**Phase Change Materials in Floor Tiles for Thermal Energy Storage**

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**ABSTRACT**

Passive solar systems integrated into residential structures significantly reduce heating energy consumption. Taking advantage of latent heat storage has further increased energy savings. This is accomplished by the incorporation of phase change materials into building materials used in passive applications. Trombe walls, ceilings and floors can all be enhanced with phase change materials. Increasing the thermal storage of floor tile by the addition of encapsulated paraffin wax is the proposed topic of research.

Latent heat storage of a phase change material (PCM) is obtained during a change in phase. Typical materials use the latent heat released when the material changes from a liquid to a solid. Paraffin wax and salt hydrates are examples of such materials. Other PCMs that have been recently investigated undergo a phase transition from one solid form to another. During this process they will release heat. These are known as solid-state phase change materials. All have large latent heats, which makes them ideal for passive solar applications. Easy incorporation into various building materials is must for these materials. This proposal will address the advantages and disadvantages of using these materials in floor tile.

Prototype tile will be made from a mixture of quartz, binder and phase change material. The thermal and structural properties of the prototype tiles will be tested fully. It is expected that with the addition of the phase change material the structural properties will be compromised to some extent. The ratio of phase change material in the tile will have to be varied to determine the best mixture to provide significant thermal storage, while maintaining structural properties that meet the industry standards for floor tile.

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## 1. INTRODUCTION

The use of solar energy to offset fuel consumption in commercial and residential buildings can be accomplished by implementing active or passive solar systems. Duffie and Beckman[14] give the following basic distinction of these two systems. Active solar systems include the use of collectors and storage systems that are not integrated with the building structure, while passive systems are integrated within the building structure. The proposed research is concerned with increasing the efficiency of passive solar applications by enhancing the thermal mass. Thermal storage capacity of floor tile will be increased with the addition of phase change materials.

Traditional passive design involves the addition of a sunspace to a structure. The purpose of this room is to store thermal energy and then subsequently release the energy to aid in the reduction of the heating load. Energy is gained directly from the sun through the glazing in the sunspace, with the majority entering through the south-facing windows. The south-facing wall should contain 0.19 to $0.38^{14}$ glazing area to floor area in order to maximize energy collected.

Floors and walls traditionally make up the thermal mass of a sunspace. Typically construction materials are concrete, masonry brick or dark clay tile. Thermal storage is usually accomplished by sensible heat storage. Heat is stored as the material temperature increases due to the solar energy entering the space. As a result, the space can easily become overheated. Solutions to prevent overheating can be accomplished in several ways. The south-facing glazing area can be decreased or an overhang can be placed over the south facing glazing to reduce the amount of direct sunlight entering the space during the summer months. Installation of fans for increased ventilation and circulation can also aid in reducing overheating. Another solution is to incorporate latent heat storage.

Heat is released during a change in phase of a material. All materials undergo phase transitions, thus have an associated latent heat. When a substance melts, vaporizes and sublimates, heat is absorbed. Heat is released when a material solidifies and condenses. During a change in phase, the temperature remains practically constant.

Since the temperature stays virtually constant during a change in phase, the temperatures of the thermal mass are lower. Lower temperatures mean less heat loss and a comfortable room temperature even during the summer months. It also results in a more consistent room temperature and reduction in overheating. Another advantage of latent heat storage is greater volumetric energy storage compared to sensible heat storage.

Phase change materials can be incorporated into building materials used in passive applications. Wood, gypsum board, lightweight concrete and floor and ceiling tile can all be enhanced with the addition of phase change materials. The ceiling, floor and walls are all large surface areas in a sunspace that are perfect candidates for latent heat storage.

## 2. EXECUTIVE SUMMARY

We refresh the reader by describing the technology that we hope to license to manufacturers of agglomerate floor tile.

One of the standard agglomerate floor tiles manufactured today consists of quart chips, quartz powder (filler), dyes, and a polyester binder. Components are mixed in what looks like a giant cement mixer. The mix, appearing and feeling much like damp sand, is placed in a vibrating vacuum assembly to remove all air and to compress the material. Next, the slabs of material are heated to cause catalysis. Later, slabs are cut and polished to produce the desired tiles.

Our proposal is to substitute micro encapsulated phase change material for much, if not all of the quartz power used in the recipe above. We may also be able to replace some of the chips without degrading the tile appearance. We will refer to this tile as PCM floor tile, hereinafter.

Putting phase change material in the floor tile dramatically increases its ability to store thermal energy. Also, the energy is stored at a nearly constant temperature. One application is the use of the tile in sunroom floors where it can absorb solar energy during the day and release it at night to reduce mechanical heating. The resultant reduced heating bills need to be sufficient to offset any additional first costs associated with the use of the phase change floor tiles.

Because agglomerate floor tiles have exceptional wear resistance properties, they are often marketed to institutional clients that have high traffic areas. Just as professional basketball teams may "have a foul to give," the residential applications we have in mind (sun rooms or other areas that receive direct sunlight) do not have the traffic of say, an airport concourse. Our challenge then is to maximize the amount of phase change material used in the floor tile without ruining the tile's physical properties. We have "wear properties to give" compared to agglomerate floor tiles because we expect the tiles to be used in less demanding applications.

To date, we have made floor tile samples that contain PCM as a substitute for the quartz filler. These tiles have structural properties that are not quite as good as agglomerate tiles without PCMs, but are significantly better than fired clay tiles often used in residential applications. We have explored variations in tile composition of the tile and how they affect tile structural properties. We have also made preliminary contact with prospective licensees and are participating in DOE's Commercialization Program.

## 3. PHASE CHANGE MATERIALS

All materials have an associated latent heat for each phase change, but only a few are appropriate for passive solar applications. They need to have a reversible transition, a high latent heat, and small changes in volume between phases and low vapor pressure. They must be chemically stable and good heat conductors. These properties also have to occur at the appropriate transition temperature. Depending on the passive application, the required transition temperature will vary. However, for a sunspace it needs to be approximately $27^{o}C(80^{o}F)$. The transition temperature is crucial to attaining the maximum heat storage during the day and maximum heat release at night.

During the heating season, the nights are longer than the daylight hours. The optimal transition temperature is one-third of the way between the lowest tolerable temperature and the highest tolerable temperature of the space.[38]

### 3.1 Phase Change Material Candidates

Traditional phase change materials that have been studied and used in applications are alkanes, paraffin waxes and salt hydrates. These materials undergo a reversible solid to liquid phase change at various transition temperatures. Studies have been performed for the feasibility of using solid-state phase change materials for latent heat storage. The biggest advantage the solid-state phase change materials have is no liquid phase to contain—the materials change from amorphous to crystalline phases while remaining "solid." Both paraffin wax and salt hydrates usually have to be encapsulated to contain the liquid phase, which adds to the final cost of the material.

Paraffin wax and salt hydrates have been successfully incorporated into building materials such as wallboard and concrete. A few products have been marketed commercially. Incorporation of solid-state phase change material in concrete has been accomplished in laboratory settings. Sheets of the solid-state phase change materials have also been used as flooring for a research simulation of the effect of latent heat storage in flooring.

The candidate building product that we are considering is floor tile. Phase change floor tile can be used in sun spaces to store energy from the sun during the day while releasing it during the night.

Salt hydrates are inorganic materials. Inorganic compounds have twice the volumetric latent energy storage compared to organic compounds. The organic compounds however, have the advantages of melting congruently, self-nucleation and are non-corrosive.[25] Salt hydrates will melt incongruently causing phase separation.

Naumann[37] reported that the incongruent melting behavior of Glauber salts results in two or three different solidification steps upon cooling below the melting temperature. This was observed at 20 degrees below the melting temperature. The application of nucleating agents reduced this effect to one degree.

### 3.2 Salt Hydrates

These materials were not considered a candidate for floor tile for several reasons. If a container is required to contain the liquid phase, metal containers cannot be used because the salt hydrates are corrosive. Crystallization of the salts can also lead to tears forming in polymer containers. They are also known to form partially hydrated or less soluble crystals due to the high rates of crystallization of the subcooled melts.[6] These less soluble crystals undergo phase transitions at much higher temperatures, thus lowering the thermal storage capabilities over time.

### 3.3 Solid-State Phase Change Materials

Materials that undergo an additional phase transition between the solid and liquid state belong to a group of solid-state phase change materials. A transition occurs from one solid state to another. This transition is associated with large latent heats of transformation. Additional advantages are, usage significantly below melting temperatures requiring very little or no

containment and easy incorporation in building materials.  There are two categories of solid-state phase change materials, layered perovskites and plastic crystals.

### 3.3.1  Layered Perovskites

Layered perovskites are chemical compounds with the general formula of:

$(n\text{-}C_n H_{2n+1} NH_3)_2 MCL_4$
      Where:
            M    =      is a divalent metal atom such as Mn, Cu, Hg or Fe.
            n    =      $8 \leq n \leq 18$

The structure is composed of regular alteration of inorganic and hydrocarbon regions.  Each inorganic layer is sandwiched between two hydrocarbon layers.  The hydrocarbon regions are composed of long chain alkylammonium groups ionicly bonded to the inorganic support.[9]  These linear alkyl chains are responsible for thermal behavior of the material.

