy Mines and Resources Agency in Canada. Their most recent results were reported at the 12th Solar Passive Conference in Portland, Oregon, July 11-16, 1987. We have also evaluated the fatty acids and esters (e.g., butyl stearate) as PCM for use in thermal energy storage applications.

We regard the fatty acid esters as the second best PCM for thermal energy storage at near ambient temperatures but not as competitors that threaten or invalidate our continuing research on the linear alkyl hydrocarbon PCM. The two most important containment methods we have developed for the alkyl hydrocarbon PCM (HDPE pellets and percolation into plasterboard) can also be carried out with the fatty acid esters. We are therefore including the use of the fatty acid esters in the two containment processes and products in pending U.S. and foreign patent applications.

The fatty acid esters are obtained primarily from animal fats in the U.S. and from palm oil in Southeast Asia. From both sources, the starting materials have very similar fatty acid composition, and consist primarily of palmitic, stearic, and oleic acids, plus minor amounts of myristic and linoleic acids. In commercial practice, the glycerides are hydrolyzed, hydrogenated (to remove unsaturation), and then esterified with monofunctional alcohols (methanol, ethanol, propanol, butanol, etc.). Thereby commercial products are made that are primarily mixed esters of stearic and palmitic acids with small amounts of myristic, etc. The mixed esters can be separated - purified by distillation.

The chemical composition of the fatty acids from palm oil and animal fats is summarized in Table 3.

The melting points of the pure stearate and palmitate esters as taken from the Handbook of Chemistry and Physics, 1985-86 edition, are contained in Table 4. The pure stearate

esters melt and freeze at higher temperatures than the corresponding palmitate esters.

The mixed ester products sell in the U.S. for about \$0.70 per pound. The "pure" 90-95% distilled products sell here from about \$1.10 per pound.

In the U.S., the commercial (less pure) grades of alkyl hydrocarbons sell for prices well below those of the fatty acid esters. Witco 45-A was available for \$0.75/lb, and will store and release 43-50 cal/gm.

The Thermotop fatty acid esters, including 98.3% pure butyl palmitate (Thermotop 15), will store and release only about 26 cal/gm over the range of melting and freezing temperatures expected in the use of these PCMs.

The fatty acid esters are likely to hydrolyze during long-term exposure to moist ionized environment (as in plaster or concrete). Also, unlike the paraffinic hydrocarbons, the fatty acid esters do not offer a homologous series of materials that can store energy at a broad temperature range (-15 to +60°C vs. 16 to 39°C).

It is believed that the fatty acid esters can support growth of molds and other microorganisms.

Accordingly, it was concluded from the above considerations, that the fatty acid esters are less attractive than the alkyl hydrocarbon PCM from the standpoint of cost/performance, and other reasons as well.

3.3 Gamma Irradiation Crosslinking of Polyethylene and Polypropylene Products

We have developed an effective method of hardening the C-18 PCM in process No. 3, wherein the alkyl hydrocarbon PCM is permeated into small crosslinked pellets of HDPE at elevated temperature. Our experimental results have shown that the crosslinked HDPE can contain up to 80% wt. of C-18 or C-16 PCM and are stable to repeated thermocycling.

In continuation of this work, we are now investigating the irradiation dose on different forms of polyethylene and polypropylene products. Several products of PP, HDPE and LDPE were first analyzed by DSC to determine the melting points. Annealing temperatures of these products were calculated as 8/9 of the melting points in degrees Kelvin. Samples were annealed at temperatures as indicated in Table 5, in a air circulated oven. Annealing of the products was performed to remove the strains of processing and thermal history. In all, 15 samples were sent to Neutron Products for irradiation to a total dose of 10 M-rad, 14 M-rad and 20 M-rad as specified in Table 5. The crosslinked products will be tested for PCM containment.

The objective of this irradiation crosslinking is to crosslink finished (molded) films, sheets, etc. which can afterward be swelled with PCM to provide thermal storage in HDPE in "other-than-pellet" forms.

