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FORM-STABLE CRYSTALLINE POLYMER PELLETS FOR
THERMAL ENERGY STORAGE: PHASE 1

Final Report, July 1, 1976—May 1, 1977

By
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January 1978
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Work Performed under Contract No. EY-76-C-05-5159

Dayton Laboratory
Monsanto Research Corporation
Dayton, Ohio

U. S. DEPARTMENT OF ENERGY

Division of Energy Storage Systems

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FOR THERMAL ENERGY STORAGE
Phase 1

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July 1, 1976 - May 1, 1977

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MONSANTO RESEARCH CORPORATION
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FOREWORD

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ABSTRACT

The objective of this project was to develop a form-stable, crystalline polymer pellet TES bed material, useful in the 120-140°C temperature range suitable for solar absorption air conditioning applications. This objective was achieved with a Si-O-Si crosslinked HDPE pellet material, demonstrated to have a high heat of fusion value (46 cal/g, ~98% of the HDPE's heat of fusion value prior to crosslinking). Further, on melt/freezing cycling of these TES pellets through 400 cycles in ethylene glycol, they retained nearly 100% of their initial heat of fusion value, and had excellent form-stability characteristics, with little or no inter-particle adhesion. Appropriate testing of this TES pellet material, from analytical (DSC) to a one gallon lab-scale TES unit, and finally to a 60 gallon prototype TES demonstration unit, consistently verified these results. C-C crosslinked PE products, which were slightly inferior to the Si-O-Si crosslinked PE in terms of good heat of fusion and form-stability properties, were also developed and are potential alternatives to the prime PE TES product.

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1. INTRODUCTION

The development of a cost-effective durable energy storage material is essential to widespread utilization of solar energy for heating and cooling of buildings. High heat storage efficiency, low cost, retention of capacity with time and use, effectiveness around 125-150°C (255-300°F), non-toxicity, non-flammability, and non-corrosivity are desirable characteristics of such a material.

Phase-change materials having high latent heats of fusion offer an advantage for thermal energy storage over sensible heat-only storage materials, in terms of saving of space by reducing the need for large and expensive storage tanks or bins. However, many phase-change materials suffer from other drawbacks, such as the incongruent melting behavior of many salt-hydrates and poor heat transfer characteristics of large blocks of paraffin wax.

A highly crystalline polymer, such as polyethylene, offers certain unique advantages as a potential thermal energy storage material. It possesses a substantial latent heat of fusion which reportedly may be as high as 58 cal/g¹, i.e., comparable to Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$), yet melts congruently in the 125-150°C (255-300°F) temperature range best suited for solar absorption air conditioning. Further, there should be little or no decrease in polyethylene's heat of fusion after cycling a great many times around its crystalline melting point, since it is a stable, recrystallizable, homogeneous material.

The potential utility of thermoplastic polyethylene pellets for thermal energy storage would be greatly enhanced if they were rendered non-flowable and non-sticking on melting. A porous bed of the pellets could then be maintained and a liquid or gaseous heat transfer medium passed through it. It was expected that this form stability could be accomplished by crosslinking of polyethylene. Crosslinking was expected to reduce crystallinity to some extent so it had to be kept to a minimum in order to retain the maximum heat of fusion of the form-stable polyethylene.

Accordingly, the principle objective of this project was to develop a form-stable polyethylene bed material which would retain a high heat of fusion and be suitable for thermal energy storage applications. In order to achieve this objective, the following tasks were undertaken:

- (1) evaluation and optimization of limited controlled chemical crosslinking techniques on polyethylene;
- (2) evaluation of the heat storage capabilities of the polyethylene crosslinked products;

- (3) optimization of the heat transfer to, through and from the polyethylene, and
- (4) construction of a prototype bed to demonstrate the practicality of this approach to energy storage.

The work performed and results obtained for each of the above tasks will be described in detail in this report. This will not be done on a strictly task-segregated basis, however, since there is considerable overlap and interdependence among these four cited tasks.

2. SUMMARY AND CONCLUSIONS

The principle areas of investigation in the development of a thermal energy storage material of form-stable, crystalline polyethylene pellets are briefly outlined here, along with major results obtained and suggestions for continued work.

2.1 DEVELOPMENT OF A FORM-STABLE, CRYSTALLINE POLYMER PELLET BED MATERIAL

The major objective of the project was to develop a form-stable, durable polymer pellet bed material useful for thermal energy storage. The base polymer chosen for this work was high density polyethylene (HDPE), due to its high initial crystallinity (and hence heat of fusion), low cost and desirable melting range directly applicable to the needs of solar absorption air conditioning.

Controlled, limited crosslinking of the polyethylene by chemical means was undertaken in order to produce form-stable, yet still highly crystalline, pellets useful as a TES bed material. The achievement of the required form-stability is demonstrated in Figure 1, which shows the melt and flow of an uncrosslinked pellet compared to form-stable pellets which do not flow on melting.

Essentially, two general methods of controlled crosslinking of HDPE were investigated: (1) crosslinking via incorporation and thermal activation of a peroxide in the PE to produce primarily C-C crosslinks between polyethylene chains; and (2) grafting of vinyl triethoxysilane onto the PE backbone, followed by crosslinking in an aqueous environment to produce primarily Si-O-Si crosslinks between polyethylene chains.

The latter method (giving products with Si-O-Si crosslinks) was found to be preferable in terms of achieving the desired goal of form-stable polyethylene pellets while retaining a very high degree of the crystallinity of the original polyethylene starting material. When first prepared on a relatively small scale (~5 pounds) these crosslinked pellets demonstrated excellent form-stability while retaining 91% of the starting HDPE heat of fusion (43 cal/g, as determined by DSC). Even better results were achieved with a subsequent scale-up (to 250 pounds) of this crosslinked PE product, as a heat of fusion of 46 cal/g was obtained by DSC, or ~98% of the original ΔH_f of the starting HDPE. This material also underwent melt/freeze cycling tests in a 60 gallon prototype TES unit, where ΔH_f values equivalent or slightly higher than the DSC values were demonstrated.

Figure 1. Normal HDPE (left) flows on melting while modified form-stable HDPE does not

Figure 2. One gallon lab-scale thermal energy storage unit containing 5-lb form-stable HDPE pellet bed

Figure 3. 60 gallon prototype TES unit containing 250 lb of form-stable PE pellets for automatic cycling durability test

In general, the C-C crosslinked PE products were somewhat inferior to the silane-grafted/crosslinked PE, in terms of both reduced heat of fusion and less form-stability, the latter particularly indicated by greater inter-particle adhesion. Nevertheless, some of these products may prove to be valuable as practical TES materials. In particular, one such C-C crosslinked product, prepared in a simple extrusion process, may be worth further consideration, particularly due to the ease of manufacture and hence projected lower cost.

2.2 EVALUATION OF PE PELLETS IN PROTOTYPE TES TEST UNITS

Evaluation of five pounds each of three prime candidate TES materials was carried out in a one gallon (4-liter) lab-scale TES unit (Figure 2), to confirm analytical characterization results obtained on small samples of C-C and Si-O-Si crosslinked PE products. The three candidate materials included two C-C crosslinked PE products and one Si-O-Si crosslinked PE product. Form-stability and heat storage capability were evaluated during and at the conclusion of up to 20 melt/freeze cycles in ethylene glycol (Prestone II antifreeze) in this unit.

Results of the testing in the one gallon unit were verified by results of smaller scale (<100 g) long-term stability testing that showed the silane-grafted/crosslinked HDPE to retain ~100% of its initial heat of fusion after 400 melt/freeze cycles, with excellent form-stability and virtually no inter-particle adhesion. The silane-grafted/crosslinked PE was thus chosen for still further scale-up (to 250 pounds) and evaluation in a 60 gallon prototype TES unit (Figure 3). Testing of the TES material in this unit continued on an automated basis up to 170 cycles with no changes in PE performance.

2.3 CONCLUSIONS

It is concluded that the principle project objective, development of a form-stable, crystalline polymer pellet TES bed material was achieved. In particular, a Si-O-Si crosslinked HDPE product, was shown to have excellent form-stability with a heat of fusion value of 46 cal/g, which is ~98% of this HDPE's initial heat of fusion before crosslinking. Further, on melt/freeze cycling of this TES material in ethylene glycol through 400 cycles, nearly 100% of its initial heat of fusion was retained, along with excellent form-stability characteristics, including little or no inter-particle adhesion.

In combination with an ethylene glycol heat transfer fluid, the output of a typical pellet bed exceeds 0.5 million BTU per 1000 gallon volume and, most importantly, this energy is all at temperatures between 120 and 140°C.

A projected one time cost for the materials in a storage bed consisting of the form-stable HDPE with ethylene glycol liquid thermal transfer is $\sim 0.4\phi$ per storable BTU. In the case of air thermal transfer, the equivalent would be $\sim 0.2\phi$ /BTU. Assuming a conservative useful life of 30 years and 333 potential cycles per year for a total of ca. 10,000 cycles, the cost per BTU stored would be 0.00004ϕ and 0.00002ϕ , respectively. These costs were determined using a best foreseeable selling price of 26ϕ /lb, and a reasonable projected ΔH_f value of 50 cal/g for these TES pellets.

Further work to confirm the long-term performance of the TES material system, and to demonstrate its utility in an air heat transfer system, is in order. Significant process improvements (and hence cost reductions) are seen as feasible with the preferred Si-O-Si crosslinked PE TES material and should be investigated. Further development of a C-C crosslinked PE product as an alternative TES material useful in this same temperature range would also warrant consideration. Finally, defining alternative form-stable polymeric TES materials useful in temperature ranges other than that considered here would be most desirable.

3. EXPERIMENTAL METHODS

This section describes the experimental methods used both in the preparation of polyethylenes with enhanced form-stability and the evaluation of such products. The evaluation was done both on a relatively small, or "analytical" scale, and on a larger "prototype demonstration" scale. TES demonstration or evaluation equipment was designed and built specifically for use in this project, thus their design basis and operation are described in detail.

3.1 ENHANCEMENT OF POLYETHYLENE FORM-STABILITY

A number of methods for enhancement of the form-stability of polyethylene were examined, all of which involved crosslinking of the high density polyethylene (HDPE) by chemical means. Essentially, these methods could be divided into two fairly broad categories: (1) those in which the crosslink formed is a carbon-carbon bond between the polyethylene backbone molecules (as shown below) and (2) those in which the crosslink formed is primarily a silicon-oxygen-silicon bond between the polyethylene backbone molecules (also shown below):

(1) Carbon-carbon crosslink
between PE backbone
molecules

(2) Silicon-oxygen-silicon
crosslink between PE
backbone molecules

The PE products obtained containing these two different types of crosslink bonds do differ in preproperties, as will be shown later. The methods of preparation for each are now described in some detail.

3.1.1 Preparation of C-C Crosslinked PE Products

Although a variety of methods were used to produce polyethylene chemically crosslinked by C-C bonds, all employed basically similar process steps: (a) a peroxide crosslinking agent was added to the PE (or in some cases was already present); (b) the decomposition of the peroxide was thermally initiated to generate free radicals and resultant crosslinking of the PE; and (c) pellets of the crosslinked PE were formed (with the exception of those cases where no "melting" of PE had occurred in step b).

The various process methods used for carrying out each of the C-C crosslinking steps given above may be summarized as follows:

- a. Incorporation of Peroxide
 - Melt Compounding
 - Mill Roll
 - Banbury
 - Interfacial Contact
 - Liquid
- b. Thermal Activation of Peroxide
 - High Pressure
 - Compression Molding
 - Extrusion
 - Low Pressure
 - Heated Liquid ($>T_M$, $<T_M$)
- c. Formation of Pellets
 - Extrusion
 - Injection Molding
 - Chopping

These methods will be described more fully and some examples given, from the work performed.