At low temperatures the alkyl chains are in an ordered planar zigzag arrangement.  The chains are in a disordered state at high temperatures.  They exhibit "liquid-like" behavior in this state.  A liquid phase is not obtained at this point because the alkyl chains are fixed on one end to the inorganic layer, thus keeping its lattice structure.[9]

One advantage is that transition temperatures are dependent on alkyl chain length so control of transition temperatures can be accomplished.  Other advantages are a relatively high thermal conductivity and chemical stability at high temperatures.[8]  Disadvantages are possible toxicity, lower value of enthalpy per unit cost and the total latent heat is reduced due to the inorganic regions of the molecules that are inert.[9]

### 3.3.2  Plastic Crystals

NASA studied a group of solid-state materials during the 1970's for passive temperature control of earth satellites.[7]  Three materials were shown to be promising for passive applications: pentaerythritol (PE), pentaglycerine (PG) and neopentyl glycol (NPG).

These materials belong to a class of compounds called polyalcohols or polyols.  Each molecule has a central carbon atom with four attached carbon atoms forming a tetrahedron.  The number of hydroxyl groups attached to the four carbon atoms distinguished the three compounds from each other.[45]  Pentaerythritol is the largest molecule, the smallest is neopentyl glycol.  Molecular structures of these materials are presented in Appendix 1 in Figures 8-10.

The most stable form of these materials is a crystalline solid.  As heat is applied the material undergoes a transition to a plastic crystal.  This behavior comes from the tetrahedral molecular shape and the hydrogen resonant bonding that occurs between neighboring molecules.[6]  The substance will eventually melt as the temperature is further increased and will eventually turn into a gas.  It is the transition from crystalline solid to a plastic crystal that is of interest.

### 3.3.3  Background on Plastic Crystals

Plastic crystals are defined as a type of mesophase.  The term mesophase, shortened from mesomorphic, was introduced by Friedel in 1922.[23]  He defined it as a phase with microscopic structures between solids and ordinary isotropic liquids.  He stated that there were two distinct types of this phase, which he described as smectic and nematic.  Earlier, the term "liquid crystal" was used to describe both these phases.  Otto Lehmann coined the phrase "liquid crystal" in 1889.  The actual discovery of this phase is attributed to an Austrian botanist, Friedrich Reinitzed, in 1888.[23]  Friedel did not agree with the term "liquid crystal" which lead to his use of smectic and nematic to describe two types of this phase.

In 1935, Timmermans recognized a third type of mesophase, "plastic crystals".  Later, Wunderlich and Grebowitz further distinguished three types of mesophases referred to as liquid crystals, plastic crystals and condis.  Condis is often confused with liquid crystals since they are similar in nature.[8]  All three types exhibit some degree of long-range order similar to crystals.  They also show a degree of mobility other than segment vibrations, which is similar to isotropic liquids.[8] This is why the term "liquid crystal" was first used to describe this phase.

The difference between these three types of mesophases are the types of disordering they display.  Liquid crystals exhibit a positional disordering.  Plastic crystals show positional disordering but also display orientational disordering.  The final type, condis, displays conformational disordering as well as positional and orientational disordering.[8]  In positional disordering, the intermolecular distances become less uniform and the molecules can arrange themselves parallel, perpendicular or randomly.  Conformational disordering is the acquisition of freedom of executing rotations about single bonds.[35]

A further distinction between liquid and plastic crystals can been seen in Figure 1.  In this figure, the phases are given for liquid, plastic and ordinary crystals.  A typical crystal on increasing temperature will transform directly into the liquid state.  This is shown by Case II in Figure 1.  Both liquefaction and isotropy occur at the same temperature.  This is not true of plastic and liquid crystals.  Liquid crystals first undergo liquefaction then become isotropic.  The opposite is true of plastic crystals were isotropy occurs first.  Case I and III both show the behavior of liquid and plastic crystals respectively.  This figure was taken from Timmermans.[45]

### 3.4  Paraffin Wax

Normal paraffin waxes are part of a family of saturated hydrocarbons.  The structure is the type $C_nH_{2n+2}$. Those with carbon atoms between five and fifteen are liquids at room temperatures and are not considered.  Normal or straight chain and symmetrically branched chain paraffin waxes are the most stable.  Typically, paraffin waxes with odd numbers of carbon atoms are more widely used because they are more available, more economical and have higher heats of fusion.
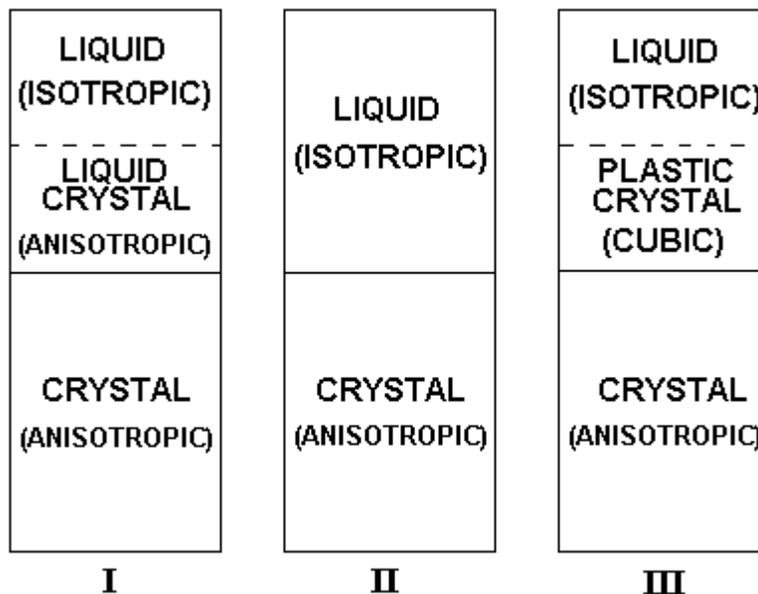
**Figure 1. Phase of a: I. liquid crystal  II.  typical crystal  III.  plastic crystal**

Paraffin waxes are composed mainly of alkanes, approximately 75%.[25] Alkanes and paraffin waxes are both organic compounds.  Paraffin can contain several alkanes resulting in a melting range rather than a melting point.  As the molecular weight increases, the melting point tends to increase as well.  Using different mixtures of alkanes, specific transition temperatures for paraffin waxes can be attained.  Paraffin waxes and alkanes at the transition temperature melt to a liquid and solidify upon cooling.  They do not have the containment problems of salt hydrates.  The only requirement is a flexible containment to allow for the small volume change from the melt.

The properties of normal paraffin wax are very suitable for latent heat storage.  They have a large heat of fusion per unit weight, non-corrosive, nontoxic, chemically inert and stable below $500^{\circ}$C $(932^{\circ}$F).  On melting, they have a low volume change and a low vapor pressure.  Mixing different molecular weight paraffin waxes together can easily vary melting temperature.  Since they are commercially available, the cost is reasonable.  Prime candidates for passive applications are tetradecane, hexadecane, octadecane and eicosane.  Paraffin wax, as well as solid-state phase change materials, has a low thermal conductivity.  However, the addition of additives such as graphite could increase the thermal conductivity.[6]

3.4.1 Outlast Technology

A Boulder, Colorado company, Outlast Technology, is incorporating encapsulated paraffin wax into fabric for outerwear using a technology originally developed for NASA.  The technology involves the microencapsulation of microscopic size droplets of paraffin wax.  These encapsulated particles of wax are then incorporated into fabrics and foams that are used for lining materials.

Outlast currently uses two grades of phase change materials in order to fit to different applications. One application is for cold weather/extremity wear designed to operate from 18.3$^{o}$C to 29.4$^{o}$C (65$^{o}$F to 85$^{o}$F). The other grade is used in four season applications designed to operate from 26.7$^{o}$C to 37.8$^{o}$C (80$^{o}$F to 100$^{o}$F).[33] The grades are composed of a mixture of paraffin waxes from a carbon count of 15 to 24. A mixture is used in order to cut production costs. Pure forms of paraffin waxes are significantly more expensive due to the refining processes involved. Capsules are on the order of 21μm. Using this process of microencapsulation and the appropriate mixture of paraffin, a suitable candidate can be found for the floor tile application.

## 4. EXPERIMENTS

### 4.1 Comparison of Thermal Properties of Phase Change Materials

Paraffin wax and solid-state phase change materials have transition temperatures and heats of fusion suitable for passive solar applications. A transition temperature around room temperature, 80$^{o}$F (27$^{o}$C) is ideal. Thermal properties of these materials are presented in Table 1.