CONCLUSIONS

1. In fire retardant compositions of melt mixed blends of C-18 PCM/HDPE, the amount of fire retardant additive and homogeneous mixing are two critical factors which control the flammability of the products. Adequate mechanical mixing of the blends is necessary to achieve homogeneity. In the ratios and concentrations tested in this series of experiments fire retardant compositions were not obtained. Further tests with higher concentrations of fire retardant are planned.
2. Commercial fatty acid esters Thermotop 13 and Thermotop 15 mainly consist of butyl palmitate with different degrees of purity. Thermotop 20 is a mixture of butyl stearate/butyl palmitate (57/43). The thermal energy storage properties of the fatty acid esters are significantly lower than those of the linear alkyl hydrocarbon PCM. Nonetheless, the fatty acid esters are the next best known alternates to the alkyl hydrocarbon PCM (in the event of a petroleum shortage).

In the "butyl stearate" PCM, the higher percentage of stearate ester in the UDRI sample (65%) appeared to provide significantly higher thermal energy storage than in the Thermotop 20 (57%).

IMMEDIATE FUTURE WORK

1. To investigate higher concentrations of fire retardants, and improved mixing techniques, to obtain HDPE/PCM melt mixed blends that are self-extinguishing, after ignition.
2. To optimize conditions for maximum fire retardancy in plasterboards by sequential percolation in C-18 PCM and Fyrol CEF.
3. To increase the amount of PCM in fire retardant plasterboards percolated in a suspension of C-18 PCM/BCL-462/Sb₂O₅. Suspensions with lesser amounts Sb₂O₅ will be made to increase the uptake of PCM in the plasterboards.

Sample: THERMOTOP-13
 Size: 4.5530 mg
 Method: DSC- 2°C/min
 Comment: 2°C/MIN, N2

DSC

File: A: RUN1483.01
 Operator: GALASKA
 Run Date: 11/05/87 10:47

General V2.2A DuPont 9900

Figure 1. DSC Graph of Thermotop 13 Cycled Between -45°C and +55°C at a Heating and Cooling Rate of 2°C/min.

Sample: THERMOTOP 13
 Size: 4.5400 mg
 Method: DSC-LOW TEMP
 Comments: 2°C/min

DSC

File: RUN1524.01
 Operator: GALASKA
 Run Date: 02/05/88 12:59

Figure 2. DSC Graph of Thermotop 13 Cycled Between 0 and 20°C at a 2°C/min. Rate of Heating and Cooling.

Sample: THERMOTOP-15
 Size: 4.8640 mg
 Method: DSC-SUB AMB
 Comment: 2°C/MIN, N2

DSC

File: A:RUN1492.01
 Operator: DANTIKI
 Run Date: 11/10/87 10:52

Figure 3. DSC Graph of Thermotop 15 Cycled Between -45°C and +55°C at a Heating and Cooling Rate of 2°C/min.

Sample: THERMOTOP 15
 Size: 4.7520 mg
 Method: DSC-SUB AMB-2
 Comment: 2 C/MIN, N2

DSC

File: A.RUN1496.02
 Operator: BACKSCHEIDER
 Run Date: 11/12/87 15:19

Figure 4. DSC Graph of Thermotop 15 Cycled Between -5°C and +20°C at a Heating and Cooling Rate of 2°C/min.

Sample: THERMOTOP-20
 Size: 5.6240 mg
 Method: DSC-SUB AMB
 Comment: 2°C/MIN, N2

DSC

File: A: RUN1493.02
 Operator: DANTI KI
 Run Date: 11/11/87 09:12

Figure 5. DSC Graph of Thermotop 20 Cycled Between -45°C and +55°C to a Heating and Cooling Rate of 2°C/min.

TABLE 1
MELT MIXED BLENDS OF HUMPHREY TECH GRADE
C-18 PCM WITH MARLEX EHN-6001 HDPE AND
FIRE RETARDANT ADDITIVES

Chemical Composition	1 Wt. Grams	2 Wt. Grams	3 Wt. Grams	4 Wt. Grams	5 Wt. Grams
1. Humphrey Chemical Co. Technical Grade C-18 PCM	80	80	80	80	80
2. Phillips Marlex HDPE Melt Index 0.2 dgs/min. EHN-6001	20	20	20	20	20
3. Monsanto Phoschek P-30 Polyammonium Phosphate	24	--	--	--	--
4. Stauffer Company Fyrol CEF Trichloroethyl Phosphate	--	24	--	--	--
5. Ethyl Corporation BCL-462 Dibromoethyl dibromo cyclohexane	--	--	16	--	--
6. Diamond Shamrock Chlorowax 70-S Heat Stabilized Chlorinated Paraffin, 70% Cl	--	--	--	16	--
7. Ferro Bromochlor 70 halogenated hydrocarbon, containing bromine and chlorine	--	--	--	--	16
8. Nyacol Products Inc. Nyacol ADP-480 Sb ₂ O ₅ 0.03 Micron Antimony Pentoxide	--	--	8	8	8