3.1.1.1 Compression Molding Activated Peroxide Crosslinking Process

The method used most extensively to produce consistent C-C crosslinked PE lab batches was that of incorporating the peroxide into molten PE on a steam-heated mill roll, followed by thermal activation via compression molding. Pellets were then formed by chopping of strips of the crosslinked, molded PE. The milling and molding equipment used is illustrated in Figure 4.

(a) Melting of PE on small steam heated mill roll prior to peroxide addition

(b) Electrically heated press for compression molding of peroxide-containing HDPE sheets from mill roll

Figure 4. Views of equipment used for incorporation of peroxide into HDPE (mill roll) and thermal activation of peroxide in molten PE (press)

Typically, 50 g of the HDPE to be crosslinked was melted on the small steam-heated mill roll at ca. 150°C (300°F) [Figure 4(a)], the peroxide was then added to the molten PE (if any "fillers" were employed, they were added prior to the peroxide) and milling continued only long enough to assure complete mixing. The PE sheet was removed from the mill roll and compression molded in an electrically heated press [Figure 4(b)], generally for 30 minutes at 170°C (350°F) and ~700 psi (if other molding conditions were used these are noted where applicable). The molded samples (generally 6" x 6" x 1/8") were then cooled slowly in the mold (rather than quenched) to RT, and next cut into strips (band-saw) to be chopped into pellets (pellet chopper). The pellets (~1/4" x 1/8" x 1/8") were then ready for testing.

3.1.1.2 Extrusion-Activated Peroxide Crosslinking Process

A second major method used to produce C-C crosslinked PE products was via extrusion of a peroxide-containing HDPE. The peroxide was added to the PE on a heated mill roll (as described in 3.1.1.1) and the resultant sheet granulated; alternately, the peroxide was incorporated at room temperature via tumble-blending of the PE pellets with an inert diluent (mineral oil) containing the peroxide. Extrusion of pellets coated with peroxide via the latter procedure is shown in Figure 5. A C. W. Brabender single screw (3/4 in. screw size) extruder with 4 heated zones was used. Temperatures of the zones could be adjusted and also screw speed altered to vary throughput times. Actual conditions used depended on the particular peroxide employed and its decomposition temperature. The extruded strand of crosslinked PE was chopped into pellets, with the pellet chopper, as shown in Figure 5. Pellet sizes could be varied -- generally they were 1/4 in. (length) by 1/4 in. (diameter) or less.

3.1.1.3 Heated Liquid Activation of Peroxide Crosslinking Process

A third method of producing C-C crosslinked HDPE was via activation of peroxide in a heated liquid medium. The temperature used could be either above or below the melting temperature, T_M , of the HDPE, depending on the decomposition temperature of the peroxide employed. Vigorous stirring was required in both cases, but particularly when the PE was above its melting point. Typical examples of the procedures used for liquid above and below T_M (135°C) are as follows:

(a) Addition of peroxide-coated pellets to extruder hopper

(b) Extrusion of crosslinked HDPE strand

(c) Chopping of crosslinked strand into pellets

Figure 5. Crosslinking of HDPE via an extrusion process

- a. Liquid Medium >T_m. 10 g of commercially available cross-linkable PE (Marlex CL-100, Phillip's Petroleum Company) pellets were heated with vigorous agitation in 200 ml of DC-200 (Dow Corning) silicone fluid (500 cs viscosity) to 200°C and kept at this temperature for 15 minutes. In spite of the vigorous stirring, much of the molten PE agglomerated into a large ball, but the rest remained as individual small spheres, which could be isolated by filtration after cooling to room temperature.
- b. Liquid Medium <T_m. In this case, it was anticipated that crosslinking would be restricted largely to the surface and amorphous portion of the pellet, since it would not be melted during crosslinking. Typically, 50 g of the HDPE pellets were stirred in 200 ml of refluxing H₂O containing 0.5 g of benzoyl peroxide (and possibly a surfactant) for ~2 hours. Then, after cooling to RT, the pellets were filtered off, washed with H₂O and air-dried prior to testing. Figure 6 shows an example of this crosslinking process with PE pellets in refluxing H₂O.

3.1.2 Preparation of Si-O-Si Crosslinked PE Products

The preparation of crosslinked PE products containing the Si-O-Si linkage between PE backbone molecules differs considerably from that previously described for the C-C crosslinked PE. It involves first the grafting of alkoxy silyl groups onto the PE backbone (in the melt), followed by crosslinking in water, or an aqueous environment, below the PE melting point. This process is described fully in U.S. Patent 3,646,155 (Dow Corning), and is briefly illustrated by the following equations by which it may be presumed to occur.

Figure 6. Surface crosslinking of HDPE pellets in refluxing H_2O containing a peroxide crosslinking agent

The processing steps which were involved in carrying out the reactions are as follows:

- a. Grafting of Alkoxysilane onto PE Backbone
Hot mill melt or
Banbury mixer melt
- b. Melt Blend Catalyst with PE Carrier
Hot mill or
Banbury mixer
- c. Incorporation of PE Catalyst Carrier with Grafted PE and Pellet Formation
Extrusion or
Injection Molding
Chopping
- d. Hydroxyl Activation of Crosslinking in Boiling H₂O or Steam

The actual procedures used are best illustrated by the following description of the preparation of a ~250 pound batch of silane-grafted/crosslinked HDPE (for testing in a 60 gallon prototype TES unit).

3.1.2.1 Preparation of 250 Pound Batch of Silane-Grafted and Crosslinked HDPE

The procedures and reactants employed in the preparation of ~110 kg (250 lb) silane-grafted and crosslinked HDPE were as follows:

- a. A charge of 2000 g of Alathon 7040 HDPE (DuPont) pellets was added to a large Banbury mixer and fluxed 4 to 5 minutes at a temperature above RT (no steam). A charge of 120 g (6 phr) vinyl triethoxy silane (Union Carbide A-151) containing 4 g (0.2 phr) benzoyl peroxide was added and 5 min of mixing with steam on (120 psi) begun. At the end of this time, cooling water was turned on and the ~1/4 lb silane-grafted PE cake removed from the Banbury (after 2 min cooling time). This procedure is demonstrated in Figure 7.
- b. The grafted PE cake was next cold pressed into round flat discs which could readily be cut into strips via a band-saw, and then granulated into flakes or pieces suited for extrusion.

(a) Addition of ~5 lb PE pellets to Banbury mixer

(b) Addition of VTS to PE after 5 min. flux in mixer

(c) silane-grafting onto molten HDPE

(d) Removal of silane-grafted PE "cake" from mixer after 5 min. mixing (with steam on) and 2 min. cooling (cold water on).

Figure 7. Grafting of Vinyl Triethoxy Silane (VTS) onto Alathon 7040 HDPE in Banbury intensive mixer

- c. The silane-grafted flakes were next co-extruded in a 95/5 (w/w) ratio with a catalyst batch (consisting of 100 parts Alathon 7040, 1 phr dibutyltindilaurate and 0.15 phr benzoyl peroxide prepared via mixing on a hot mill roll, and granulated into flakes) using a 1 inch extruder (2 passes, all zones at 165°C) (330°F) and chopped into pellets. This is shown in Figure 8.
- d. These silane-grafted HDPE pellets were next crosslinked by heating in 88°C water for 48 hours, removed, rinsed thoroughly with H₂O, and air-dried. The crosslinking procedure and the final dried Si-O-Si crosslinked PE pellets are shown in Figure 9.

The procedure described above for producing Si-O-Si crosslinked HDPE represented some improvements and simplifications over earlier procedures employed. Initially, the hot mill roll had been employed in the grafting reaction of alkoxysilyl onto the PE backbone. However, this being a relatively "open" system, excess silane was lost on addition to the PE, and use of a Banbury mixer (which is closed under pressure) was found to be preferable. Also, the granulated PE flakes and silane charge had been tumble-blended at room temperature to mix the two prior to melt-blending; however, this was found not to be necessary when a larger Banbury mixer was used for grafting. It is expected that further processing simplifications could be achieved with the additional scale up needed for the production of Si-O-Si crosslinked PE in substantial quantities.

3.2 ANALYTICAL EVALUATION OF CROSSLINKED PE PRODUCTS

In order to characterize the crosslinked PE products and evaluate their potential utility for TES applications, certain quantitative and qualitative analytical tests were performed. The starting HDPE candidates also were similarly characterized, both to serve as the controls and to select the ones most suited for potential TES materials via form-stability enhancement. The analytical characterization methods used will be described briefly in this section.

3.2.1 Thermal Characteristics by Differential Scanning Calorimetry

The primary method used for performance characterization of the crosslinked PE products (and starting HDPE's) was differential scanning calorimetry (DSC). It was used to determine the crystalline melting (T_M) and recrystallization temperature (T_C) and the heat of fusion (ΔH_f) on melting of the polyethylene products.

(a) co-extrusion of granulated,
silane-grafted PE with PE
catalyst-carrier
(95/5 w/w ratio)

(b) PE pellets after co-extrusion
-- prior to crosslinking

Figure 8. Co-extrusion and pelletizing of silane-grafted
PE + PE catalyst carrier

(a) Addition of PE pellets to steam-heated kettle (containing H_2O) for crosslinking reaction

(b) Air-dried silane-grafted and crosslinked PE pellets

Figure 9. Crosslinking of silane-grafted Alathon 7040 HDPE and drying of pellets

The importance of the ΔH_f value to TES applications is that it is a measure of how much energy can be stored by the material. The DSC instrument employed was a Perkin-Elmer Model DSC-1 (shown in Figure 10). In operation, the polymer sample to be measured by DSC (~10 mg) is placed in a crimped aluminum sample pan in the instrument sample holder. A reference holder contains an empty sample pan. Both are heated according to a predetermined time/temperature program (typically 10°C/min was used).

A typical DSC plot of PE melting (Figure 10) has the temperature on the X axis and the signal proportional to any power difference required to keep the two heaters on the same temperature on the Y axis. When the sample undergoes a thermal transition, such as melting, the area under the curve is a direct measure of the heat of transition. The areas measured under the melting curves could be attributed to the PE heat of fusion, as contributions from specific heat were compensated for by the baseline method used.

As shown in Figure 10, melting of the PE occurs over a finite temperature range; the physical reason for this behavior is reported to be the higher surface free energy of small crystallinities.² However, this temperature interval for fusion decreases with increasing molecular weight and narrowing molecular weight distribution. Thus, use of high molecular weight, but narrow MWD, PE is favored for reducing this temperature interval on melting.

Differences observed between T_M , the melting temperature peak, and T_C , the recrystallization temperature peak (generally about 10-15°C below T_M), were attributed primarily to the DSC test conditions and were not considered inherent to the polymers themselves. This was further verified by results of larger scale testing in prototype TES units and is discussed in detail in Section 4.1.

The absolute values (in cal/g) for the polyethylene heat of fusion were determined by the periodic calibration of the instrument with a material having a known heat of fusion. Indium was the primary standard used here, but dotriacontane was also employed as a second standard.

3.2.2 Thermal Form Stability

An essential characterization test performed on all crosslinked PE products (and starting materials) was a determination of their thermal form stability in air (and, in some cases, in a liquid heat transfer medium). Testing of the form stability and "tackiness" on melting of the PE products in air and at

(a) Perkin-Elmer Model DSC-1 showing sample pan being placed in instrument

(b) Portion of DSC scan showing crystalline melting of a crosslinked HDPE resin (T_M = peak, ΔH_f = area under curve)

Figure 10. Determination of thermal fusion properties of HDPE crosslinked products by Differential Scanning Calorimetry

ambient pressure was readily and rapidly accomplished by heating of three or four touching pellets to $\sim 200^{\circ}\text{C}$ on a Fisher-Johns melting point apparatus (Figure 11).