**Table 1. Thermal Properties of Phase Change Materials**

| Material | Transition Temperature | Heat of Fusion | Density |
|---|---|---|---|
| **Solid-State PCM** | | | |
| Pentaerythritol (PE) | 370.4$^{o}$F (188$^{o}$C) | 269 J/g (115 Btu/lbm) | 1390 kg/m$^3$ (86.8 lb/ft$^3$) |
| Pentaglycerine (PG) | 192.2$^{o}$F (89$^{o}$C) | 139 J/g (59.8 Btu/lbm) | 1220 kg/m$^3$ (76.2 lb/ft$^3$) |
| Neopentyl Glycol (NPG) | 118.4$^{o}$F (48$^{o}$C) | 119 J/g (51.2 Btu/lbm) | 1060 kg/m$^3$ (66.2 lb/ft$^3$) |
| 60%NPG and 40%PG | 78.8$^{o}$F (26$^{o}$C) | 76 J/g (32.7 Btu/lbm) | 1124 kg/m$^3$ (70.2 lb/ft$^3$) |
| **Normal Paraffin** | | | |
| Tetradecane C$_{14}$ | 41.9$^{o}$F (5.5$^{o}$C) | 228 J/g (98 Btu/lbm) | 825 kg/m$^3$ (51.5 lb/ft$^3$) |
| Hexadecane C$_{16}$ | 62.1$^{o}$F (16.7$^{o}$C) | 237 J/g (102 Btu/lbm) | 835 kg/m$^3$ (52.1 lb/ft$^3$) |
| Octadecane C$_{18}$ | 82.4$^{o}$F (28.0$^{o}$C) | 244 J/g (105 Btu/lbm) | 814 kg/m$^3$ (50.8 lb/ft$^3$) |
| Eicosane C$_{20}$ | 98.1$^{o}$F (36.7$^{o}$C) | 244 J/g (105 Btu/lbm) | 856 kg/m$^3$ (53.4 lb/ft$^3$) |
| **Outlast** | | | |
| Kenwax 18 | 88.2$^{o}$F (31.2$^{o}$C) | 165 J/g (71 Btu/lbm) | 765 kg/m$^3$ (47.8 lb/ft$^3$) |
| Kenwax 19 | 98.24$^{o}$F (36.8$^{o}$C) | 151 J/g (65 Btu/lbm) | 811 kg/m$^3$ (50.6 lb/ft$^3$) |

The transition temperature of the solid-state phase change materials in the pure form is not low enough for use in passive applications. By mixing these compounds in various ratios, the transition temperature can be lowered. The ideal ratio was determined to be a mixture of 60% neopentyl glycol and 40% pentaglycerine. Both Benson[4,6] and Font[18] have presented this ratio in their research. It also has been repeated in the laboratory during early research for this project.

Benson[6] reported the number of intermolecular hydrogen bonds largely controls the amount of energy absorbed at transition. Altering the number of hydrogen bonds can have a significant effect on the energy absorbed and the transition temperature. This can be accomplished by mixing the pure forms of the solid-state materials with each other. The materials readily form binary mixture with each other either by dissolution in water or in their molten forms.

Pure octadecane is very close to the defined ideal passive temperature. Outlast uses mixtures of normal paraffin wax, Kenwax 18 and 19, for the phase change material. The paraffin content of these two mixtures is listed in Appendix 2. By mixing normal alkanes of different molecule weights, the melting or transition temperature can be altered from that of the pure form.

One obvious effect of mixing phase change materials is that the latent heat is lowered. The mixture of 60% NPG and 40% PG, as presented in Table 1, results in more than 50% decrease in the latent heat storage capabilities. Kenwax mixtures experience a decrease, although not as drastic. Outlast determined that the latent heat of a blend can be found from a linear equation, presented below:

Final Blend J/g = (wt.% $_{mPCM1}$ x J/g $_{mPCM1}$) + (wt.% $_{mPCM2}$ x J/g $_{mPCM2}$) + …

Studies performed by Benson[6] and Font[21] did not show a linear relationship between the molar percentage of neopentyl glycol and pentaglycerine, and latent heat. The latent heat decreases from the pure form of pentaglycerine as neopentyl glycol was added until the mixture contained 60% NPG. At that mixture, the latent heat, as well as the transition temperature, began to increase to the latent heat for the pure form of neopentyl glycol. Results of analysis done by Benson and Font are presented in Appendix 1.

Octadecane in its pure form has the highest heat of fusion with a transition temperature close to the ideal passive temperature. Its latent heat storage is more than three times greater than the NPG/PG mixture. Based on thermal storage capabilities, octadecane is the superior material, followed by the Kenwax 18.

## 4.2  Under Cooling Effects of Phase Change Materials

Paraffin wax and solid-state phase change materials show the behavior of under or super cooling. This behavior occurs when the material does not solidify at the same temperature at which it melted. Solid-state phase materials have shown more than a twenty-degree difference. The difference is not as noticeable in paraffin waxes.

Measurements have been made using a differential scanning calorimeter (DSC) to show the undercooking effect. The DSC is an apparatus that controls the cooling and heating of a

material. Materials were heated at $5^oC$ per minute beyond the transition temperature and then allowed to cool at the same rate. The difference between the transition temperature during heating and cooling is presented in Table 2. Measurements were taken for the solid-state phase change material by Benson, and Outlast took measurements for Kenwax 18 and 19.

Nucleating agents, such as powder graphite, can be also added to help further reduce under cooling. Benson[6] showed the addition of 0.1%-powdered graphite aided in the reduction of under cooling.

**Table 2. Under Cooling for DSC Measurements Taken at $5^oC$/min**

| Material | ΔT Between Heating and Cooling Transition Temperature |
|---|---|
| 60%NPG and 40%PG | 27.2 |
| Kenwax 18 | 8 |
| Kenwax 19 | 8 |

Studies by Yamagishi[48] presented the result of the use of derivatives of n-paraffin waxes to cancel under cooling effects. 1-Tetradecanol was selected as the nucleating agent for tetradecane. Results showed a 2% addition of the nucleating agent canceled the undercooking effects.

Further analysis by Yamagishi[48] found the size of an encapsulated particle of paraffin to affect the degree of under cooling. As the size of the particle is decreased the crystallization temperature decreases, thus increasing the degree of under cooling. This is due to the fact that as the size decreases, the number of nuclei to start crystallization in each particle decreases. Particles from the range of 100-to1000 μm show a constant difference of approximately $10^oC$ between melting and crystallization temperatures. However, particles in the range of 5 to 100 μm had a drop from a $10^oC$ difference to a more than $20^oC$ difference. Again the addition of nucleating agents can reduce this difference.

## 4.3 Potential Energy Storage Capabilities of Phase Change Materials

Based on the latent heat and the density of the phase change materials, the potential energy storage can be calculated. Assuming a floor tile composed of 100% phase change material, the energy storage per square area is presented in Table 3. Two common thicknesses of tiles were used for the analysis.

Results presented in Table 3 shows octadecane to have twice the potential energy storage of the solid-state phase change mixture. Kenwax 18 has one and one half times more potential energy storage over the solid-state mixture. As expected, the thicker tile has the greater heat storage and would be the best selection for the floor tile.

It should be mentioned that the potential energy storage of Kenwax and octadecane does not include the encapsulation material. The microencapsulation shell is approximately one micron

thick with the core taking 80-85% of the weight.[11] Results from Table 4 should be reduced to account for the encapsulation shell.

**Table 3.  Potential Energy Storage of 100% Phase Change Floor Tile**

| Material | ½" Floor Tile | ¾" Floor Tile |
|---|---|---|
| 60%NPG/ 40%PG | 1.08 MJ/m$^2$ (95.6 Btu/ft$^2$) | 1.63 MJ/m$^2$ (143.5 Btu/ft$^2$) |
| Kenwax 18 | 1.60 MJ/m$^2$ (141.4 Btu/ft$^2$) | 2.40 MJ/m$^2$ (212.1 Btu/ft$^2$) |
| Octadecane | 2.52 MJ/m$^2$ (222.3 Btu/ft$^2$) | 3.78 MJ/m$^2$ (333.4 Btu/ft$^2$) |

Table 4 shows the effect of an 80% to 85% reduction.  Octadecane still has a storage potential approximately twice as great as the solid-state phase change mixture.  The effect on the Kenwax 18 is more noticeable.  Its energy storage potential is still larger, but is more on the scale of the solid-state phase change mixture.  The preferred phase change material based on the potential energy storage is octadecane.

**Table 4. Potential Energy Storage Adjusting for Encapsulation Shell**

| Material | ½" Floor Tile | ¾" Floor Tile |
|---|---|---|
| Kenwax 18 | 1.28 - 1.36 MJ/m$^2$ | 1.92 – 2.04 MJ/m$^2$ |
| Octadecane | 2.02 – 2.14 MJ/m$^2$ | 3.02 – 3.21 MJ/m$^2$ |

Potential energy storage is a theoretical value and not obtainable in real floor tile.  It can be assumed that in an actual floor tile the phase change materials would only occupy, at best, 50% of the total tile.  The remainder of the tile is composed of the binder and agglomerate, such as quartz.  However, the optimum potential energy does provide a useful gauge in the benefit of using one type of phase change material over another.  Based on potential energy storage the phase change with the largest latent heat storage would be the best choice.

## 4.4  Binders

The focus of this research is to incorporate a phase change material into an agglomerate floor tile.  Prototype tiles will have three main components.  A binder, phase change material and a combination of quartz rock chips and quartz powder.  The quartz rock and powder are for strength and appearance.  The type of binder will depend on the phase change material used for the tile.