TABLE 2
DIFFERENTIAL SCANNING CALORIMETER ANALYSIS
OF THERMOTOP FATTY ACID ESTERS AND
HUMPHREY TECH GRADE C-16 AND C-18 ALKYL HYDROCARBON PCM

Tradename and Chemical Composition	DSC Temp Cycle (°C to °C)	DSC Rate Heating & Cooling (°C/min)	T _m (°C)	T _c (°C)	T _m -T _c (°C)	Δ H _f (cal/gm)	ΔH _c (cal/gm)
1. Thermotop 13 Butyl Palmitate 89% "Impurities" 11%	-45°C to +55°C	10.0	16.4	9.7	6.7	31.9	27.7
	-40°C to +55°C	0.1	13.6	12.2	1.7	33.4	21.2
	-45°C to +55°C	2.0	13.7	10.0	3.7	43.1	26.7
	-5°C to 20°C	2.0	13.4	11.0	2.3	20.3	20.2
2. Thermotop 15 Butyl Palmitate 98.3% "Impurities" 1.7%	-45°C to +55°C	2.0 ---	15.0 ---	11.0 1.7	4.0 ---	42.9 ---	25.2 4.5
	-5°C to +20°C	2.0 ---	13.7 3.3	11.3 1.9	2.4 1.4	25.9 4.2	25.6 4.3
3. Thermotop 20 Butyl Stearate 57% Butyl Palmitate 43%	-45°C to +55°C	2.0	21.5	18.5	3.0	30.3	30.0
4. UDRI "Butyl Stearate" Butyl Stearate 65% Butyl Palmitate 35%	-45°C to +55°C	10.0	23.3	17.4	5.9	35.7	35.8
5. Humphrey Chem. Co. Tech Grade C-18 Alkyl Hydrocarbon	-45°C to +55°C	10.0	27.2	19.3	7.8	51.0	49.9
	-45°C to +55°C	2.0	26.2	22.5	3.7	49.0	48.9
6. Humphrey Chem. Co. Tech Grade C-16 Alkyl Hydrocarbon	-45°C to +55°C	10.0	18.5	9.8	8.7	45.1	44.4
	-45°C to +55°C	2.0	15.8	12.3	3.5	43.6	43.8

TABLE 3¹
ACID COMPOSITION OF FATS AND NONDRYING OILS (1)

Fat or Oil	Iodine Value	Titer of Acids (°C)	Fatty Acids, %							
			Caprylic	Capric	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic
Coconut	8-10	20-23	8.0	7.0	48.0	17.5	8.2	2.0	6.0	2.5
Babassu	12-16	23-24	6.5	2.7	45.8	19.9	6.9	---	18.1	---
Palm kernel	15-18	20-25	3.0	3.0	52.0	15.0	7.5	2.5	16.0	1.0
Palm	51-58	38-47	---	---	---	1.0	42.5	4.0	43.0	9.5
Olive	80-85	17-21	---	---	---	---	0.0	4.0	83.0	7.0
Castor ²	81-89	3	---	---	---	---	---	0.3	8.0	3.6
Peanut ³	85-90	28-32	---	---	---	---	7.0	5.0	60.0	21.0
Rape ⁴	94-106	12-18	---	---	---	1.0	1.0	1.0	20.0	15.0
Beel tallow	32-47	37-47	---	---	---	2.0	32.5	14.5	48.3	2.7
Lard (leaf)	46-66	36-43	---	---	---	1.1	30.4	17.9	41.2	5.7
Whale blubber ⁵	110-150	22-24	---	---	---	8.0	12.1	2.3	33.4	9.0

¹ Data of Werner G. Smith Company.

² Contains 87.8% ricinoic acid.

³ Contains 4.0% arachidic acid and 3.0% lignoceric acid.

⁴ Contains 1.0% lignoceric acid and 50.0% erucic acid.