The apparatus is simply a small "hotplate" equipped with a thermometer, to indicate the temperature at which melting occurs, and a magnifying lens to enhance viewing of the melting process. The melting of two PE pellets which are crosslinked and form-stable along with one unmodified PE pellet is shown in Figure 11. The uncrosslinked PE pellet flows on melting while the crosslinked form-stable ones do not even deform.

A second method for testing thermal form stability of crosslinked PE pellets, particularly in relation to their tendency to adhere to one another on melting, was to cycle the PE pellets around their melting point in a liquid heat transfer medium, such as ethylene glycol. This was conveniently done in a small open test tube or beaker on a hot plate. Those crosslinked PE products which otherwise appeared to be potentially promising candidate TES materials, as evidenced by their form-stability in air and heat of fusion values, were tested in this practical manner.

3.2.3 Other Methods (Density, Melt Flow, Gel Content)

On selected crosslinked PE products (and candidate HDPE starting materials) other analytical characterization data were obtained, as deemed necessary. The characterization data obtained and methods used were as follows:

- (a) Density (as a measure of crystallinity). Since the density of a polyethylene is directly proportional to its crystallinity (and this in turn relates to the heat of fusion value), it was of interest to measure the densities of some crosslinked PE products and/or starting materials (if information was not available from the manufacturer). A standard ASTM buoyancy method was used (ASTM D-792).
- (b) Melt Index (as a measure of molecular weight). The "melt index" of polyethylene, as determined by its melt flow through a capillary, is inversely related to its molecular weight, i.e. the higher the molecular weight of the PE the lower its melt index. This information is useful in various ways, such as determining if grafting has occurred in the silane-grafting onto PE (which should increase molecular weight and lower the melt index) and determining if crosslinking has occurred (no M.I. will be obtainable, as the crosslinked PE will not flow through the capillary). A standard ASTM method (D-1238) was used for determining melt indices.

(a) Fisher-Johns Melting Point Apparatus

(b) Pellets of uncrosslinked PE (left) and crosslinked PE (right) at room temperature

(c) Uncrosslinked PE (left) and crosslinked PE (right) at 140°C. Note melt and flow of the uncrosslinked material in contrast to the form stable crosslinked pellet

Figure 11. Characterization of thermal form stability of PE pellets using Fisher-Johns melting point apparatus

- (c) Gel Content (as a measure of degree of crosslinking). One indication of the amount or degree of crosslinking achieved in a crosslinked PE product is its gel content, as determined by extraction in what is normally a solvent for uncrosslinked PE. The crosslinked polyethylene will be swollen by the solvent but not dissolve, while any uncrosslinked PE will be solubilized.

Normally, fully crosslinked PE's will have gel contents of 60-80% or more. In the work conducted, however, it was desirable to limit the crosslinking (to maximize crystallinity); hence lower gel contents were generally considered desirable.

The gel contents were determined by extraction of the crosslinked PE's (and uncrosslinked starting materials as well) in refluxing ethyl benzene for 16 hr, employing Soxhlet extraction thimbles (placed directly in the solvent) to hold the PE samples. This procedure is very similar to one recommended by Phillip's Petroleum Co. for determination of gel contents in crosslinked PE. Details of the Phillip's Co. Procedure are given in Appendix A.

3.3 EVALUATION OF CROSSLINKED PE PRODUCTS IN PROTOTYPE UNITS

From the initial analytical characterization data obtained on the crosslinked PE products, certain prime candidate TES materials were selected for further scale-up and evaluation. These were evaluated in the following quantities and manner:

- a. Long-term evaluation of durability and form stability of the three prime candidate TES materials, on a small (<100 g) scale.
- b. Evaluation of heat storage capability and stability of the three prime candidate TES materials in a medium scale (1 gallon volume) TES demonstration unit (~5 lb PE bed).
- c. Evaluation of heat storage capability and stability of one selected TES material (based on above results) in a prototype TES demonstration unit (60 gal volume) using ~250 lb PE bed.

The methods for evaluation and equipment design, construction, and operation will be described for each of the above in this section.

3.3.1 Long-term Form Stability and Durability of Candidate TES Materials

The long-term form stability and durability of these prime candidate crosslinked PE TES materials were evaluated using two tests. These were:

- a. Melt-freeze cycling in ethylene glycol, and
- b. Maintenance above the PE melting point in refluxing ethylene glycol.

The equipment used for these tests is shown in Figure 12. Figure 12(a) shows the TES candidate samples (PE pellets) in ethylene glycol (Prestone II) as they were cycled around their melting points. Figure 12(b) shows the same PE pellet samples which were maintained in the molten state in refluxing ethylene glycol.

Periodically, samples (pellets) were withdrawn from each test medium for evaluation of durability as determined by retention of the heat of fusion (ΔH_f). Visual observations of form stability and tendency of the pellets to adhere to themselves were made daily and in detail at the time of sample collection.

3.3.2 Laboratory Scale 1 Gallon (4-Liter) Prototype Unit

A prototype lab scale TES unit was constructed to meet three basic needs in this program:

- (1) To confirm in larger scale the DSC test data and provide a higher level of confidence in both heat of fusion properties and form-stability of the candidate polymers.
- (2) To measure heat dissipation rates and determine the necessity for fillers and other surface configurations to increase the heat exchange rate through HDPE pellets.
- (3) To evaluate the materials and the design of the unit itself to identify the materials requirements and optimum design for the 60 gallon demonstration model unit.

The TES unit consists of four basic components: a storage chamber to hold the form-stable polyethylene pellets; a heating unit to heat the ethylene glycol heat exchange fluid; a cooling radiator to remove heat from the system; and a metering pump to circulate the heat exchange fluid.

(a) Melt-freeze cycling of PE pellets in ethylene glycol; left - pellets prior to melting; right - molten pellets

(b) Maintenance of PE pellets above M.P. in refluxing ethylene glycol

Figure 12. Long-term form stability and durability evaluation of three prime candidate crosslinked PE TES materials

During the heating cycle, the pump continuously circulates the heat exchange fluid (ethylene glycol) through the heating unit to the storage chamber, where the hot glycol raises the temperature of the form-stable polyethylene pellets up through their phase change to as high as 160°C. Thermal energy is thus stored as sensible and phase change heat.

By isolating the heater and circulating the heat exchange fluid between the radiator and the storage chamber, thermal energy is transferred out of the chamber and then removed from the system by the radiator. The amount of energy charged to or removed from the storage chamber can be calculated when the inlet and outlet fluid temperatures and the circulating fluid volumes are known. The energy recovered is therefore the energy stored by the polyethylene as sensible and phase change heat, plus the sensible heat of the heat exchange fluid and the mass of the chamber itself.

3.3.2.1 Prototype Unit Components

The storage chamber (Figure 13-a), a 4 in. x 18 in. hard glass cylinder, has a volume of approximately 1 gallon (4-liter) and can hold about 5 pounds (2200 g) of TES pellets (depending on the pellet size, shape, density and packing efficiency).

The heat exchange fluid flow is from top to bottom during the heating phase and from bottom to top in the cooling (heat discharge) phase. This flow pattern was selected, first, because it conforms to the natural convective flow and avoids convective mixing in the chamber. Secondly, it improves the efficiency of both heating and cooling. The coldest fluid is removed from the bottom, heated, and returned to the top of the chamber.

The flow is reversed during cooling to discharge the highest temperature from the top and return the cooled fluid to the bottom. The cooled fluid can then remove a maximum amount of heat from the lower cooler zones of the chamber and be "pre-heated" before entering the hot upper zone. The system therefore permits a maximum amount of energy to be removed at higher, more useful temperatures.

Copper and brass resistance heaters, and to a lesser extent the copper plumbing initially used in the prototype unit, were found to react with the stabilized ethylene glycol (antifreeze) at high temperatures. This reaction, which probably caused formation of copper oxalate, rapidly corroded the chromolax immersion heaters. The scale (salt) thus produced inhibited free flow in the system. These heaters were replaced with stainless steel (Figure 13-b), which eliminated the problem, and pointed up the need for a careful selection of materials for the larger working model unit.

(a) One gallon (4-liter) thermal storage chamber

(b) Stainless steel immersion heater

Figure 13. One gallon (4-liter) prototype TES test unit components

Two stainless steel immersion heaters (13-b) with a combined power of 800 watts raised the chamber temperature from room temperature to $\sim 160^{\circ}\text{C}$ in approximately four hours. After the initial cycle, the chamber was then cooled to only $\sim 80^{\circ}\text{C}$, whereupon the heating time required to return to 160°C was approximately three hours. Circulation in the heater was from bottom to top conforming to natural convective flow.

Cooling was accomplished by circulating the heat exchange fluid through a heat exchanger or radiator submerged in a water bath. This technique provided a means to control the operating temperature range. By maintaining the cooling water at 100°C (the glycol was further cooled in circulating through the pump and back to the storage chamber), a reproducible lower operating temperature of $\sim 80^{\circ}$ was readily achieved. The procedure shortened the cycle time required and simulated the real, useful temperatures required for most heating and cooling applications (such as absorption air conditioning).

The validity of the determination of thermal energy stored in or recovered from the TES unit depended upon the accurate measurement of the circulation rate. The pump chosen (Figure 14-a) was a Hills McHanna precision metering pump with an adjustable piston stroke length. Controllable and reproducible (to $\sim 2\%$) flow rates from 30 to 150 ml/min were attained. At a pumping rate of 150 ml per min, the fluid in the storage chamber was changed every 12 min. A 30 ml/min rate corresponded to a complete exchange every 1.0 hour.

Thermocouples, shown as T_1 to T_{11} in Figure 14-b, were used to monitor the temperatures at critical points throughout the system. T_3 and T_4 at the inlet and outlet of the storage chamber were the sensing points used to define the heat storage capacity of the system. Overall views of the 4-liter TES test unit are shown in Figure 15.

3.3.2.2 Operation of the Prototype TES Unit

The system was designed to separate the two phases of operation, heating and cooling, to minimize the effects of sensible heat storage by the relatively large mass of the plumbing and system components. During the heating phase, valves 1, 3 and 5, shown in Figure 14-b (a schematic drawing of the system) are opened. Valves 2, 4 and 6 are closed, isolating the radiator. Circulation is clockwise, bottom to top through the heater and top to bottom through the storage chamber. Reversing the valve positions isolates the heater and produces a clockwise circulation through the radiator and storage column for the cooling phase.

(a) Hills-McHanna piston type metering pump

(b) Schematic drawing indicating placement of thermocouples

Figure 14. One gallon (4-liter) prototype TES test unit pump and schematic of design

(a) Overall view before insulating

(b) In operation after insulating

Figure 15. Views of the one gallon (4-liter) TES test unit

The temperatures at thermocouples T_3 and T_4 at the inlet and outlet of the storage chamber were critical parameters for determining the energy stored in or removed from the chamber. Knowing the temperature of the circulating glycol at these two points, and the weight of glycol circulated (pumping rate), the total instantaneous stored heat energy was: $Q_{T_0} = \text{glycol weight } (W_g) \times \text{specific heat of glycol } (C_g) \times \text{temperature differential between } T_3 \text{ and } T_4 (\Delta T)$. Over a period of time t , the total stored energy was: $Q_T = (W_g \cdot C_g \cdot \Delta T)t$.

Cooling phases were considered more definitive than heating phases because the time required for cooling and therefore the radiant heat loss from the apparatus was less.

Temperatures at six points within the storage chamber as well as the inlet and outlet fluid temperature and the fluid flow rates were carefully recorded. Measurements of the heat stored or recovered were based upon the chamber inlet and outlet fluid temperatures. Thus, the total flow path external to the storage chamber (to the water bath heat exchanger and return through the pump to the storage chamber) was considered a single radiator, the net effect of which was $T_{\text{out}} - T_{\text{return}}$.

The process used to calculate the heat recovered from the storage chamber and to compare the relative thermal storage properties of the candidate crosslinked PE pellets is summarized in these five steps:

1. Compute Q_r , the heat recovered ($T_{\text{out}} - T_{\text{return}}$) by integrating the inlet and outlet temperature versus mass curves.