### 4.4.1  Binder for Solid-State Phase Change Materials

Initially unsaturated polyester, with styrene as a liquid monomer, was used as the binder. However, the tile mixture would not cure when the solid-state phase change material was added. It was assumed the phase change material was preventing the cure.

Polyesters use carboxylic acids and polyfunctional alcohols like neopentyl glycol, to impart flexibility, toughness and stain and chemical resistance.  Neopentyl glycol is often used in the polyester synthesis for improved stain and chemical resistance.  Propylene glycol is typically

used with the unsaturated monomer styrene. It is believed that with the addition of neopentyl glycol and pentaglycerine, cross-linking was being prevented.

Epoxies were then investigated as possible binders for solid-state phase change materials. An epoxy resin and curing agent produced by Shell Chemicals was the second binder tested. EPON 828 and curing agent 3140 was combined with the phase change materials and quartz. This mixture did cure to form a piece of prototype tile. The amount of phase change material was small, but DSC runs did show a phase transition at the appropriate transition temperature.

EPON 828 is an undiluted clear difunctional bisphenolA/epichlorohydrin derived liquid epoxy resin.[16] This material is cross-linked with an appropriate curing agent to form a material with good adhesive, mechanical, dielectric and chemical resistance properties. The curing agent 3140 is a low viscosity reactive polyamide and high imidazoline, which is based on dimerized fatty acid and polyamines.[15]

Solid-state phase change materials have also been shown to react adversely with the epoxy resin. The solid-state materials, NPG, PG, PE and the 60/40 NPG/PG mixture all have available hydroxyl groups to react with epoxy groups. The solid-state phase change material was causing the rate of cross-linking to increase by acting like a curing agent. This resulted in a decrease in the thermal storage capability of the phase change material, since some of phase change material was being used during the cure.

4.4.2  Binder for Paraffin Wax

It is expected that paraffin wax will not react adversely with epoxies or polyesters. The material used for the encapsulation is relatively inert. Encapsulation of melamine resin was determined by Yamagishi[48] not to react with the brine solutions $CaCl_2$, NaCl, glycol or silicon oil. Outlast Technology uses melamine-formaldehyde as the encapsulation material and found it was durable and did not react adversely with other materials.

Melamine-formaldehyde resin belongs to the family of thermosets. The high cross-linking nature of the cure product results in superior hardness, strength and rigidity. High chemical and abrasion resistance are other strong attributes of the material. It is widely used in decorative laminate such as Formica. The molecular structure is given in Appendix 3. Sites can remain active if cross-linking is not complete, which may react with the tile binder. However it is not seen as a risk, as the encapsulation process is expected to be a complete cure.

4.5  Cost Analysis of Components

An area for concern is the final cost of the floor tile. The type of binder and phase change material used effects final costs. It is assumed that the amount of quartz rock and powder would be the same regardless of binder and phase change material used. The type of binder will depend on the phase change material selected. Solid-state phase change material requires an epoxy to be used, while polyesters can be used with encapsulated paraffin particles. Table 5 shows that the costs of general-purpose polyesters are half the cost of epoxies.

**Table 5. Binder Approximate Costs**

| Binder | Price |
|---|---|
| **Epoxy** | |
| Basic grades | $1.30 to $1.50 / lb |
| Specialty grades | $2.00 to $4.00 / lb |
| Shell EPI_CURe 3140 | $1.65 / lb |
| Shell EPI-CURe 3234 | $1.65 / lb |
| Shell Resin 828 | $1.65 / lb |
| **Polyesters** | |
| General purpose | $0.65 to $0.70 / lb |
| Ashland chlorendic polyester HETRON 197-3 | $1.81 / lb |
| Ashland isophthalic polyester AROPOL 7241 | $1.44 / lb |

Bulk costs of the phase change materials depend on the current commercial use of the materials. Neopentyl glycol is used in paint and resin production, which reduces the cost of the raw product. However pentaglycerine is not as widely used and will increase the final cost of the solid-state phase change mixture significantly.

Paraffin waxes are widely used in many different applications and can be obtained in many different grades. The level of processing assigns grades. A pure form of octadecane, 99%, is more expensive than the 97% form. Kenwax used by Outlast is a mixture of paraffin waxes and does not undergo as much refinement, so the cost is even less. However a decrease in the latent heat storage is accompanied with the use of unrefined paraffin, as values in Table 1 show.

Encapsulation processing for the paraffin wax makes up most of the final costs as seen in Table 6. The table also shows the bulk costs of the raw phase change materials.

**Table 6. Final and Bulk Cost of Phase Change Materials**

| Material | Price |
|---|---|
| **Solid-State Phase Change Materials** | |
| Eastman NPG | $0.74 / lb |
| Eastman NPG-90 | $0.67 / lb |
| PG | $9 - $12 /lb |
| **Paraffin Wax** | |
| Outlast Kenwax 18 and Kenwax 19 | $0.59/lb |
| Technical Grade Octadecane (~95%) | $2.71/lb |
| **Encapsulation Final Costs** | |
| Outlast Kenwax 18 and Kenwax 19 | $8.60/lb |
| Technical Grade Octadecane (~95%) | $11.13/lb |

The final costs of the encapsulated paraffin and solid-state material are not very different. In order to obtain the 60% NPG and 40% PG mixture, a processing step to combine the raw materials needs to be included in the final cost. This added cost is not reflected in Table 6. The

final cost would still be expected to be on the same order of the encapsulated paraffin. It is expected cost would be drastically reduced on a large-scale production for both materials.

An advantage paraffin wax has over the solid-state material is in the choice of binder. Encapsulated paraffin wax can be bonded with quartz chips using a polyester resin, which significantly reduces the overall cost of the floor tile. Solid-state materials have to use an epoxy for the binder, which is twice the cost of polyesters.

## 4.6 Structural Integrity of Encapsulated Particles

Structural integrity is a concern for encapsulated particles. Polyesters often involve an exothermic cure, which could possibly reach temperatures high enough to degrade the encapsulation. Encapsulated particles used by Outlast were tested by thermogravimetry analysis to $300^{o}C$ without any noticeable damage.

Thermal stability of melamine resin has been shown to be dependent on the curing time and on several pyrolysis steps. Mass lost during thermogravimetry analysis became smaller with increased curing times.[27] Heat resistance is expected to be enough to tolerate the curing temperatures of the polyester.

Encapsulated wax particles of a diameter of 5 μm were subjected to the thermal cycling tests by Yamagishi.[48] Tests were performed for a temperature range to allow melting and solidification. After 5000 cycles, the particles examined under a microscope showed no damage.

Another concern is any damage that may result from the procedure to manufacture the tile. Currently, the manufacturing process for agglomerate tile using polyester as a binder is accomplished by mixing the components in a concrete mixer. The mixture is then agitated under a vacuum to remove air bubbles. It is then heated to induce the curing process. Agitation is not seen as a risk, but the batch mixing could possibly cause damage. However, the size of the encapsulated particles compared to the quartz chips is significantly smaller, so damage is expected to be minimal if any at all. Quartz chips are on the order of several centimeters.

Yamagishi[48] performed tests on the structural stability of an encapsulated paraffin particle, similar to the particles used in the Outlast technology. Encapsulated wax in a brine slurry as a heat transfer fluid was the focus of the research. The slurry was circulated using a pump system. Breakage rate was found to increase with increasing circulation times. It was found that the structural stability of the particle depended on the diameter of the particle. Smaller particles withstood pressures of a slurry flow and pressure from volumetric expansion. Volumetric expansion was not a problem due to the flexibility of the shell.

A particle will be broken when the external pressure equals the internal pressure. The internal pressure in a spherical microencapsulated particle was defined by Yamagishi[48] to be related to the wall tension, thickness and particle diameter.

$$P = 4 \, \sigma \, t \, / d$$

Where:

| | | |
|---|---|---|
| $\sigma$ | = | tension of the microencapsulated particle |
| t | = | wall thickness |
| d | = | diameter |

The particles were also subjected to agitation from a magnetic stirrer. It was found that the agitation did not damage particles from the size of 5 to 1000 μm.[48]

Research performed by Roy[40] found that the structural strength of particles of wax encapsulated with polyvinyl alcohol was dependent on the wall thickness. Particles with a wall thickness comprising 30% of the total particle volume withstood thermal cycling better than particles with a 15% wall thickness. Particles used by Yamagishi had wall material comprising 14 to 20% of the total volume. Outlast particles are 20% wall material. The encapsulation material used by both Yamagishi and Outlast is melamine resin, which is more durable than polyvinyl alcohol.

Outlast uses the encapsulated particles in phase change fabrics for thermal comfort outdoor wear. Foams are soaked with a solution of the particles. The particles have to be durable enough for wear and washing in a machine. A concern expressed by Outlast is that high shear stress may cause damage to the particle. The tile manufacturing process is not expected to exert high shear stress on the particles.

## 4.7  Final Material Selection

### 4.7.1  Phase Change Material

Encapsulated octadecane has been selected as the phase change material. The material will be supplied by Outlast.