⁵ Contains 1.5% of a C₁₄-monounsaturated acid, 15% palmitoleic acid, and 18.7% C₂₀ and C₂₂ highly unsaturated acids.

(1) Organic Chemistry, Fieser and Fieser, page 340, D.C. Heath and Company, Boston, MA, 1944.

TABLE 4
MELTING POINTS OF STEARIC AND PALMITIC ACID ESTERS FROM
1986-86 HANDBOOK OF CHEMISTRY AND PHYSICS

Stearic Acid and Esters Methyl thru Butyl	Melting Temperature (°C)	Palmitic Acid and Esters Methyl thru Butyl	Melting Temperature (°C)
1. Stearic Acid	71.2	1. Palmitic Acid	63.0
2. Methyl Stearate	39.1	2. Methyl Palmitate	30.0
3. Ethyl Stearate	31.3	3. Ethyl Palmitate	α 24.0 β 19.0
4. Propyl Stearate	28.9	4. Propyl Palmitate	20.4
5. Isopropyl Sterate	28.0	5. Isopropyl Palmitate	13.4
6. N-Butyl Stearate	27.5	6. N-Butyl Palmitate	16.9

TABLE 5
SAMPLES FOR NEUTRON PRODUCTS GAMMA
IRRADIATION CROSSLINKING

I. <u>Irradiate to a Total Dose of 10 M-Rad in N₂</u>				Annealing Temp. (°C)
1.	870623-1	6"x6"x0.125"	Sheets, Crystalline Polypropylene	116
2.	870623-2	6"x6"x0.030"	Sheets, Crystalline Polypropylene	116
3.	870623-3	6"x6"x0.125"	Sheets, HDPE	85
4.	870623-5	6"x6"x0.030"	Sheets, HDPE	88
5.	870623-5	6"x6"x0.003"	Film, HDPE, Grocery Bag	86
6.	870623-6	6"x6"x0.125"	Sheets, LDPE	68
7.	870623-7	6"x6"x0.030"	Sheets, LDPE	68
8.	870623-8	6"x6"x0.004"	Film, LDPE	66
9.	870623-9	6"x6"x0.001"	Film, LDPE Dry Cleaners Garment Bag	67
10.	870623-10	6"x6"x ---	HDPE Fabric	100
11.	870623-10B	1 qt. Containers & Lids	HDPE "Flower Pots"	100
12.	870623-10A	1000 grams	Marlex TR-416 Black Pellets	---
II. <u>Irradiate to a Total Dose of 14 M-Rad in N₂</u>				
13.	870623-13		Marlex 6006 Pellets	---
III. <u>Irradiate to a Total Dose of 20 M-Rad in N₂</u>				
14.	870623-11	6"x6"x ---	HDPE Fabric	100
15.	870623-12	1000 grams	Marlex 6006 Powder	---

MONTHLY PROGRESS REPORT NO. 20
CONTRACT NO. DE-FG03-86SF16308
COVERING JANUARY AND FEBRUARY, 1988

1. BACKGROUND

During the last three years under the sponsorship of the DOE Solar Passive Division, the UDRI has investigated four (three organic and one inorganic) phase change material (PCM) systems for utility in thermal energy storage for solar passive heating and cooling applications. From this research, on the basis of cost, performance, containment, and environmental acceptability, we have selected as our current, and most promising series of candidate phase change materials, the C-15 to C-24 linear crystalline alkyl hydrocarbons. Ultra-pure C-16 to C-18 alkyl hydrocarbons (PCM) that melt and freeze sharply in the temperature range desired for solar passive applications are available from Humphrey Chemical at a premium price. These alkyl hydrocarbons have heats of fusion of 55-60 cal/gm, are self-nucleating, and exhibit little or no supercooling. However, crystalline paraffin waxes that can provide acceptable thermal energy storage are commercially available at much lower cost from several petroleum refining companies (Witco, Shell, Exxon, Union). These paraffins have melting points ranging from 15-80°C, and are available at a quoted price of \$0.15/lb to \$0.28/lb, for some grades, in tank-car quantities. The lower melting members of this family of commercial alkyl hydrocarbons have been evaluated "neat" and in "blends".

Containment costs and attendant problems have been the bane of many of the PCM systems developed in the past. During the past year, we have defined four economic and effective methods of packaging the candidate PCM materials in common construction materials. Importantly, the containment methods appear to also provide a means for adequate heat transfer; and the processes are of the type that could be rapidly implemented by commercial manufacturers of building materials.