2. Compute the contribution to Q_r from sensible heat storage by the glycol: $Q_g = M_g \cdot C_g \cdot \Delta T$

where M_g = mass of glycol in the chamber

C_g = specific heat of glycol

ΔT = average temperature change through the cooling cycle

3. Compute the contribution to Q_r from sensible heat storage by the polyethylene: $Q_p = M_p \cdot C_p \cdot \Delta T$

where M_p = mass of polymer in chamber

C_p = specific heat of polymer

ΔT = average temperature change through the cooling cycle

4. Determine Q_A , the net heating effect of the storage chamber apparatus exclusive of polymer and heat exchange fluid (discussed below).

5. Compute the net phase change heat, Q_F , recovered:

$$Q_f = Q_r - (Q_p + Q_g) \text{ and}$$

$$\Delta H_f = Q_F / M_P$$

In order to measure the energy stored by the TES pellets, the net effect of the mass of the storage chamber apparatus, exclusive of the heat exchange fluid and the polymer, was considered. Since sensible heat was stored by the apparatus during heating and lost to both the heat exchange fluid and to the outside air during cooling, the net effect of the apparatus, Q_A , negative or positive, depended upon cooling time. When the cooling time was short, the energy stored by the apparatus was greater than that lost by radiation and the net effect was an increase in recovered heat. Conversely, when lower discharge rates and longer cooling times were used, the effect was reversed.

Tests were made to determine Q_A as a function of time by heating and cooling the column at several different rates, using only ethylene glycol. Approximate values for Q_A were determined for the one gallon (4-liter) apparatus. The experimental determinations of Q_A showed significant variations probably caused by differences in ambient temperature and drafts. Because the mass of the apparatus was large compared to that of the glycol, errors in the determined Q_A values were translated to proportionally larger errors in the calculated heat of fusion, and the one gallon (4-liter) TES values for ΔH_f should not be considered absolute. However, approximate ΔH_f values, determined from tests with cooling times similar to those used in determining a common Q_A , would provide a valid means of comparing ΔH_f properties of the candidate TES materials, and this process was used.

3.3.3 60 Gallon Prototype Model TES Test Unit

3.3.3.1 Design and Construction

The design of the 60 gallon prototype test model was similar to that of the lab unit but larger in scale, with the components upgraded for continuous automated operation. A schematic drawing of the unit showing the component locations, flow paths and monitoring points is shown in Figure 16. The unit cycles continuously between heating and cooling phases, switching automatically at predetermined outlet temperatures of 140° and 115°C.

The function of the unit was as follows: During the heating (storage) cycle for the TES material, the pump circulated ethylene glycol (heat exchange fluid) through the array of electrical heaters (Figure 17-a), which heated the liquid from 115°C (after the first cycle started at 23°C) to approximately 140°C. Ethylene glycol was then circulated in series through the storage tank (Figure 17-b) where the form-stable polyethylene pellets were heated through their phase change by the circulating fluid until the temperature at the outlet

Figure 16. Schematic drawing of the automated 60 gallon (200 liter) TES unit

(a) 18 KW heater

(b) 60 gallon TES chamber

Figure 17. Views of the 60 gallon TES prototype test unit

of the storage tank reached 140°C. The heating cycle took approximately 1 hour. The fluid direction was then reversed in the storage tank and the hot glycol diverted through the water-cooled, four pass shell and tube heat exchanger, shown in Figure 18-a.

The cooling cycle required approximately 20 minutes. When the temperature of the ethylene glycol solution at the outlet (top) reached 115°C, the solenoid valves were reversed and the heating cycle again initiated.

A stainless steel gear pump (Figure 18-b) with a variable speed Reeves drive was originally selected as most appropriate for the desired controlled pumping rate. The pump was rated for delivery of up to 18 GPM (68 liters/min) of fluid at 1750 RPM motor speed. The flow system was equipped with a pressure relief valve and a pressure switch designed to stop the system in case of an accidental overpressure. A flowmeter was provided for visual indication of the ethylene glycol flow.

Heating of the ethylene glycol fluid was accomplished with a bank of six immersion (230 volts) electrical heaters rated at 18 KW. The heaters were selected to give a maximum power density of 30 watts/in.². This is the maximum heating density recommended for the ethylene glycol (boiling and cavitation occur at higher heating densities).

Power input to the heaters was controlled by a Fenwell thermocouple temperature controller. High temperature cutout was provided in case of accidental malfunction of the immersion heaters.

Liquid flow direction control in both heating and cooling loops was accomplished with six stainless steel solenoid valves. Three of the valves were normally open and three were normally closed. Temperature switches located at the top and bottom outlets of the storage tank controlled the position of the solenoid valves.

The TES storage tank (Figure 19-b) is a 60-gallon (200-liter), stainless steel tank rated at 75 psig. The top of the tank has a removable lid for easy access to the TES material. The top of the tank is also connected to a 12-gallon (45-liter) expansion tank designed to accommodate the thermal expansion of ethylene glycol and the polyethylene pellets that totaled at least 10%.

Cooling of the ethylene glycol was accomplished in a four pass stainless steel shell and tube heat exchanger. Temperature control of the water cooling medium is provided by a temperature switch located at the cooling water outlet. Recirculating

(a) Water-cooled heat exchanger unit to provide cooling times of ~ 0.3 hour

(b) Reeves variable speed, constant volume gear pump with flow up to 18 GPM

Figure 18. Views of components for the 60 gallon prototype TES test unit

(a) Control panel and recorder

(b) Overall view

Figure 19. Components and a general view of the 60 gallon prototype TES test unit

ethylene glycol liquid is constantly filtered through a stainless steel filter. An indicator was provided to monitor the operating pressure of the unit.

The TES assembly is mounted on a 3 ft. x 7 ft. (1 m. x 2 m.) steel platform that readily can be transported. The operating controls and recorder were mounted in a electrical panel integral with the test stand (Figure 19-a). For operation of the unit, 230 volts, 3-phase, 60 cycle, 50 ampere electrical power and city water connections are required. The assembled TES unit before being insulated is shown in Figure 19-b. Three inches of asbestos/cement boiler insulation was applied to the storage tank and heat chamber.

This TES storage test unit was designed to be a versatile test instrument. Heating and cooling and the heat exchange fluid rates can be varied. These capabilities were necessary for an accurate definitive characterization of the energy storage achieved, and to optimize the various design parameters. It is important to note that the design of a production TES system would be considerably less complicated, and hence less costly.

4. RESULTS AND DISCUSSION

This section describes in detail the results obtained in the development of the form stabilized HDPE TES products. Included are analytical characteristics of the unmodified HDPE's, as well as the crosslinked PE's, and thermal performance of the prime candidate TES materials in prototype beds.

4.1 ANALYTICAL EVALUATION OF HDPE AND CROSSLINKED PE PRODUCTS

The analytical characterization and evaluation of the various PE's is discussed in the following order: (1) baseline or unmodified HDPE's; (2) C-C crosslinked PE products; (3) Si-O-Si crosslinked PE products, and (4) secondary treatments of the above resins and products, such as incorporation of fillers.

4.1.1 Characterization of Unmodified HDPE Resins

At the beginning of this work, a number of manufacturers of high density polyethylene were contacted for samples of their resins. Since the density of polyethylene is directly proportional to its crystallinity (and hence its heat of fusion) only the highest density PE resins were chosen for examination as TES materials.

Table I lists the important physical properties (related to use as TES materials) and source of a number of candidate HDPE resins. The density and melt index data were supplied by the manufacturer, and the thermal properties determined by DSC in our laboratory. These HDPE resins encompassed a wide molecular weight range as evidenced by melt indices (M.I.) from 0.15 to 8.0; however, these differences produced essentially no effect on the ΔH_f of the uncrosslinked polyethylene resins.

The variation in heat of fusion (ΔH_f) among the candidates was not large and served to eliminate only the lowest from further consideration. These ΔH_f values, while not as high as some reported in the literature¹, corresponded favorably to those reported for highly crystalline PE's as determined by DSC under comparable instrument operating conditions.³

As shown in Table I, the recrystallization temperature, T_c (peak), of these HDPE resins occurred as much as 10-15°C below the crystalline melting temperature, T_m (peak). However, this was not considered to be due to any "supercooling", as is frequently observed in the melting of inorganic salt-hydrates.

This difference in melting and recrystallization temperatures was not observed experimentally in the prototype TES unit, as will be later described in Section 4.2.2. There recrystallization was typically

Table I
PHYSICAL PROPERTIES OF CANDIDATE HDPE RESINS

Manufacturer	HDPE Resin Designation	Density ^a (g/cc)	Melt Index ^a (g/10 min)	Thermal Fusion Properties ^b		
				T _M (°C)	T _C (°C)	ΔH _f (cal/g)
Phillips Petroleum Co.	Marlex EHM 6001	0.960	0.15	133	120	44
Phillips Petroleum Co.	Marlex EHM 6006	0.964	0.75	132	121	48
Phillips Petroleum Co.	Marlex EMN 6030	0.964	3.0	132	120	47
Phillips Petroleum Co.	Marlex CL-100 (crosslinkable PE)	-	-	130	119	45
DuPont Co.	Alathon 7040	0.96	6.0 (narrow MWD)	132	120	47
U.S. Industrial Chemical Co.	Petrothene LS-606	0.962	8.0	132	111	47
U.S. Industrial Chemical Co.	Petrothene LB-747	0.959	0.8	133	115	45
Dow Chemical Co.	Resin 69065	0.965	0.60	133	117	44
Dow Chemical Co.	Resin 70065	0.965	0.70	133	112	44
Monsanto Co.	MPE 315	-	-	129	110	40

^aManufacturers data.

^bAs determined by DSC (at MRC) - T_M = melting temperature (peak).

T_C = recrystallization temperature (peak).
See Section 4.1.1

ΔH_f = heat of fusion.

observed at $\sim 130^{\circ}\text{C}$, the same temperature at which PE melting occurs. Thus the melting and recrystallization temperature differences observed in the DSC characterizations were due primarily to the DSC testing conditions themselves (rapid heating/cooling rates, inferior sample/probe contact, etc.). In the bulk of the work reported here, therefore, only T_M is given, as determined by DSC. DSC values of T_C (not given) generally ranged, as stated above, $10\text{--}15^{\circ}\text{C}$ below T_M .

The choice of HDPE resins to use in the production of cross-linked PE's was made on the basis of selecting PE's with the highest heats of fusion, covering a reasonable range of molecular weights. The first six HDPE resins listed in Table I were all used (at least to some extent) in making the cross-linked PE's for potential TES materials.

In the course of the work, additional DSC determinations of the thermal properties of these starting HDPE resins were made, as needed, for control values. They may have, in some cases, differed slightly from those cited in Table I, due to differences in sample lots of HDPE polymer, different DSC operating conditions, etc. Crosslinked PE product % ΔH_f retained values were always determined using identical polymer lots and DSC conditions as used for the corresponding controls.

4.1.2 Evaluation of Carbon-Carbon Crosslinked PE Products

The HDPE products chosen for evaluation were crosslinked in various ways, as described in Section 3.1.1, to enhance their form stability. These included incorporation of peroxide and thermal activation at (a) an elevated pressure via compression molding or (b) extrusion, or (c) at ambient pressure in a heated liquid medium (as outlined in Figure 20). One of the starting HDPE products (Marlex CL-100) contained a proprietary peroxide crosslinking agent; hence no added peroxide was used in crosslinking of this PE resin.