This decision was based on the thermal properties. Octadecane has more than twice the latent heat storage of the 60%NPG/40%PG mixture. Under cooling effects are significantly less for octadecane. Currently, the cost of the encapsulated material is the largest drawback of the octadecane. This cost, however, is expected to decrease with large-scale production.

By selecting encapsulated octadecane, polyester may be used as the binder. Polyester is typically more than half the cost of epoxies. The encapsulated material should not react adversely with the binder, as the solid-state phase change material.

### 4.7.2  Binder

Since encapsulated octadecane was selected for the phase change material, a polyester binder can be used. The polyester resin selected is a styrene-based resin that is used by Granirex. It requires heating to $80^{\circ}$C to initiate the curing process. A curing agent is also used to aid the curing process.

Room temperature and UV cured resins were researched as a possible replacement. The UV cured resins typically are used for coatings and do not possess the mechanical strength required for a floor tile application. Suitable room temperature cured resins were not found.

A polyester resin was experimented with that would gel at room temperature, but was still required to be heated in order to reach full strength. The resin was supplied by Granirex.

## 4.8 Potential Energy Saving Analysis

Potential energy storage of encapsulated paraffin wax and solid-state phase change materials have been calculated and presented in Table 3.

### 4.8.1 Expected Solar Gain

Phase change enhanced floor tile is to be used in a sunspace as additional thermal storage. The sunspace is assumed to have the appropriate amount of south facing glazing for the maximum solar gain during the winter months. Assuming Denver, Colorado as the location, the monthly-absorbed radiation can be determined from the following equation.

$$\overline{S} = \overline{H}_b \overline{R}_b (\overline{\tau\alpha})_b + \overline{H}_d (\overline{\tau\alpha})_d \left(\frac{1+\cos\beta}{2}\right) + \overline{H}\rho_g (\overline{\tau\alpha})_g \left(\frac{1-\cos\beta}{2}\right)$$

Where:

$\overline{H}_b$ = monthly average daily beam radiation on a horizontal surface

$\overline{H}_d$ = monthly average daily diffuse radiation on a horizontal surface

$\overline{H}$ = monthly average daily radiation on a horizontal surface

$(\overline{\tau\alpha})$ = average transmittance-absorptance for beam (b), diffuse (d) and ground (g)

$\overline{R}_b$ = monthly average ratio of beam radiation on a tilted plane to that on the plane of measurement (usually horizontal)

$\rho_g$ = ground reflectance

$\beta$ = collector slope

The collector slope of the south facing glazing has an orientation of 90°. Ground reflectance was assumed to be 0.3 for each month. Monthly average daily radiation was obtained from weather data for Denver. Remaining values were calculated using equations from Duffie and Beckman.[14] Results are presented in Table 7.

Total monthly radiation incident on the windows of the sunspace, $\overline{H}_T$, was also calculated and presented in Table 7. The percentage of the total radiation absorbed into the sunspace is presented in the last column of Table 7. Calculations were done assuming there was no overhang above the south facing glazing to shade during the summer. As a result, the absorbed radiation during the summer months is higher than a typical sunspace with appropriate shading.

Based on the results for the heating months, September through April, the average percentage of solar radiation that will be absorbed into the sunspace is 70%.

**Table 7. Estimated Monthly Absorbed Solar Radition per Area of South Glazing**

| Month | $\overline{H}$ [MJ/m$^2$] | $\overline{H}_d$ [MJ/m$^2$] | $\overline{H}_b$ [MJ/m$^2$] | $\overline{H}_T$ [MJ/m$^2$] | $\overline{S}$ [MJ/m$^2$] | $\overline{(\tau\alpha)}$ |
|---|---|---|---|---|---|---|
| Jan | 9.54 | 2.72 | 6.82 | 18.59 | 14.27 | 0.77 |
| Feb | 12.79 | 3.64 | 9.15 | 18.35 | 13.45 | 0.73 |
| Mar | 17.37 | 4.80 | 12.57 | 17.01 | 11.96 | 0.70 |
| Apr | 21.33 | 6.07 | 15.26 | 13.63 | 8.81 | 0.65 |
| May | 24.24 | 7.10 | 17.14 | 11.49 | 7.10 | 0.62 |
| Jun | 26.68 | 7.16 | 19.52 | 10.94 | 6.57 | 0.60 |
| Jul | 25.8 | 7.13 | 18.67 | 11.27 | 6.72 | 0.60 |
| Aug | 23.21 | 6.42 | 16.79 | 12.93 | 8.14 | 0.63 |
| Sep | 19.6 | 5.10 | 14.50 | 16.25 | 11.01 | 0.68 |
| Oct | 14.77 | 3.84 | 10.93 | 19.02 | 13.80 | 0.73 |
| Nov | 10.03 | 2.94 | 7.09 | 17.89 | 13.43 | 0.75 |
| Dec | 8.3 | 2.50 | 5.80 | 17.39 | 13.50 | 0.78 |

In order to verify there will be enough radiation absorbed to fully charge the floor tile, the results from Table 7 and Table 4 have to be multiplied by the appropriate areas. Results from Table 3 and Table 4 are per unit area of the floor, while results from Table 7 are per unit area of south facing glazing. A floor area of 346.5 ft$^2$ and a glazing area of 352 ft$^2$ were chosen. Based on the results from Table 8 and Table 9 there is enough absorbed energy per day to fully charge the floor tiles containing either phase change material at both tile thicknesses.

**Table 8. Potential Energy Storage for a Floor Area of 346.5 ft$^2$**

| Material | Daily Energy Storage ½" Floor Tile [MJ] | Daily Energy Storage ¾" Floor Tile [MJ] |
|---|---|---|
| 60%NPG/ 40%PG | 34.8 | 52.5 |
| Kenwax 18 | 41.2 – 43.8 | 61.8 – 65.7 |
| Octadecane | 65.0 – 68.9 | 97.2 – 103.3 |

4.8.2  Solar Load Ratio Calculation

It has been determined that there is enough absorbed solar radiation daily to fully charge phase change materials in floor tile. The next step is to determine the potential savings that can be achieved with the addition of phase change materials to floor tiles. An empirical method for estimating the monthly solar and auxiliary energy requirements for passive systems, called the solar load ratio (SLR), was used for a rough estimate. The monthly solar load ratio is a dimensionless parameter defined as:

$$SLR = \frac{\text{solar energy absorbed per month}}{\text{building heating load per month}}$$

**Table 9. Absorbed Average Daily Radiation through South Glazing of Area 352 ft$^2$**

| Month | Absorbed Solar Radiation [MJ] |
|-------|-------------------------------|
| Jan | 466.7 |
| Feb | 439.9 |
| Mar | 391.1 |
| Apr | 288.2 |
| May | 232.1 |
| Jun | 215.0 |
| Jul | 219.8 |
| Aug | 266.2 |
| Sep | 360.1 |
| Oct | 451.2 |
| Nov | 439.1 |
| Dec | 441.4 |

A parameter correlated to the SLR is the solar savings fraction (SSF). It is defined as the following.

$$SSF = \frac{\text{solar saving}}{\text{net reference load}}$$

The net reference load is the heat loss from the non-solar parts of a building. This includes walls, floors, ceilings and the roof of everything but the sunspace. Solar savings is the difference between the net reference load and the auxiliary heat required by the building.

Net reference load = (NLC) (DD)
Solar Savings = Net Reference Load - Auxiliary Heating Load

Where:
$\quad$ NLC $\quad = \quad$ net load coefficient
$\quad$ DD $\quad = \quad$ monthly degree day

The net load coefficient is found by summation of the load coefficient of each building element. Load coefficient is the overall heat transfer coefficient, times the area of the element. The following definition of NLC was used for this analysis.

NLC = 24 [ $(UA)_{wall}$ + $(UA)_{roof}$ + $(UA)_{glazing}$ + $(UA)_{perimeter}$ + $(UA)_{infiltration}$ ]

Where:
$\quad$ $(UA)_{wall}$ $\quad = \quad$ $(A_{wall}/R_{wall})$

$$(UA)_{roof} = (A_{roof}/R_{roof})$$
$$(UA)_{glazing} = (1.1 \times (A_{glazing}/\text{Number of glazing}))$$
$$(UA)_{inflitraion} = (0.018)(ACH)(ADR)(\text{Volume of building})$$

| | | |
|---|---|---|
| R | = | Resistance of element |
| ACH | = | Air changes per hour |
| ADR | = | Air density ratio |

Glazing losses were only considered for the east, west and north facing windows. ADR is dependent on the elevation of the site. For a building in Denver, Colorado the value is 0.83. ACH is determined from the design criteria and chosen to be 0.28. Resistance values can be found from ASHRAE.[50]

**Table 10. Coefficients used for NLC Calculation**

| Building Element | (UA) [W / K] |
|---|---|
| Walls | 30.7 |
| Roof | 24.8 |
| E,W,N Windows | 2.9 |
| Floor Perimeter | 22.3 |
| Infiltration | 27.4 |

From the solar savings fraction the auxiliary heat required and the solar savings for the building can be calculated by the following equations.

$$\text{Auxiliary heat} = (NLC)(DD)(1\text{-SSF})$$
$$\text{Solar savings} = (NLC)(DD)(SSF)$$

Parameters to determine the above variables have been defined for several reference designs. In the early eighties, Los Alamos National Laboratories developed reference designs representing direct gain, trombe walls and sunspace passive systems. A reference design that simulates a passive system with an attached sunspace was chosen for this analysis. Balcomb[2] gives parameters for several different reference designs. A summary of the major dimensions of the building is given in Table 11.