The four processes are as follows:

1. Direct incorporation of PCM into the wet mix of building materials,
2. Direct incorporation into rubber or plastics medium for floor and wall tiles,
3. Indirect incorporation by first swelling the PCM into crosslinked polyethylene pellets or powder, which are then incorporated into building materials,
4. Direct incorporation by percolating the melted PCM into the open space in porous building materials.

As is well known, all organic PCM after ignition will continue to burn in a normal air atmosphere. In the processes where the PCM is completely encapsulated in a non-burning matrix of plaster or concrete (processes 1 and 3), the building material will not burn. However, in process No. 4, where the PCM is percolated into plasterboard (in high concentrations), the plasterboard after ignition will continue to burn slowly until the PCM is exhausted. In process 2, where the PCM is compounded into rubbers and plastics, the resulting composite will also burn; unless the polymer matrix is made fire retardant with effective additives.

We have preliminarily addressed the flammability problem in this otherwise attractive process by incorporating a state-of-the-art fire retardant system, consisting of chlorinated paraffin and antimony oxide, into the PCM to thereby render it self-extinguishing. However, there are difficulties in applying this technology effectively in process No. 4. Accordingly, more research on this specific process, and on the whole area of fire retardance is required. This will be a subject of major emphasis in the forthcoming year's work.

However, other areas will also be intensively investigated. We will complete laboratory tests of commercially available linear alkyl hydrocarbon PCM that can provide the most cost-effective performance for solar passive applications. We will complete extensive thermocycling tests of building panels containing PCM, and prepare model panels for tests by others. Finally, we plan to continue our efforts toward commercializing the results, through

further cooperation with major materials manufacturers, and aggressive marketing of the technology.

2. SUMMARY OF CURRENT RESEARCH

As noted in our last (December) Progress Report, the allocated funds for this program have been depleted. Accordingly, the results of work reported for January contains only the results of DSC tests on potentially fire retardant phase change materials that were already in progress, or completed.

During January and February, 1988, we completed the analysis by differential thermal scanning calorimetry of 1-bromooctadecane, and 1-bromohexadecane, obtained from Humphrey Chemical Company (at no charge).

The differential scanning calorimetry analyses were performed at two rates of heating and cooling ($10^{\circ}\text{C}/\text{min.}$ and $2^{\circ}\text{C}/\text{min.}$). The DSC data are summarized in Tables 1 and 2. Graphs of the DSC data are contained in Figures 1 to 4. Further, we plotted the DSC determined melting (T_m) and freezing (T_c) temperatures versus the rate of heating and cooling on semi-log graph paper in Figures 5 and 6. Thereby, we determined by extrapolation the rate of heating and cooling where the melting and freezing temperatures become congruent. From these data, we have drawn several tentative conclusions regarding the overall merit of these halogenated PCM for thermal energy storage in solar passive applications.

2.1 Fire Retardance

Because they contain about 21% bromine, these PCMs may be readily made fire retardant by the addition of antimony pentoxide. This hypothesis is, however, yet to be tested experimentally. The fact that the fire retardant and phase change materials are contained in the same molecule should be a decided advantage over the separate additive approach; since, we can be more confident that the concentration of the PCM and fire retardant are uniformly

distributed throughout the plasterboard, etc. This should also simplify the "percolation" process, since fewer components have to be monitored.

When additional funds become available, we plan to evaluate the fire retardance of plasterboard percolated with halogenated PCM. We also intend to obtain and test dibrominated octadecane and hexadecane from Humphrey Chemical Company.

2.2 Thermal Energy Storage Properties

The thermal energy storage, ΔH_m and ΔH_c of the two brominated alkyl hydrocarbons, as shown in Tables 1 and 2, is significantly lower than that of the corresponding unmodified octadecane and hexadecane by at least 20%. The heat of fusion, and crystallization of the two halogenated PCM (about 40 and 30 cal/gram, respectively) is still comparable to that of fatty acid ester or other competing phase change materials.

The difference in DSC determined melting and freezing temperatures (degree of supercooling) is also greater in the halogenated PCM than for the unmodified alkyl hydrocarbon PCM (at the same rate of heating and cooling).