4.1.2.1 C-C Crosslinked PE Products Via Compression Molding Activated Peroxide Process

Table II shows a comparison of three HDPE resins, varying in molecular weights (melt indices). All were crosslinked by compression molding activation of dicumyl peroxide [which has a half-life of 0.15 hr at 150°C (302°F)], that had been incorporated by milling. There were some differences in absolute ΔH_f values among the four crosslinked HDPE resin products. Also, the % ΔH_f retained (of the sample's initial value) differed significantly among these samples, apparently varying somewhat

Figure 20. Illustration of processes for production of C-C crosslinked HDPE pellets

Table II

THERMAL PROPERTIES OF HDPE RESINS CROSSLINKED WITH DICUMYL PEROXIDE VIA COMPRESSION MOLDING

HDPE Resin	Melt Index (dg/min)	Concentration Dicumyl Peroxide (phr)	Thermal Form-Stability ^a		DSC Characterization ^b					ΔH_f Retained, (%)
			Pellets Flow on Melting	Pellets stick together on Melting	Cycle	T _M (°C)	ΔH_f (cal/g)	Ave. ΔH_f (cal/g)		
Petrothene LS-606	8.0	none	yes	yes (fused)	1 2	131 132	39.6 46.9	43	-	
Petrothene LS-606	8.0	0.5	no	yes (slightly)	1 2	130 129	41.1 39.6			40
Alathon 7040	6.0	none	yes	Yes (fused)	1 2 3	130 133 133	41.6 42.7 42.7	42	-	
Alathon 7040	6.0	0.5	yes	yes (slight)	1 2 3	131 130 130	35.4 35.7 33.8			35
Alathon 7040	6.0	1.0	no	no	1 2	128 129	31.9 31.0	31	75	
Marlex EMN 6030	3.0	none	yes	yes	1 2 3	131 132 133	42.3 46.1 45.4	45	-	
Marlex EMN 6030	3.0	0.5	no	no	1 2 3	129 128 128	35.5 35.5 34.1			35
Marlex EMN 6030	3.0	1.0	no	yes (v. slight)	1 2	130 128	31.3 30.4	31	67	
Marlex EMN 6006	0.8	none	yes (forms flat discs)	yes	1 2 3	132 134 134	39.6 45.8 46.6	44	-	
Marlex EMN 6006	0.8	0.5	no	no	1 2 3	126 127 127	31.5 32.8 31.2			32
Marlex EMN 6006	0.8	1.0	yes (v. slight at edges)	yes (v. slight)	1 2	121 120	28.9 26.9	28	64	

^aOn heating touching pellets in air to 200°C in Fisher-Johns m.p. apparatus.

^bDSC Conditions Used: 10°C/min. heating and cooling rate, range 8,
0.75 in./min chart speed, indium calibration
standard; T_M = melting temperature (peak),
 ΔH_f = heat of fusion.

T_C - See discussion Section 4.1.1 on T_M vs T_C .

inversely to molecular weight (or directly with melt index). This relationship is shown graphically in Figure 21. It should be emphasized that there may not be sufficient data (in terms of the range of molecular weights covered or number of HDPE samples included) to verify that this would always be the case. Other factors could also be involved.

Nevertheless, it did show that the HDPE resins of prime interest as potential TES materials were the highest melt index samples, USI's Petrothene LS-606 and DuPont's Alathon 7040. The latter resin, claimed by the manufacturer to be of a narrow molecular weight distribution, appeared to offer a potential advantage of greater product uniformity in the crosslinked product. Subsequent crosslinking studies were carried out with both of these HDPE resins.

The production of C-C crosslinked PE using the Alathon 7040 and the Petrothene LS-606 HDPE resins as starting materials was investigated with varying concentrations of different peroxide crosslinking agents. Typical results are given in Tables III and IV. (Additional data on crosslinking of these two resins may be found in Tables B-I and B-II in Appendix B.)

In the crosslinking of Alathon 7040 with dicumyl peroxide (DCP), which has a half-life of 9 min at 150°C, it was found that 0.5 parts per hundred resins (phr) peroxide concentration was sufficient to achieve form-stability and still retain nearly 80% of the resin's initial heat of fusion value (Table III). The slightly higher ΔH_f and poorer form stability attained with 0.75 phr DCP suggests that some DCP may have been lost in the addition process. The use of Lupersol 101 peroxide (half life of 24 min @145°C) resulted in a significantly higher ΔH_f being attained at a comparable level of form-stability. These (and other similar results) suggested its use, in preference to DCP, in a scale-up (to a 5 lb evaluation quantity) of this process for making a C-C crosslinked Alathon 7040 resin TES material.

The C-C crosslinked PE products prepared using Petrothene LS-606 (Table IV) as the starting HDPE resin all exhibited excellent retention of their initial ΔH_f value; however, none of them were as completely form-stable as desired. All exhibited some tendency to "stick" together. Again, the use of comparable levels of Lupersol 101 peroxide in crosslinking resulted in a higher ΔH_f retention, but the "form-stability" was less than optimum.

The combined effect of half-life differences (Lupersol 101 being slower to decompose), and molar concentration differences at the same weight level used (Lupersol 101 being ~93% of that of DCP) may well account for the observed product differences.

Figure 21. Melt Index vs. % ΔH_f retained for HDPE resins crosslinked with 0.5 phr dicumyl peroxide via compression molding

Table III

THERMAL PROPERTIES OF C-C COMPRESSION MOLDED CROSSLINKED ALATHON 7040 HDPE RESIN

Peroxide Crosslinking Agent		Thermal Form-Stability ^b		DSC Characterization ^c				
Name	Concentration (phr)	Pellets Flow on Melting	Pellets Stick Together on Melting	Cycle	T _M (°C)	ΔH _f (cal/g)	Ave. ΔH _f (cal/g)	ΔH _f Retained (%)
none	-	yes	yes (fused)	1	130	41.6	42	-
				2	133	42.7		
				3	133	42.7		
dicumyl peroxide	0.25	yes (v. slight)	yes (slightly)	1	130	34.4	36	86
				2	131	36.8		
dicumyl peroxide	0.50	no	no	1	129	33.4	33	79
				2	129	32.5		
dicumyl peroxide	0.75	no	yes (slightly)	1	130	34.2	34	81
				2	129	34.2		
dicumyl peroxide	1.0	no	yes (slightly)	1	128	31.9	20	76
				2	129	31.0		
Lupersol 101 ^a	0.5	no	yes (slightly)	1	134	40.9	40	95
				2	132	38.8		

^aTradename for 2,5 dimethyl-2,5-bis(t-butylperoxy) hexane (Lucidol Division, Pennwalt Corporation).

^bTouching pellets heated in air to 200°C on Fisher-Johns m.p. apparatus.

^cDSC Conditions Used: 10°C/min heating and cooling rate, range 8, 0.75 in./min chart speed, indium calibration standard; T_M = melting temperature (peak), ΔH_f = heat of fusion.

T_C - See Section 4.1.1 for discussion of T_M vs T_C.

Table IV

THERMAL PROPERTIES OF C-C COMPRESSION MOLDED CROSSLINKED PETROTHENE LS-606 HDPE RESIN

Peroxide Crosslinking Agent		Thermal Form-Stability ^b		DSC Characterization ^c				
Name	Concentration (phr)	Pellets Flow on Melting	Pellets Stick Together on Melting	Cycle	T _M (°C)	ΔH _f (cal/g)	Ave. ΔH _f (cal/g)	ΔH _f Retained (%)
none	-	yes	yes (fused)	1	129	39.5	45	-
				2	132	47.7		
				3	133	46.7		
dicumyl peroxide	0.3	yes (slightly)	yes (firmly)	1	130	42.4	42	93
				2	130	41.0		
dicumyl peroxide	0.5	no	yes (slightly)	1	131	41.4	41	91
				2	131	39.9		
dicumyl peroxide	0.7	no	yes (slightly)	1	130	41.2	41	91
				2	130	40.2		
Lupersol 101 ^a	0.3	yes (slightly)	yes	1	130	43.5	44	98
				2	130	44.0		
Lupersol 101	0.5	no	yes (firmly)	1	132	44.5	44	98
				2	131	43.0		
Lupersol 101	1.0	no	yes	1	131	44.1	43	96
				2	129	41.6		

^a2,5 dimethyl-2,5-bis(t-butyl peroxy) hexane^bTouching pellets heated in air to 200°C on Fisher-Johns m.p. apparatus.^cDSC Conditions Used: 10°C/min heating and cooling rate, 0.75 in./min chart speed, indium calibration standard; T_M = melting temperature (peak), ΔH_f = heat of fusion (crystalline melting).T_C - See Section 4.1.1 for discussion of T_M vs T_C.

Figure 22 shows the variations observed in % ΔH_f retained with increasing concentration of dicumyl peroxide initiator for both the LS-606 and Alathon 7040 HDPE resins. While the LS-606 resin demonstrated higher ΔH_f retention, form-stability at comparable peroxide levels was not as good. In order to achieve equivalent form-stability, additional crosslinking agent would be required, which in turn would further reduce the ΔH_f value. The differences observed between these resins may be due at least in part to their different molecular weights and molecular weight distributions. This could be particularly true if the Petrothene LS-606 contained a high portion of low molecular weight polymer. The Alathon 7040 reportedly has a narrow molecular weight distribution.

The use of Alathon 7040 PE as a starting material for TES products thus appeared to offer, among the various HDPE resins examined, a good balance of properties in terms of heat of fusion retained and form-stability achieved. Additional data comparing it to some of the other crosslinked PE products, particularly on melt-freeze cycling in ethylene glycol, is given in Table B-III of Appendix B and supports this choice. It was therefore used in most of the subsequent work, particularly in scale-up to 5 lb batches for TES prototype evaluations.

4.1.2.1.1 Marlex CL-100 HDPE Crosslinking

One additional HDPE resin crosslinked via compression molding to produce a C-C crosslinked products was Phillip's Marlex CL-100, which contains a proprietary crosslinking agent. Thus, no peroxide was added to it, prior to compression molding (or any other crosslinking procedure undertaken with it). Results are given in Table V, which also contains data on the other crosslinking procedures employed with this HDPE resin.

Adequate form stability was achieved with the compression molded samples of this HDPE resin. However, ΔH_f values (and % ΔH_f retained) were low, relative to results achieved with other HDPE resins, regardless of molding conditions. Since there is no control over the amount of crosslinking agent present, further modification to improve the ΔH_f achieved after crosslinking via compression molding was not possible. The results of other methods of crosslinking this HDPE resin will be discussed subsequently in sections 4.1.2.2 and 4.1.2.3.

4.1.2.2 C-C Crosslinked Products Via Extrusion Activated Peroxide Process

The second major process by which C-C crosslinked PE was produced was via extrusion activation of HDPE containing a peroxide.

Figure 22. Example of % ΔH_f retained with increasing DCP concentration for two different compression-molded crosslinked PE products - one with good form stability (Alathon 7040) and one with inadequate form stability (LS-606).

Table V

THERMAL PROPERTIES OF C-C CROSSLINKED PHILLIF'S MARLEX CL-100 HDPE RESIN

Crosslinking Method	Thermal Form-Stability ^a		DSC Characterization ^b				
	Pellets Flow on Melting	Pellets Stick Together on Melting	Cycle	T _M (°C)	ΔH _f (cal/g)	Ave. ΔH _f (cal/g)	ΔH _f Retained (%)
none	yes	yes	1	127	39.9	42	-
			2	130	44.6		
Heat to 208°C for 15 min in DC-200 silicone fluid (with stirring)	no	no	1	128	32.5	33	79
			2	128	33.0		
Compression mold-15 min/350°F	no	no	1	124	26.9	27 ^c	64
			2	123	27.1		
Compression mold-30 min/350°F	no	no	1	124	29.1	29 ^c	69
			2	123	29.0		
Compression mold-15 min/400°F	no	no	1	123	27.5	27	64
			2	122	27.3		
Extrude ~140°C	yes	yes	-	-	-	-	-

^aOn heating touching pellets in air to 200°C in Fisher-Johns m.p. apparatus.