The building's heating load was determined by calculating the expected heat loss through the walls, roof, windows, perimeter and infiltration. Standard values for insulation and infiltration were used, as defined by ASHRAE.[50] Sunspace losses are not considered in this calculation. Losses from the sunspace are considered in the correlation for the specific reference design. Balcomb[2] has reported these values for the reference designs.

**Table 11. Dimensions of Passive Reference Design**

| Parameter | Dimension |
|---|---|
| Total Volume of Building | 1240 ft$^2$ |
| Projected area of solar gain | 270 ft$^2$ |
| Sunspace floor area | 346.5 ft$^2$ |
| South Facing Glazing Area | 352 ft$^2$ |

Calculations were performed in a spreadsheet. Solar savings were first calculated for the reference design without any phase change storage. Latent heat storage was included in the calculation by assuming the heat gained would reduce the heat losses from the building. Increases in solar savings due to the addition of phase change materials are presented in Table 12. These increases are in addition to savings attained by passive heat gains without latent heat storage.

**Table 12. Increase in Solar Savings from Basic Reference Design**

| Phase Change Material | ½" Floor Tile | ¾" Floor Tile |
|---|---|---|
| 60%NPG/ 40%PG | 8.5% | 12.0% |
| Kenwax 18 | 11.9% | 16.7% |
| Octadecane | 17.3% | 23.9% |

Based on the results in Table 12, the addition of latent heat storage does make an impact on the heating load. As expected, octadecane has the largest increase in savings. Again the calculations did not include the volume taken by the encapsulation. If the encapsulation material is included, results of the Kenwax 18 and octadecane would have to be decreased from 85% to 80%.

The solar load ratio is a widely used method since it can be performed either with hand analysis or simple spreadsheets. Calculations are simplified by the use of reference designs. Annual results have been reported by Duffie and Beckman[14] to be within 3-4% of more detailed simulations.

4.8.2.1 Possible Annual Savings

Actual effects of the savings are dependent on the annual heating loads and costs. The size of the load determines the amount of impact a 10% increase in energy savings has on the annual heating bill. Lower fuel costs would not see as large as savings as high fuel costs. An analysis was performed assuming a heating and annual heating load of 50 MBtu at a heating cost of $11.6/MBtu. Results are presented in Table 13.

It should be noted that the annual heating cost savings presented in Table 13 are only the savings for adding latent heat storage. Passive savings gained from sensible heat storage have not been included. The savings, of course, would increase as the heating load increases and as the cost of fuel increases.

**Table 13. Annual Heating Cost Savings**

| Phase Change Material | ½" Floor Tile | ¾" Floor Tile |
|---|---|---|
| 60%NPG/ 40%PG | $49.30 | $69.60 |
| Kenwax 18 | $69.02 | $96.86 |
| Octadecane | $100.34 | $138.62 |

4.8.3 Future Simulations

The solar load ratio calculation provided a good estimate of possible savings by the addition of phase change materials in passive applications. However it does not fully show the effect of latent heat storage in the floor. It is also a static calculation, where a dynamic simulation would fully represent the latent heat storage in the floor.

An hourly energy analysis program, the Building Loads Analysis and System Thermodynamics (BLAST) program, can be used for a dynamic simulation. The program has the ability of simulating heat transfer and thermodynamics in buildings to characterize the possible energy savings of using phase change floor tile. BLAST does not explicitly simulate phase change in building materials such as walls and floor, however specifying layers of high thermal capacitance can mimic it. Initial simulations have not produced the result expected. Further investigation into the behavior of the simulation code is required.

Another thermal analysis code, SUNREL, developed by the National Renewable Energy Laboratory (NREL), simulates phase change in materials. Simulations need to be performed with the code and compared to the SLR method. Early simulations have yet to produce reliable results.

## 4.9  Tile Mixture

The original recipe supplied from Granirex serves as a base for the prototype tile mixture. It is composed of seven ingredients. A catalyst and wetting agent, silane, are added to the resin before the other components. The catalyst is 2% the weight of the resin and the silane is 1% of the weight. Table 14 lists the proportions of the components. The pigment used is carbon black.

**Table 14. Granirex Recipe Proportions**

| Component | Density [g/cm$^3$] | Mass Fraction F |
|---|---|---|
| Quartz Chips, Mesh 6 (q-6) | 2.65 | 0.05 |
| Quartz Chips, Mesh 10 (q-10) | 2.65 | 0.06 |
| Quartz Chips, Mesh 34 (q-34) | 2.65 | 0.43 |
| Quartz Chips, Mesh 84 (q-84) | 2.65 | 0.13 |
| Quartz Powder, Mesh 325 (pow) | 2.65 | 0.24 |
| Resin | 1.094 | 0.08 |
| Pigment | 1.75 | 0.002 |

4.9.1  Varying Binder Proportions

We expected that the mixture of resin and quartz would be the consistency of wet sand before it was molded and cured. When a mixture was prepared following original recipe, the mixture was dry. It was quite obvious that there was not enough resin in the mixture. A press was used to compress the mixture in the tile mold. Approximately 500-1000 psi was applied. Since there was not enough resin, the compaction was not sufficient. As can be seen in Figure 2, the surface is not smooth and there are visible gaps.
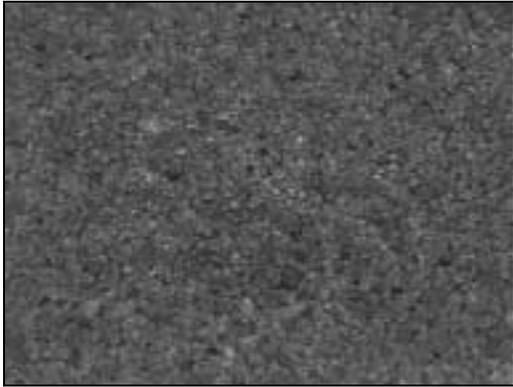
**Figure 2. Sample tile with resin mass fraction of 8% (No phase change material)**

By increasing the resin mass fraction from 8% to 12% a mixture with the consistency of wet sand was achieved. The resulting cured surface is smooth and there are no visible gaps, as shown in Figure 3.



**Figure 3. Sample tile with resin mass fraction of 12% (No phase change material)**

The integrity of the cured tile from Figure 2 was not good. Edges of the tile crumbled easily under light pressure and the components were not compactly compressed. A quick compression test resulted in the sample crumbling apart under less than 1000 psi of pressure. The tile sample from Figure 3 had strong edges that did not crumble.

4.9.2  Addition of Phase Change Material

Encapsulated octadecane will be added to the tile mixture by replacing the quartz powder. Powder is mainly used as filler so it can be replaced by another material, namely the phase change material. The main goal is to add the phase change material without adversely affecting the physical properties of the tile.
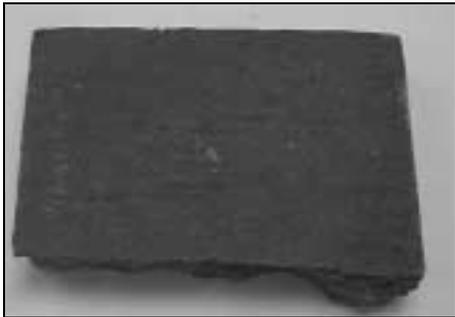
In order to maximize the amount of phase change material, another component will have to be replaced in addition to the powder. The q-34 chips will be replaced until the structural integrity of the tile decreases beyond acceptable limits.

Samples have been made that replaced 100% of the powder that resulted in a successful cure. However, as with the first samples made with the powder, the resin amount was not enough to bind the components together properly. Edges crumbled easily and it withstood less than 1000 psi in compressive pressure before crumbling apart. Another problem was encountered with the addition of the phase change material. The phase change material tended to clump together in small balls approximately 1/16" in diameter. Several different ways of treating the phase change material were tried. First the material was dried in a dissector with no added benefit. The material was then mixed with the resin before the quartz was added. This helped, but clumps still formed. In Figure 4 the white dots are the clumps of phase change material.
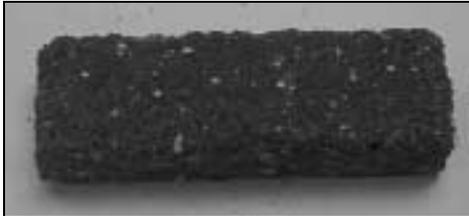


**Figure 4. Sample tile with phase change material incorporated with visible clumps.**

By running the mixer at a higher speed, the material was fully incorporated. The material was not dried in a dissector. Figure 5 shows the difference in the surfaces. There are no visible phase change material clumps.