Note also that the cooling curves in Figures 1 and 2, for 1-Bromo-octadecane show a pronounced double peak, indicating a second transition in the PCM. This phenomenon has heretofore only been observed in the even carbon atom alkyl hydrocarbons having 20 or more carbon atoms. The double peak in cooling is not present in the DSC curves for 1-bromohexadecane. This PCM shows a single transition in both heating and cooling that is especially narrow in the cooling phase (Figures 3 and 4).

We have plotted the melting and freezing temperatures of the 1-octadecane and 1-hexadecane versus the rate of heating and cooling of semi-log graph paper in Figures 5 and 6. The supercooling of 1-bromooctadecane at 10°C/min. is 14.66°C; and at 2°C/min. 10.63°C (Table 1). From the semi-log plot of Figure 5, the melting and freezing temperature would be expected to coincide at 0.04°C/min. rate of heating and cooling, at a temperature of

about 23°C (exactly in the range desired for solar passive applications).

We believe this new process of extrapolating to congruent melting and freezing on semi-log graphs provides a useful means of numerically comparing the supercooling tendencies of these and other PCMs.

2.3 Cost/Performance of the Halogenated Phase Change Materials

The selling price of the 1-bromooctadecane is very substantially higher than that of the Humphrey Technical Grade C-18 (\$3.10/lb. vs. \$0.85/lb.). Thus, one would need to carefully evaluate the cost/effectiveness of the halogenated PCM compared with the unmodified alkyl hydrocarbon PCM plus fire retardant additives.

Please remove and destroy the present page 8 from your copy of the December 1987 Progress Report, and insert the enclosed corrected page 8 in its place.

CONCLUSIONS

1. The concept of an inherently fire retardant PCM is certainly worth further study, in any continuing research to determine its cost/effectiveness.
2. The semi-log plots of melting and freezing temperatures versus the rate of heating and cooling appears to be a useful method of numerically evaluating the supercooling tendencies of candidate phase change materials.

IMMEDIATE FUTURE WORK

1. No further experimental work under this contract is possible until additional funding is provided.

esters melt and freeze at higher temperatures than the corresponding palmitate esters.

The mixed ester products sell in the U.S. for about \$0.70 per pound. The "pure" 90-95% distilled products sell here from about \$1.10 per pound.

In the U.S., the commercial (less pure) grades of alkyl hydrocarbons sell for prices well below those of the fatty acid esters. Witco 45-A was available for \$0.30/lb, and will store and release 43-50 cal/gm.

The Thermotop fatty acid esters, including 98.3% pure butyl palmitate (Thermotop 15), will store and release only about 26 cal/gm over the range of melting and freezing temperatures expected in the use of these PCMs.

The fatty acid esters are likely to hydrolyze during long-term exposure to moist ionized environment (as in plaster or concrete). Also, unlike the paraffinic hydrocarbons, the fatty acid esters do not offer a homologous series of materials that can store energy at a broad temperature range (-15 to +60°C vs. 16 to 39°C).

It is believed that the fatty acid esters can support growth of molds and other microorganisms.

Accordingly, it was concluded from the above considerations, that the fatty acid esters are less attractive than the alkyl hydrocarbon PCM from the standpoint of cost/performance, and other reasons as well.

3.3 Gamma Irradiation Crosslinking of Polyethylene and Polypropylene Products

We have developed an effective method of hardening the C-18 PCM in process No. 3, wherein the alkyl hydrocarbon PCM is permeated into small crosslinked pellets of HDPE at elevated temperature. Our experimental results have shown that the crosslinked HDPE can contain up to 80% wt. of C-18 or C-16 PCM and are stable to repeated thermocycling.

Sample: HUMPHREY 1-BROMOOCTADECANE
Size: 4.9980 mg
Method: DSC-LOW TEMP
Comment: 10°C/MIN

DSC

File: RUN1557.01
Operator: GALASKA
Run Date: 02/24/88 11:51

Figure 1. Analysis of Thermal Energy Storage Properties of I-Bromooctadecane at a Heating and Cooling Rate of 10°C/minute by Differential Scanning Calorimetry.