^bDSC Conditions Used: 1.25°C/min heating and cooling rate, range 4, 0.75 in./min chart speed, indium calibration standard; T_M = melting temperature (peak), ΔH_f = heat of fusion; T_C - see Section 4.1.1 for discussion of T_M vs T_C.

^c10°C/min heating and cooling rate, range 8, used for these samples.

The primary reason for attempting to produce form-stable PE TES materials in this manner was the advantage it would offer in process simplification for scale-up to any large production. Alathon 7040 was the primary HDPE resin used for this process. Results are given in Table VI.

The main differences observed among the extruded products obtained related to the relative smoothness of the extruded strand. If the extruded strand was smooth in appearance (as it is normally, in extrusion of uncrosslinked PE), then the product pellets were not completely form-stable, and flowed to some extent on melting. On the other hand, if the extruded rod was "spiralled" (an indication that melt fracture was occurring and that the polymer was crosslinking in the extruder), then the pellets were form-stable and did not flow on melting. Figure 23 shows typical examples of these spiralled Alathon 7040 extruded rods and pellets chopped from them.

Better results could be achieved, and the process simplified even further, when the peroxide was incorporated via tumble-blending of the pellets with peroxide (in an inert diluent at RT) as opposed to peroxide incorporation on a hot mill roll. Also, the Lupersol 130 peroxide (which is somewhat less reactive than the Lupersol 101 peroxide) proved to be more effective at a lower concentration level than the Lupersol 101, if adequately high extruder temperatures were maintained. The processing conditions given for the last sample listed in Table VI were essentially those used to produce five pounds of a C-C cross-linked Alathon 7040 HDPE (via extrusion activation of peroxide) for further testing as a candidate TES material.

As indicated previously in Table V, extrusion of the Phillip's Marlex CL-100 crosslinkable PE at $\sim 140^{\circ}\text{C}$ did not result in a form-stable product. Quite possibly the extrusion temperature was too low and/or the dwell time in the extruder too short to be effective in activating the crosslinking agent contained in this HDPE. No additional work was performed to extrusion crosslink the Marlex CL-100 HDPE resin.

4.1.2.3 C-C Crosslinked PE Products Via Heated Liquid Activated Peroxide Process

The remaining method used for production of C-C crosslinked PE was thermal activation of peroxide in a heated liquid medium (containing pellets) at atmospheric pressure. The peroxide either was first incorporated into the PE or simply added to the liquid medium.

(a) "Spiralled" rod produced
in extrusion process

(b) Spiralled rod and pellets
chopped from it

Figure 23. Spiralled rods and chopped pellets of C-C crosslinked Alathon 7040 HDPE produced via extrusion - activated peroxide process

Table VI

THERMAL PROPERTIES OF EXTRUSION CROSSLINKED ALATHON 7040 HDPE

<u>Crosslinker</u> <u>Type</u>	<u>Concentration</u> <u>(phr)</u>	<u>Blending</u> <u>Cond.</u>	<u>Extruder</u> <u>Die Temp.</u> <u>(°C)</u>	<u>Ext'd. Rod</u> <u>Appearance</u>	<u>Pellets</u> <u>Flow on Melting</u>	<u>T_M^c</u> <u>(°C)</u>	<u>ΔH_f^c</u> <u>(cal/g)</u>	<u>Retained</u> <u>ΔH_f</u> <u>(%)</u>
	none	-	-	smooth	yes	132	46	100
Lupersol 101 ^a	0.5	hot mill	175	spiral	no	132	39	84
Lupersol 101	0.5	RT/wet	145	smooth	yes	-	-	-
Lupersol 101	0.5	RT/wet	165	spiral	slightly	130	36	78
Lupersol 130 ^b	0.5	hot mill	180	smooth	slightly	134	45	98
Lupersol 130	0.5	hot mill	200	rough	v. slightly	132	40	87
Lupersol 130	0.5	RT/wet	175	spiral	no	130	35	76
Lupersol 130	0.25	RT/wet	175	spiral	no	132	38	83

^a2,5 dimethyl-2,5, bis-(t-butyl peroxy) hexane (half-life = 24'/145°C).

^b2,5 dimethyl-2,5, bis (t-butyl peroxy)-hexyne-3 (half-life = 18'/160°C).

^cby DSC characterization - 10°C/min heating and cooling rates.

4.1.2.3.1 Liquid Medium $>T_M$ of PE

If the peroxide crosslinking agent was already incorporated into the HDPE (as is the case with the Marlex CL-100 resin which contains a proprietary crosslinking agent), the PE was then crosslinked by heating in a liquid medium above its melting point. Results of this approach are shown in Table V for Marlex CL-100 resin. Good form-stability was achieved with retention of nearly 80% of the PE's initial ΔH_f value.

However, the major problem encountered with this method was that in heating the PE above its m.p. severe agglomeration occurred, and most of the crosslinked PE product ended up in the form of a large lump, rather than individual pellets. Vigorous agitation during the entire procedure did not remedy the problem, and hence it was concluded that this method was not practicable on a larger scale.

4.1.2.3.2 Liquid Medium $<T_M$ of PE

In view of the above results, an alternate approach was taken to producing form-stable crosslinked PE products by simply heating in a liquid medium. This was to keep the temperature of the liquid below the T_M of the PE; hence there would be no melting of the pellets and no chance for agglomeration. Since a peroxide which is activated at a temperature below T_M would have to be used, it was not incorporated into the PE, but simply added to the liquid. This would, of course, confine any crosslinking that might occur to the surfaces and outer layers of the PE pellets.

The results obtained using this method of crosslinking PE pellets are summarized in Table VII. Additional data on "surface" crosslinking of Alathon 7040 alone is given in Table B-V, Appendix B. The effect of various molecular weights of the HDPE resin starting material was examined.

Essentially, the results obtained showed excellent ΔH_f retention with this process and some increase in pellet form-stability, which was at least minimally affected by the starting PE molecular weight. The higher molecular weight (lower M.I.) PE pellets demonstrated slightly superior form stability on melting than did the lowest molecular weight (highest M.I.) PE. However, in no case was sufficient form-stability achieved to consider these crosslinked pellets as really useful TES materials. Any crosslinking which had occurred was probably limited to the pellet surfaces, and was not sufficient to give the desired form-stability.

Table VII
THERMAL CHARACTERISTICS OF SURFACE CROSSLINKED HDPE'S
 (2 phr benzoyl peroxide)

<u>HDPE Resin</u>	<u>M.I.</u> <u>(dg/min)</u>	<u>Form-Stability^b</u>		<u>Pellets</u> <u>stick</u> <u>together</u> <u>on Melting.</u>	<u>DSC Characterization^c</u>		
		<u>Reflux Time^a</u> <u>(hr)</u>	<u>Melting Character</u> <u>of Pellets</u>		<u>T_M</u> <u>(°C)</u>	<u>ΔH_f</u> <u>(cal/g)</u>	<u>ΔH_f</u> <u>Retained</u> <u>(%)</u>
Marlex 6006	0.75	6	slight flattening	v. slightly	131	43	96
Marlex 6030	3.0	6	slight flattening	slightly	131	43	98
Alathon 7040	6.0	6	slight flow	slightly	131	45	98
Alathon 7040	6.0	24	v. slight flow	slightly	131	44	96

^a PE pellets in refluxing H₂O containing benzoyl peroxide + Pluronic F-68 surfactant.

^b On heating touching pellets in air to 200°C on Fisher-Johns m.p. apparatus.

^c DSC Conditions Used: 10°C/min heating and cooling rates, 0.75 in./min chart speed, range 8, indium calibration standard; T_M = melting temperature (peak); ΔH_f = heat of fusion; ΔH_f retained - compared to control values of 45, 44, and 46 cal/g for Marlex EHM 6006, EMN 6030, and Alathon 7040 respectively.

T_C - See Section 4.1.1 for discussion of T_M vs T_C.

One possible way of rendering these surface crosslinked PE pellets more useful for TES applications would be to put them through a single melting step, after the initial surface-crosslinking, to "set" their final pellet shape. This also would reduce the simplicity of the process, which was one of its chief advantages.

4.1.3 Evaluation of Si-O-Si Crosslinked PE Products

The second major type of crosslinked HDPE examined as a potential TES material was that which contained a siloxane (-Si-O-Si-) bond between the polyethylene backbone chains. Preparation of this type of crosslinked PE is described in Section 3.1.2.

There are two major differences between this type of cross-linked PE product and the C-C crosslinked PE products. These are: (1) crosslinking in this system occurs below the PE melting point and hence largely in the amorphous regions, leaving the polymer's crystallinity essentially unaffected; and (2) the Si-O-Si linkage between PE chains is no doubt a more "flexible" one than is the C-C linkage of two PE backbone molecules, and thus subsequent melting and recrystallization (after crosslinking) may be expected to occur without significant loss of crystallinity. Both of these factors would influence the heat of fusion obtained and thus potential utility was a TES material.

Table VIII summarizes the process conditions used and the results obtained in the preparation of a number of small batches of silane-grafted (and crosslinked) PE. Additional data is given in Tables B-VI, B-VII and B-VIII, Appendix B. The HDPE resin chosen for use in much of this work was Alathon 7040, one of the prime reasons being that its melt index (6.0) falls in the recommended range of 5-10.⁴ Also, good results were achieved with it, in terms of form-stability enhancement and high ΔH_f retention, in the C-C crosslinked PE products.

The first PE resin listed in Table VIII is a commercially available (Nortech Division of Northern Petrochemical Co.) silane-grafted low density polyethylene (LDPE). It was co-extruded with a catalyst-containing LDPE (also from Nortech) and crosslinked in boiling H₂O. Although form-stability was achieved, the low density of the starting resin precluded attainment of a high ΔH_f value. Hence this material is included solely as a reference base.

Silane-grafting of a HDPE resin (Alathon 7040) was therefore undertaken following published procedures.⁴ A number of silane-grafted samples of Alathon 7040 were preparing using a steam-heated mill roll for grafting, with subsequent crosslinking in boiling H₂O. Retention of the PE's original ΔH_f was excellent, but form-stability was not as good as desired, even with the use of a relatively high vinyl triethoxysilane (VTS) concentration.

Table VIII

THERMAL PROPERTIES OF SILANE-GRAFTED AND CROSSLINKED PE

Starting PE Resin	Silane-Grafting Process ^(a)		Crosslinking Process	Pellets Flow on Melting	DSC Characterization ^(c)			
	VTS Conc. (phr)	Grafting/Catalyst Incorporation			^(b) T_M (°C)	ΔH_f (cal/g)	ΔH_f (d) Retained (%) (crosslinked)	Melt Index ^(e) (g/10 min/190°C)
Norchem XLM	-	Commercial silane-grafted LDPE co-extrude with catalyst-containing LDPE (95/5 ratio) at MRC	1. none	yes	99	11	-	2.0
			2. 30 min/boiling H ₂ O	no	100	14	100	-
Alathon 7040	3	Graft via hot milling and co-extrude with catalyst-containing (1 phr DBTDL) Alathon 7040 (95/5) ratio	1. none	yes	132	44	-	-
			2. 72 hr/boiling H ₂ O	v. slightly	131	46	100	-
Alathon 7040	10	Graft via hot milling and co-extrude with catalyst-containing (1 phr DBTDL) Alathon 7040 (95/5 ratio)	1. none	yes	132	45	-	1.8
			2. 48 hr/boiling H ₂ O	v. slightly	132	46	100	not obtainable
Alathon 7040	8	Graft via hot-melt Banbury mixing and co-extrude with catalyst-containing (1 phr DBTDL) Alathon 7040 (95/5 ratio) (5 lb batch prepared)	1. none	yes	131	43	-	1.65
			2. 40 hr/boiling H ₂ O	no	132	43	93	not obtainable

(a) VTS = vinyl triethoxysilane; DBTDL = dibutyltin dilaurate

(b) Pellets heated in air to 200°C in Fisher-Johns m.p. apparatus.