**Figure 5. Sample time with phase change material incorporated without visible clumps.**

**4.10 Prototype Testing Research**

Prototype testing has been separated into two categories, physical and thermal. Physical testing is important to ensure that the tile is comparable to commercially available agglomerate floor tile. Thermal analysis will be done to determine the heat storage capability of the tile and to verify that transition occurs within the appropriate temperature range. The final prototype tile is not expected to have the highest thermal storage or maximum physical strength, but rather be in the middle range of thermal and physical properties.

4.10.1 Physical Testing

Prototype tiles will be subjected to physical testing typical of commercially available agglomerate floor tile. Tests performed by three manufacturers of an agglomerate floor tile

composed of quartz chips and a polyester resin are listed in Appendix 4.  Each test performed by the manufacturer is marked.  Physical tests will be selected from this list.

There is overlap in the majority of the tests performed for each type of floor tile which identifies an industry standard.  The tests performed by Granirex are of the most importance since the recipe for the prototype tile is based on the Granirex recipe.  A list of the seven tests that have been selected for this project are listed in Table 15.

**Table 15. Selected Physical Tests**

| Test |
| --- |
| ASTM C-170 Compressive strength |
| Impact Resistance |
| ASTM C-97 Absorption and bulk specific gravity |
| ASTM C-880 Flexural Strength |
| ASTM C-484 Thermal Shock |
| ASTM C-241 Abrasion Resistance |
| Morphology |

These tests were selected based on the importance of the test to show the physical strength of the tile.  Tests for tile that may be used outdoors were eliminated, such as the freeze thaw and resistance to de-icing chemicals tests.  It is expected that the phase change tile will be for strictly for indoor usage.  Other tests such as smoke density and flame spread were eliminated because they were not physical strength tests. The tests are also complex and involved and it was felt that they are unnecessary to perform at this time.

All prototype tiles will undergo acclimation before any testing is performed.  Tiles will be held at a set temperature for a specified amount of time.  Humidity will not be controlled.  It will be assumed no change within the time testing will occur.  Results from the tests will be compared to the results obtained from Granirex, and to a standard tested along with the prototypes.  The standard will be a piece of floor tile obtained from Granirex.

4.10.1.1  Initial Testing

The listed tests in Table 15 do not have to be performed on each prototype tile.  This would be time consuming and a needless use of materials.  Results from a select group of tests will be significant to eliminate a majority of the prototype tiles.  Once the first elimination is made, the remaining tests can be performed.  Two tests have been selected for the initial round of testing.  These are compressive strength and 3-point flexural tests. They were selected based on the information they would provide on the strength of the tile and the ease of performing the test.

A morphology analysis will also be performed on a tile with and without phase change material. This is important to fully understand the behavior of dispersion of the phase change material through the mixture.  It will also help to verify whether or not the phase change material is clumping together.

4.10.2  Thermal Testing

Testing performed with a differential scanning calorimeter (DSC) requires samples in the order of milligrams.  These can be obtained either by drilling samples from prototype tiles that have cured, or allowing samples to cure in the pans used for DSC analysis.  Both procedures involve inconstancies and are dependent on the homogeneity of the batch.  Samples can be taken from regions with very little phase change material, showing results that may not be accurate. However multiple samples from a batch should help to eliminate some of the uncertainty.

Another possible testing technique would be to test the entire prototype tile. This requires an apparatus that is capable of providing a constant heat flux.  The temperature can then be monitored throughout the temperature range watching for indication of a phase change.

Test samples will be batches cured in the sample DSC pan.  At least five DSC samples will be made from each batch.   More extensive thermal testing can be performed after the first elimination.  This would involve testing an entire tile.  If this procedure does not give reliable results, samples will be taken from the prototype tiles.

## 5.  PROTOTYPE MANUFACTURE

Prototype tiles have been manufactured with varying amounts of resin and phase change materials.  All tiles are made with a four-inch square mold shown in Figure 6.  The mixture is added to the mold and pressed under 500-1000 psi of pressure.  Figure 7 shows the mold in the press.  While the mixture is still in the mold it is heated to approximately $85^{o}C$ for twenty minutes.  After twenty minutes the tile is removed and the curing process is finished in an oven set to $100^{o}C$ for approximately four hours.  This second cure in the oven is done to ensure that all the resin has cured.  One method of determining this state is the lack of polyester odor from the tile.
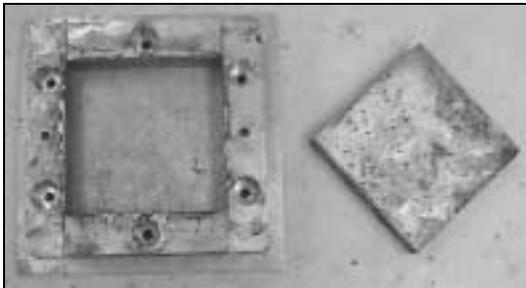


**Figure 6.  4" Tile Mold**

The tile mixture is combined together in a kitchen mixer.  Catalyst and the wetting agent are added to the resin and these are mixed for 30 seconds.  Quartz chips are then added and mixed for another minute.  Next, quartz powder is incorporated into the mixture slowly.  Once all the powder is added to the mixture it is mixed for another two minutes.  Tiles have completed the curing process after resting for 24 hours at room temperature after curing in the oven.  At this point the tiles can be cut in the appropriate sizes for testing.  A wet-saw with a diamond blade is used to cut the tiles.
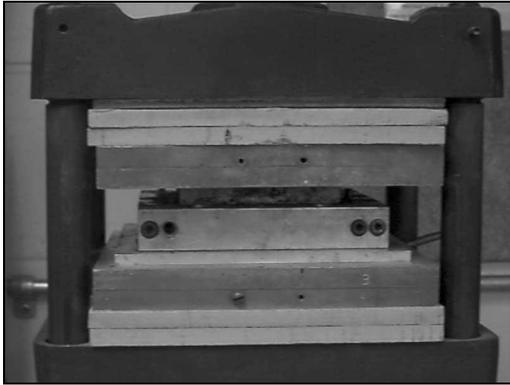
**Figure 7.  Tile mold in the press.**

## 6.  RESULTS AND DISCUSSION

Performance of the tiles will be based on the results of both physical and thermal tests.  Physical tests are important in order to have a comparison to like tiles on the market.  Thermal tests are needed to verify that the tile is storing latent heat and that the phase change is happening at the appropriate temperature.

### 6.1 Preliminary Compression Testing

The compression test was performed on a set of initial samples since it was easy to perform and gave a good metric on the bonding strength of the resin. It became apparent that there was not enough resin in the mixture.  The tiles all crumbled under 1000 psi of pressure.  Expected strength of the tiles was 25,000 psi.  Based on the results of those tested, it was decided to increase the amount of resin in the mixture.  This is not a concern, as resin percentage in the mixture is not fixed.  The amount of resins required can be sensitive to humidity and the container used for mixing. It will wet the container, which leads to less resin being incorporated into the mixture.

By increasing the resin mass fraction from 8% to 12%, a much wetter mixture was obtained. This resulted in a properly compacted and cured tile.  Several other samples were made with resin amounts varying between 8% and 12%.  These samples need to undergo a round of compression testing to determine a mixture with the minimum amount of resin that does not reduce the structural integrity.

Next, samples were made that included the phase change material.  The quartz powder was replaced with the phase change material in the mixture.  In order to overcome the dispersing problem, the mixture was mixed at a higher speed and for a longer period of time.  This resulted in the material being dispersed throughout the mixture.

## 6.2  Preliminary Thermal Testing Results

Samples were taken from mixtures with and without phase change materials and cured in a DSC pan.  The result from the heating run of a test is given in Table 16.

**Table 16.  Preliminary DSC Testing**

|  | Peak Transition Temperature | Latent Heat |
|---|---|---|
| Tile Sample | 29.0$^{o}$C | 130 mJ/mg |
| Expected Results | 31.2$^{o}$C | 165 mJ/mg |

Based on these initial results, the incorporated phase change material is undergoing a phase change at the appropriate temperature.  The latent heat is also on the order of expected values.  When similar runs were performed with solid-state phase change materials, the latent heat was significantly reduced from expected values due to an adverse reaction with the epoxy.

## 7.  CONCLUSION

Early evaluation of the potential energy storage of phase change materials in floor tile for passive solar applications have been promising.  Using encapsulated octadecane in a 3/4" thick floor tile, annual heating savings can be increased by 24%.  Solid-state phase change material has possible energy savings of half that amount.  It was therefore concluded octadecane would be the best material for this application.  The analysis done to date has been for a static model and the results are expected to be a low estimate of the possible energy savings.  A dynamic analysis may provide more realistic results and higher savings.

Each prototype tile will contain quartz chips and powder, polyester resin and encapsulated paraffin wax.  Tiles will be made with varying amounts of quartz powder, encapsulated wax and resin.  The amount of quartz chips will be held constant to ensure structural integrity of the tile.  Resin will be varied from 5% to 10% of the total mixture.  Proportions of encapsulated wax and quartz powder will be directly dependent on each other.  The ideal case would be a tile containing all phase change material and no quartz powder.

Ten design points, each containing different amounts of resin, quartz powder and encapsulated wax were identified.  Prototype tiles will be manufactured at each of these points.  Two to four batches will be made for each design point depending on the size and number of prototype tiles required.  The materials will be supplied by the companies, Granirex and Outlast Technology.  Manufacture of the prototype tile will be done in labs at Colorado State University (CSU).  Prototype tiles will be subjected to both physical and thermal testing.  Samples will be made to the size recommended by the test standards.