Sample: HUMPHREY 1-BROMOOCTADECANE
Size: 4.9960 mg
Method: DSC-LOW TEMP
Comment: 2°C/MIN

DSC

File: RUN1558.01
Operator: GALASKA
Run Date: 02/24/88 08:42

Figure 2. Analysis of Thermal Energy Storage Properties of I-Bromooctadecane at a Heating and Cooling Rate of 2°C/minute by Differential Scanning Calorimetry.

Sample: 1-BROMOHEXADECANE
Size: 4.2800 mg
Method: DSC-LOW TEMP
Comment: 10°C/min

DSC

File: RUN1526.01
Operator: GALASKA
Run Date: 02/09/88 09:41

Figure 3. Analysis of Thermal Energy Storage Properties of I-Bromohexadecane at a Heating and Cooling Rate of 10°C/minute, by Differential Scanning Calorimetry.

Sample: 1-BROMOHEXADECANE
Size: 4.2800 mg
Method: DSC-LOW TEMP
Comments: 2°C/min

DSC

File: RUN1527.01
Operator: GALASKA
Run Date: 02/09/88 10:52

Figure 4. Analysis of Thermal Energy Storage Properties of 1-Bromohexadecane at a Heating and Cooling Rate of 2°C/minute, by Differential Scanning Calorimetry.

Figure 5. Effect of Rate of Heating and Cooling on the Temperature of Melting and Freezing of 1-Bromooctadecane.

Figure 6. Effect of Rate of Heating and Cooling on the Temperature of Melting and Freezing of 1-Bromohexadecane.

TABLE 1

Differential Scanning Calorimeter Analysis of the
Thermal Energy Storage Properties of 1-Bromooctadecane
at 10 and 2°C/minute Scan Rate

Sample: 1-bromooctadecane

Disk:

Run No.: 10°C/min

File Name: RUN 1557.01

* Double Peak

Run No.	T _m (°C)	T _c (°C) *	T _m -T _c (°C)	Heat of Fusion		Heat of Recryst.	
				(J/g)	(cal/g)	(J/g)	(cal/g)
1	30.18	15.17	15.01	178.2	42.58	171.8	41.05
2	29.91	15.29	14.62	178.1	42.56	172.6	41.24
3	29.77	15.42	14.35	179.9	42.99	171.4	40.96
Ave	29.95	15.29	14.66	178.7	42.71	171.9	41.08

Sample: 1-bromooctadecane

Disk:

Run No.: 2°C/min

File Name: RUN 1556.01

* Double Peak

Run No.	T _m (°C)	T _c (°C) *	T _m -T _c (°C)	Heat of Fusion		Heat of Recryst.	
				(J/g)	(cal/g)	(J/g)	(cal/g)
1	27.87	17.23	10.64	173.1	41.36	172.5	41.22
2	27.80	17.16	10.64	177.5	42.41	172.6	41.24
3	27.93	17.32	10.61	177.1	42.32	172.3	41.17
Ave	27.87	17.24	10.63	175.9	42.03	172.5	41.21

TABLE 2

Differential Scanning Calorimetry Analysis of the
Thermal Energy Storage Properties of 1-Bromohexadecane at
10 and 2°C/minute Scan Rate

Sample: 1- bromohexadecane

Disk:

Run No.: 10°C/min

File Name: RUN 1526.01

Run No.	T _m (°C)	T _c (°C)	T _m -T _c (°C)	Heat of Fusion		Heat of Recryst.	
				(J/g)	(cal/g)	(J/g)	(cal/g)
1	19.08	4.10	14.98	153.7	37.68	151.2	36.13
2	19.17	4.49	14.68	153.4	36.65	150.0	35.84
3	18.75	3.09	15.66	151.3	36.15	151.1	36.11
Ave	19.00	3.89	15.11	152.8	36.83	150.8	36.03

Sample: 1- bromohexadecane

Disk:

Run No.: 2°C/min

File Name: RUN 1527.01

Run No.	T _m (°C)	T _c (°C)	T _m -T _c (°C)	Heat of Fusion		Heat of Recryst.	
				(J/g)	(cal/g)	(J/g)	(cal/g)
1	17.50	5.95	11.55	150.8	36.03	147.6	35.27
2	17.12	5.81	11.31	145.3	34.72	146.1	34.91
3	17.00	5.97	11.03	142.9	34.15	145.4	34.74
Ave	17.21	5.91	11.30	146.3	34.97	146.4	34.97

END

**DATE
FILMED**

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