(c) DSC Conditions Used: 10°C min heating and cooling rates, range 8, 0.75 in./min chart speed, indium standard, T_M = melting temperature (peak); ΔH_f = heat of fusion; T_C - see discussion Section 4.1.1 on T_M vs T_C .

(d) As compared to ΔH_f of starting PE resin.

(e) ASTM D-1238.

It was found, however, that use of a Banbury mixer (which is a closed system, thus preventing loss of silane) was a preferred way to carry out silane grafting onto the molten PE. Good form-stability was achieved, along with very high retention of ΔH_f in the crosslinked product. Accordingly, a five pound sample of the silane-grafted and crosslinked PE, corresponding to the last sample listed in Table VIII, was prepared for evaluation in the lab-scale TES prototype unit.

Subsequently, after preliminary evaluation of three candidate TES materials (Section 4.2.2) in the 1 gallon lab-scale TES unit, this silane-grafted and crosslinked Alathon 7040 HDPE was chosen for further evaluation in the 60 gallon prototype TES unit. It was then prepared in ~250 pound quantity, as described in Section 3.1.2.1. Several processing improvements and simplifications were made based on results of preliminary ~5 lb batches were made in the large Banbury mixer (see Table B-VIII, Appendix B). These included reduction of the VTS requirement to 6 phr (from 8 phr).

It is anticipated that further processing improvements could yet be made, thus further simplifying the large-scale production of this potentially useful TES material. The unique combination of high retention of crystallinity (and hence heat of fusion) combined with very good form-stability exhibited by this Si-O-Si crosslinked HDPE product makes it an especially attractive candidate for TES applications.

4.1.4 Additional Treatments of Crosslinked PE Products

Two additional treatments of the crosslinked PE products were carried out:

- a. Addition of "fillers" to the crosslinked PE products, activated via compression molding, primarily for the purpose of improving thermal conductivity in the PE pellets.
- b. Annealing or thermal treatment of both peroxide- and silane-grafted/crosslinked PE's for the purpose of possibly increasing ΔH_f in the crosslinked product and/or removing residual mechanical stresses.

The results of each of these treatment will be described only briefly in this section, as neither brought about any significant product improvement, and their use is not now considered essential for the success of a PE pellet TES bed material.

4.1.4.1 Incorporation of Fillers into C-C Crosslinked PE

The results of adding small quantities of finely divided carbon black and aluminum powder fillers into crosslinked Alathon 7040 and Petrothene LS-606 HDPE's are given in Tables IX and X. The results obtained with addition of small amounts (0.5-4.0 phr) of either carbon black or aluminum to the C-C crosslinked Alathon 7040 had an adverse affect on both sample appearance and tendency of the pellets to self-adhere on melting. The latter effect was most pronounced at the lowest filler concentrations. There was some decline in ΔH_f also, with increasing filler concentration (though not consistently, which may indicate poor sample uniformity). Overall, results were not encouraging, particularly in view of probable requirements for much higher filler concentrations, with increased heat transfer capabilities as the goal.

Essentially similar results were obtained with the C-C cross-linked Petrothene LS-606 samples containing these same fillers as shown in Table X. The effect on ΔH_f with increasing filler concentration was less pronounced than with Alathon 7040, but sample appearance and pellet self-adhesion were worse - particularly with the aluminum powder as filler.

Overall, use of a filler, in quantities sufficient to effect improvement in heat transfer characteristics of the crosslinked HDPE, would not be expected to have benefits otherwise (in terms of desirable thermal properties, such as ΔH_f retention and form-stability), but would have degrading effects instead. Subsequently, results of evaluation of prime candidate cross-linked PE TES materials in the 1 gallon TES unit indicated that heat transfer properties of the unmodified pellets were satisfactory, and no "fillers" were needed to improve them. Hence, this aspect of the work was not pursued further.

4.1.4.2 Annealing or Thermal Treatments of Crosslinked PE Products

Another "treatment" of PE products aimed at improving ΔH_f and form retention was annealing (or other thermal treatment). Both C-C and Si-O-Si crosslinked and the corresponding uncross-linked PE's were examined.

Some effects of thermal treatments of the uncrosslinked HDPE's are given in Table XI-A and on subsequently crosslinked HDPE's in Table XI-B. In neither case were results encouraging. A slight increase noted in the first DSC melting cycle after thermal treatment (Table XI-A) did not persist through subsequent melting cycles. This being the case, it would be expected that subsequent crosslinking (during or after the first melt cycle) would produce no substantial improvement in

Table IX

EFFECT OF FILLERS^(a) ON THERMAL PROPERTIES OF C-C CROSSLINKED ALATHON 7040 HDPE

Filler ^(b)	Conc. (phr)	Sample Appearance	Pellets ^(c) Stick Together on Melting	DSC Characterization ^(d)		
				T _M (°C)	ΔH _f (cal/g)	ΔH _f Retained ^(e) (%)
none	-	fairly smooth surface	no	132	38	83
Carbon black	0.5	somewhat pitted surface	slightly	129	34	74
Carbon black	1.0	somewhat pitted surface	v. slightly	130	35	76
Carbon black	2.0	somewhat pitted surface	no	129	37	80
Carbon black	4.0	somewhat pitted surface	no	124	27	59
Aluminum powder	0.5	smooth surface	v. firmly	131	41	89
Aluminum powder	1.0	pitted surface	v. firmly	130	34	74
Aluminum powder	2.0	fairly smooth surface	slightly	128	33	72
Aluminum powder	4.0	smooth surface	v. slightly	128	30	65

(a) Filler + Lupersol 101 peroxide (0.5 phr) hot milled into PE, then samples compression molded 30 min/350°F and pelletized.

(b) Carbon, black - Cabot's Black Pearls; Aluminum powder - Merk.

(c) After heating touching pellets in air to 200°C on Fisher-Johns m.p. apparatus.

(d) DSC Conditions Used: 10°C/min heating and cooling rate = 0.75 in./min chart speed, indium calibration standard;
T_M = melting temperature (peak); ΔH_f = heat of fusion.
T_C = See Section 4.1.1 for discussion of T_M vs T_C

(e) As compared to ΔH_f of 46 cal/g for uncrosslinked Alathon 7040 control.

Table X

EFFECT OF FILLERS^(a) ON THERMAL PROPERTIES OF C-C CROSSLINKED PETROTHENE LS-606

Filler ^(b)	Conc. (phr)	Sample Appearance	Pellets ^(c) Stick Together on Melting	DSC Characterization ^(d)		
				T _M (°C)	ΔH _f (cal/g)	ΔH _f Retained ^(e) (%)
none	-	fairly smooth surface	v. slightly	131	40	85
Carbon black	0.5	pitted surface, color not uniform	firmly	130	39	83
Carbon black	1.0	pitted surface	v. slightly	131	39	83
Carbon black	2.0	pitted surface	v. slightly	130	38	81
Carbon black	4.0	pitted surface	v. slightly	130	39	83
Aluminum powder	0.5	very pitted surface	v. slightly	132	41	87
Aluminum powder	1.0	pitted surface	v. firmly	130	36	76
Aluminum powder	2.0	pitted surface	v. firmly	128	35	73
Aluminum powder	4.0	pitted surface	v. firmly	130	39	83

(a) Filler plus dicumyl peroxide (0.5 phr) hot milled into PE, then compression molded 30 min/350°F/1000 psig.

(b) Carbon black - Cabot's Black Pearls; Aluminum powder - Merk.

(c) After heating touching pellets in air to 200°C on Fisher-Johns m.p. apparatus.

(d) DSC Conditions Used: 10°C/min heating and cooling rates- 0.75 in./min chart speed, indium standard, T_M = melting temperature (peak); ΔH_f = heat of fusion; T_C - see Section 4.1.1 for discussion of T_M vs T_C.

(e) As compared to ΔH_f of 47 cal/g for uncrosslinked Petrothene LS-606 control.

Table XI-A

EFFECT OF THERMAL TREATMENT ON ΔH_f OF UNCROSSLINKED HDPE

HDPE Resin	Thermal Treatment	Change in Value of ΔH_f after Treatment ^(a) (cal/g)	
		(1st DSC melting cycle) ^(b)	(2nd DSC melting cycle) ^(b)
Marlex EHM 6001	I. Annealed one week at 110°C	+2.1	none
Marlex EHM 6006	II. Annealed 2 days/122°C	+1.4	none
Marlex EHM 6006	III. Melted at 150°C and iso-thermally recrystallized (24 hr/125°C)	+1.5	-1.0
Marlex EMN 6030	Treatment II	none	-1.7
Marlex EMN 6030	Treatment III	-1.2	-2.3
Alathon 7040	Treatment II	+3.0	-1.7
Alathon 7040	Treatment III	+5.1	+0.6

(a) Comparison with control ΔH_f values for each resin (Table XI-B, or Table I).

(b) DSC Conditions Used: 1.25°C/min heating and cooling rates, range 4, 0.75 in./min chart speed, indium calibration standard; ΔH_f = heat of fusion.

Table XI-B
EFFECT OF THERMAL TREATMENTS ON C-C CROSSLINKED HDPE's

HDPE Resin	Thermal Pre-Treatment	Crosslinked ^(a)	Pellets Flow on Melting	DSC Characterization ^(b)		
				T_M (°C)	ΔH_f (cal/g)	ΔH_f Retained (%)
Marlex 6006	none	no	yes	134	46	-
Marlex 6006	none	yes	v. slightly	120	28	60
Marlex 6006	I, annealed 2 days/ 122°C	yes	no	124	29	64
Marlex 6006	II, Isothermally recrystallized at 125°C	yes	v. slightly	123	28	60
Marlex 6030	none	no	yes	133	46	-
Marlex 6030	none	yes	no	128	31	67
Marlex 6030	Treatment I	yes	no	123	29	64
Marlex 6030	Treatment II	yes	no	124	29	64
Alathon 7040	none	no	yes	133	43	-
Alathon 7040	none	yes	no	129	32	74
Alathon 7040	Treatment I	yes	no	129	34	80
Alathon 7040	Treatment II	yes	no	128	32	74

(a) Crosslinked via compression molding (30 min/350°F) activation of 0.1 phr dicumyl peroxide incorporated into PE on steam heated mill roll.

(b) DSC Conditions Used: 10°C/min heating and cooling rates, range 8, 0.75 in./min chart speed, indium calibration standard; T_M = melting temperature (peak); ΔH_f = heat of fusion.

ΔH_f over the untreated, crosslinked PE. Results given in Table XI-B do indeed bear out this expectation. Since all the work was carried out essentially simultaneously, the results given in Table XI-A were not known until those given in Table XI-B also had been obtained.

Although thermal treatments on PE products which were melted during the crosslinking could have no effect on improving ΔH_f , this would not necessarily be the case where crosslinking was done below the PE melting point. Hence, a brief investigation of the effect of annealing on silane-grafted PE's (before and after crosslinking) was undertaken. Results are given in Table XII.

Essentially, results were the same as with the C-C crosslinked PE products - very little increase in ΔH_f prior to crosslinking was observed, and no increase in the crosslinked ΔH_f either. It may be noted that the ΔH_f of the uncrosslinked silane-grafted control is the same as that of the starting Alathon 7040 resin itself, and a large increase in ΔH_f may simply not be achievable with this HDPE resin through annealing treatments.

Although not shown in Table XII, the same effect was noted here as previously in Table XI-A, namely an increase in ΔH_f on the first DSC melting cycle, which did not persist through subsequent DSC melting cycles (values as high as 50 cal/g were obtained on the first cycle, but declined to 46-48 on the 2nd and 3rd cycles).