Physical tests have been broken down into two phases, initial and final.  This significantly reduces the number of prototype tiles that need to be manufactured.  Results from the initial phase of testing will be used to select two or three of the best performers.  These selected tiles will then be subjected to the final round of testing.  A majority of the tests will be performed at CSU, although two or three of the tests will have to be out-sourced.

Eighty-prototype tiles have to be made for the initial phase of testing. Seventy-six have to be manufactured for the final round of testing if two are selected after the initial testing phase. Thermal testing will occur during the initial phase of testing. Samples will be cured in the DSC pans and subjected to analysis. At least five samples will be made from each batch at each design point.

Based on the results of the thermal and physical tests, the best proportion of phase change material in a tile will be selected. This will be accomplished by a statistical analysis of the testing results. The potential annual savings can be calculated for this proportion of phase change material. It can then be determined if the cost savings are worth the initial investment of installing the floor tile.

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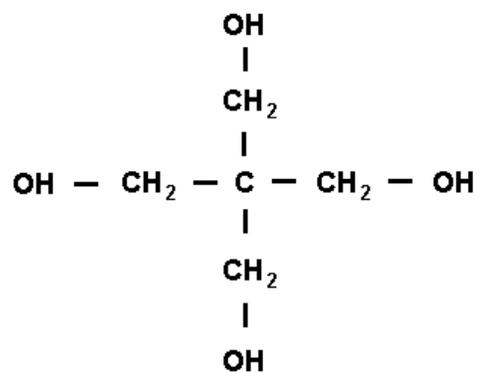
## 9.  APPENDIX 1

**Solid-State Phase Change Materials**

$$
\begin{array}{c}
OH \\
| \\
CH_2 \\
| \\
OH - CH_2 - C - CH_2 - OH \\
| \\
CH_2 \\
| \\
OH
\end{array}
$$

**Figure 8. Molecular structure of pentaerythritol, C – (CH2OH)4**

$$
\begin{array}{c}
CH_3 \\
| \\
CH_3 - C - CH_2 - OH \\
| \\
CH_2 \\
| \\
OH
\end{array}
$$
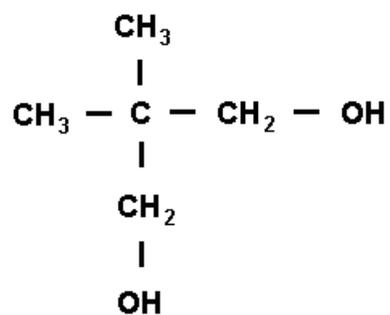
**Figure 9. Molecular structure of pentaglycerine, (CH3) – C – (CH2OH)3**

$$
\begin{array}{c}
OH \\
| \\
CH_2 \\
| \\
CH_3 - C - CH_2 - OH \\
| \\
CH_2 \\
| \\
OH
\end{array}
$$
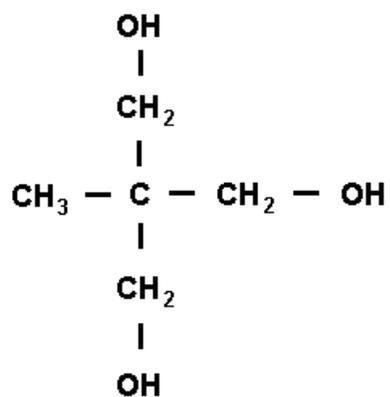
**Figure 10. Molecular structure of neopentyl glycol, (CH3)2 – C – (CH2OH)2**
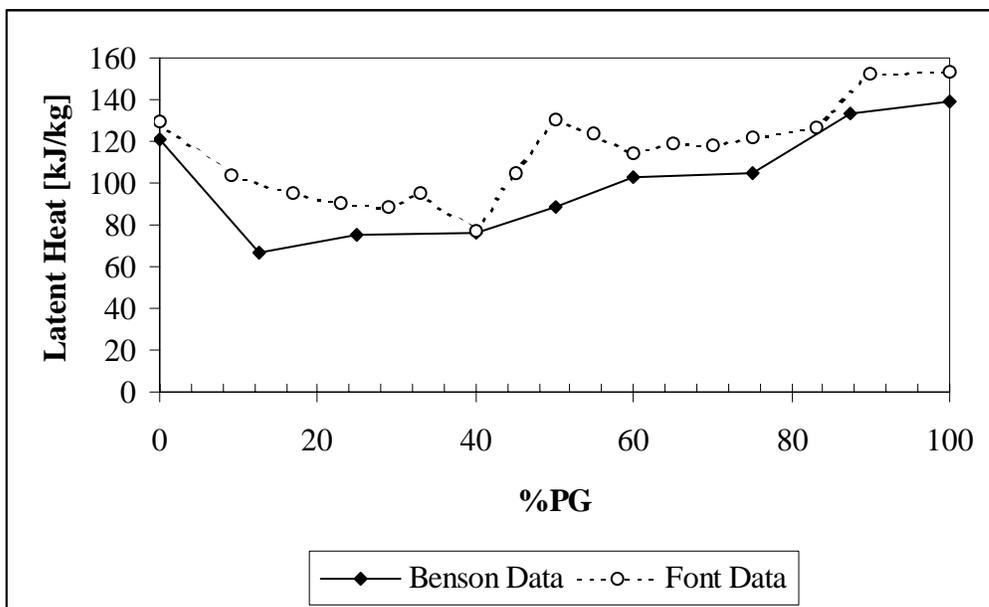
**Thermal Analysis**



**Figure 11. Latent Heat for Binary Mixture of Neopentyl Glycol and Pentaglycerine**

**APPENDIX 2**

**Kenwax 18 Normal Paraffin Content**

**Table 17. Kenwax 18 Paraffin Content**

| Normal Paraffin Content | % |
|---|---|
| C-15 | 0.83 |
| C-16 | 6.83 |
| C-17 | 19.31 |
| C-18 | 28.66 |
| C-19 | 27.22 |
| C-20 | 11.88 |
| C-21 | 2.78 |
| C-22 | 0.44 |
| C-23 | 0.08 |
| C-24 | 0.08 |

**Kenwax 19 Normal Paraffin Content**

**Table 18. Kenwax 19 Paraffin Content**

| Normal Paraffin Wax | % |
|---|---|
| C-15 | 0.083 |
| C-16 | 0.633 |
| C-17 | 6.169 |
| C-18 | 19.052 |
| C-19 | 26.522 |
| C-20 | 22.942 |
| C-21 | 14.442 |
| C-22 | 4.656 |
| C-23 | 0.903 |
| C-24 | 0.137 |

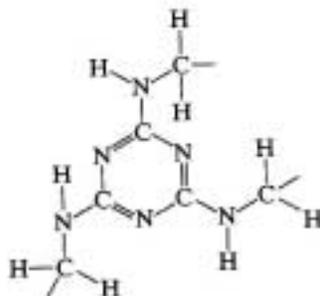# 11. APPENDIX 3

## Melamine-Formaldehyde



**Figure 12. Molecular Structure of Melamine-Formaldehyde**

## 12. APPENDIX 4

**PHYSICAL TESTS**

**Table 19. Physical Tests Performed on Agglomerate Floor Tile by Various Manufacturers**

| Test | Granirex | Quartzstone | Verona Marble Co. Quartzo 88 |
|---|---|---|---|
| ASTM C-615 Granite Dimension Stone | X | | |
| ASTM C-97 Absorption and bulk specific gravity | X | x | x |
| ASTM C-170 Compressive strength | X | x | |
| ASTM C-648 Breaking Strength | X | x | |
| ASTM C-880 Flexural Strength | X | | |
| ASTM C-484 Thermal Shock | X | x | X |
| ASTM C-531 Thermal Coefficient of Expansion | X | | |
| ASTM C-1026 Frost Resistance | X | x | X |
| ASTM C-501 Relative Resistance to Wear | X | x | |
| ASTM C-241 Abrasion Resistance | X | x | X |
| ASTM C-1028 Coefficient of Friction | X | x | X |
| ASTM D-2299 Stain Resistance | X | | |
| ASTM C-672 Resistance to De-Icing Chemicals | X | x | X |
| ASTM G-23 Ultra Violet Performance | X | | |
| ASTM E-84 Flame Spread | X | | X |
| ASTM E-662 Smoke Density | X | | X |
| ASTM C-99 Modulus of Rupture | | | X |
| ASTM C-307 Tensile Strength | | | X |
| ASTM D-695 Compression Strength | | | X |
| ASTM D-1042 Dimensional Stability | | | |
| ASTM D-2583 Indentation Hardness | | | |
| ASTM D-2047 Coefficient of Friction | | | |
| ASTM D-54384 Stain Resistance | | | X |
| ASTM C-291 Wear Resistance/Hardness | | | X |
| Impact Resistance | X | x | |
| Mohs Hardness | X | | |
| ANSI A-137.1 Ceramic Standard | X | | |
| NES 713-1985  Mean Toxicity Index | | | |