4.2 LAB AND PROTOTYPE-BED EVALUATIONS OF TES PRIME CANDIDATES

From the analytical results on the various C-C and Si-O-Si crosslinked PE products described in Section 4.1, three prime candidate TES materials were selected for further evaluation. Defining the best of these three was done in the following manner:

- a. Small quantities (<100 g) were evaluated for long-term stability and durability by melt-freeze cycling and maintenance of the PE's in the melt (thermal analytical characterization via DSC was done to illustrate retained properties);
- b. the three candidate PE's were prepared in ~5 lb quantities and evaluated in a 1 gallon (4-liter) lab-scale TES unit for potential usefulness as TES materials;

Table XII

EFFECT OF THERMAL TREATMENT ON SILANE-GRAFTED/CROSSLINKED ALATHON 7040 PE

No.	Resin Description	Crosslinked (48 hr/Boiling H ₂ O)	Thermal Treatment	DSC Characterization ^(a)		
				T _M (°C)	ΔH _f (cal/g)	Increase in ΔH _f (%)
1	Silane-grafted PE pellets	no	none	132	47.0	(control)
2	Same as (1)	no	90 hr/90°C	132	47.7	1.5
3	Same as (2)	yes	same as (2) (prior to crosslinking)	132	47.6	1.3
4	Same as (1)	no	90 hr/110°C	133	47.5	1.1
5	Same as (4)	yes	same as (4) (prior to crosslinking)	131	48	2.1

^(a) DSC Conditions Used: 10°C/min heating and cooling rates, range 8, 20 mm/min chart speed, indium standard; T_M = melting temperature (°C); ΔH_f = heat of fusion.

T_C - See Section 4.1.1 for discussion of T_M vs T_C.

- c. one of these three was then selected for further scale-up evaluation and prepared in ~250 lb quantity for testing in a 60 gallon prototype TES test unit.

The three candidate TES materials selected were: (1) a compression molded thermal activated peroxide-crosslinked HDPE; (2) an extruded thermal activated peroxide-crosslinked HDPE; and (3) a silane-grafted and crosslinked HDPE. The latter was chosen for further evaluation in the 60 gallon TES unit. All three candidate TES materials used Alathon 7040 as the starting HDPE resin.

4.2.1 Long-Term Stability and Durability Characterization of TES Prime Candidates

As a baseline for long-term stability/durability testing of the prime candidate TES materials, complete analytical characterization was conducted on each, to serve for comparison with later test results. The characterization data are summarized in Table XIII.

While all three candidates showed ΔH_f retention >80% after crosslinking, the silane-grafted/crosslinked material (Sample 3) was clearly superior (91% retention of ΔH_f) to the C-C crosslinked PE's. It also, as expected, had the highest pellet density; in fact it was higher than the starting Alathon 7040 resin (probably due in part to addition of the Si-O-Si groups).

One other area in which the silane-grafted/crosslinked PE appeared to be superior to the C-C crosslinked products was that of sample uniformity. The uniformity was indicated by the narrow range of gel content values obtained with it ($\pm 4\%$) as opposed to the C-C crosslinked PE samples, which varied by up to $\pm 24\%$ in gel contents. All of the gel contents were lower than that normally observed in crosslinked PE's (i.e., 60-80%). Thus the objective of controlled, limited (i.e., less than usually used) crosslinking to maximize heat of fusion was achieved.

The three prime candidate TES materials were evaluated for long-term stability and durability (ΔH_f retention) as follows: (1) by melt-freeze cycling in ethylene glycol and (2) by continuous maintenance above their m.p. in refluxing ethylene glycol, as described in Section 3.3.1. The results of these evaluations are given in Table XIV.

Only a slight or no variation in ΔH_f was observed for any of the candidate TES materials for up to 700 melt/freezing cycles or 3186 hours (133 days) of continuous maintenance in the melt. The largest variation (either increasing or decreasing ΔH_f)

Table XIII
THERMAL FUSION AND OTHER PROPERTIES OF CROSSLINKED PE PRIME CANDIDATES AND PRECURSORS

TES Sample No.	Material Ref. No.	Crosslinking Conditions			DSC Characterization ^(a)			Gel Contents ^(c)		Melt Index ^(d) g/10 min/190°C	Pellet ^(e) Density (g/cc)
		Agent	Conc. (phr)	Process	T _M (°C)	ΔH _f (cal/g)	ΔH _f ^(b) Retained (%)	Average (%)	Range (%)		
1	Alathon 7040 (Lot 555526)	-	-	-	132	46	-	3.3	0-7	5.8	0.96
	198408	Lupersol 101	0.5	compression molded 30 min/350 psi	131	39	84	19	0-29	N.O.	0.950
2	Alathon 7040 (Lot 656015)	-	-	-	131	47	-	0	0-0.1	6.3	0.96
	198429-2	Lupersol 130	0.25	extruded @180°C	130	38	81	~20??	0-48	N.O.	0.947
3	198097 Alathon 7040 (Lot 656015)	Vinyl tri- ethoxy silane- grafted	8	not crosslinked	131	43	91	22	19-26	1.65	-
	198097-2	Vinyl tri- ethoxy silane- grafted	8	40 hr/boiling H ₂ O	132	43	91	44	39-47	N.O.	0.974

(a) DSC Conditions Used: 10°C/min heating and cooling rate, range 8, chart speed 20 mm/min., indium standard. ΔH_f values given are averages of 5 separate DSC samples. T_M = melting temperature (peak); T_C - see Section 4.1.1 for discussion of T_M vs T_C.

(b) As compared to ΔH_f for starting Alathon 7040 HDPE resin.

(c) After 16 hour extraction in refluxing ethyl benzene. Values are averages of 5 or more separate samples.

(d) ASTM D-1238. N.O. = not obtainable (could not be extruded).

(e) Densities by buoyancy method on pellets themselves - manufacturer's data given for starting Alathon 7040 resin.

Table XIV
LONG-TERM THERMAL DURABILITY AND STABILITY OF THREE TES PRIME CANDIDATE CROSSLINKED-HDPE SYSTEMS

TES Sample No.	Crosslinking System	Stability Test	No. of Melt/Freeze cycles or time in melt	Observations on Pellet Form Stability/Fusion		DSC Characterization ^(a)			Overall Change in ΔH_f (%) ^(c)
				Pellet Original Shape Retained	Pellets Fused or "Stuck" Together	T_M (°C)	ΔH_f (cal/g)	Change in ΔH_f (%) ^(b)	
1	Peroxide/compression molded	1. Melt/freezing cycling in ethylene glycol	none	-	-	131	39		0
			50 cycles	yes	slightly	129	38	-2	
			100 cycles	yes	somewhat	130	41	+3	
			150 cycles	yes	yes, some	129	38	-6	
			200 cycles	yes	yes, some	129	38	0	
			300 cycles	yes	yes, some	128	38	0	
			400 cycles	yes	yes, some	130	38	0	
			700 cycles	yes	yes, some	130	38	0	
		2. Maintained in molten state in refluxing ethylene glycol	770 hr	yes	yes	129	38	-2	-2
			1450 hr	yes	yes, firmly	127	38	-8	
			3186 hr	yes	yes, firmly	121	29	+8	
2	Peroxide/extruded	1. Melt/freezing cycling in ethylene glycol	none	-	-	130	38		+6
			50 cycles	yes	considerably fused	129	39	+2	
			100 cycles	yes	fused	130	39	0	
			150 cycles	yes	fused	129	40	+2	
			200 cycles	yes	fused	128	38	-5	
			300 cycles	yes	fused	127	37	-2	
			400 cycles	yes	fused	130	38	+3	
			700 cycles	yes	fused	130	40	+5	
		2. Maintained in molten state in refluxing ethylene glycol	770 hr	yes	yes	129	39	+2	0
			1450 hr	yes	yes, firmly	129	39	0	
			3186 hr	yes	yes, firmly	129	38	-2	
3	Silano-grafted/ boiling H ₂ O crosslinked	1. Melt/freezing cycling in ethylene glycol	none	-	-	132	43		0
			50 cycles	yes	no	132	44	+2	
			100 cycles	yes	no	132	45	+2	
			150 cycles	yes	no	132	44	-2	
			200 cycles	yes	v. slightly	132	44	0	
			300 cycles	yes	v. slightly	131	44	0	
			400 cycles	yes	v. slightly	132	44	0	
			700 cycles	yes	v. slightly	132	43	-2	
		2. Maintained in molten state in refluxing ethylene glycol	770 hr	yes	no	131	43	0	-2
			1450 hr	yes	yes, some	130	44	+2	
			3186 hr	yes	yes, slightly	132	42	-4	

(a) DSC Conditions Used: 10°C/min heating and cooling rates, range 8, chart speed 20 mm/min, indium standard, ΔH_f = heat of fusion
 T_M = melting temperature (peak); T_C - see Section 4.1.1 for discussion of T_M vs T_C .

(b) % change compared to initial ΔH_f value of the crosslinked PE for the first sample in the test, then to preceding ΔH_f value for each succeeding sample in the test.

(c) At completion of test, as compared to original ΔH_f value.

occurred with Sample 2, the extruded/peroxide cross-linked HDPE, which had a net +5% increase in ΔH_f over the 700 melt/freezing cycle test period. Most of the changes noted in Table XIV were within what could be expected to be normal variations between different DSC samples of the same crosslinked HDPE materials.

There were decided differences observed among these three samples in terms of self-adhesion of the pellets, however. By far, the best of the three candidate materials in this respect was the silane-grafted /crosslinked PE (sample 3) which showed very little or no tendency to adhere to itself (on cooling of the pellets to RT) after 700 melt/freezing cycles or 133 days in the melt.

The peroxide/compression molded crosslinked PE (sample 1) pellets did adhere somewhat on cycling and definitely after 60 days in the melt. The, not too bad, but worst case was the extruded/peroxide crosslinked PE (sample 2) which was fused completely after 100 melt/freezing cycles and also when kept in the melt continuously. However, it should be noted that even in this most extreme case, the "voids" between the pellets were maintained, so that ethylene glycol could still circulate through them. Further, most of the "fused" chunks of this material still could be broken up into smaller pieces, on cooling to R.T.

The results of the above evaluations, and those made in the one gallon TES unit, on these three prime candidate TES materials led to the choice of the silane-grafted/crosslinked HDPE product as the candidate for further scale-up and evaluation in the 60 gallon TES unit. Accordingly, a 250 lb batch of this Si-0-Si crosslinked PE was prepared, as described in Section 3.1.2.1. Analytical characterization data obtained on it, along with a limited amount of "long-term" stability data, are presented in Table XV. The Alathon 7040 starting HDPE resin and silane-grafted (but not crosslinked) precursors are also included for comparative purposes.

These results show excellent retention of the initial ΔH_f of the starting HDPE in the grafted/crosslinked product - 98%, which was the highest achieved in any crosslinked HDPE product having satisfactory form-stability. A very slight tendency of these PE pellets to self-adhere on melting did not appear to present any problem in TES bed applications, as adequate void space for fluid circulation was maintained in the melt, and the pellets broke apart readily on cooling to R.T. Uncrosslinked (but silane-grafted) PE precursor pellets on the other hand, adhered firmly together on melting and did not break apart when cooled to RT.

Table XV

THERMAL FUSION PROPERTIES OF 250 LB SI-O-SI CROSSLINKED FE PRODUCT AND PRECURSOR MATERIALS

Material Ref. No.	Graft/Crosslinking Conditions			Melt/Freeze Cycles, Ethylene Glycol, No.	Pellet Self-adhesion after Melting ^(a)	DSC Characterization ^(b)		
	Grafting Agent	Conc. (phr)	Crosslinking Process			T _M (°C)	ΔH _f (cal/g)	ΔH _f Retained ^(c) (%)
Alathon 7040 (Lot 656015)	-	-	-	-	fused into one mass	131	47	-
204236	vinyl triethoxy- silane	6	-	-	stick firmly together, can't break apart/RT	132	45	96
204328	vinyl triethoxy- silane	6	48 hr/88°C H ₂ O	-	very slight, break apart readily/RT	132	46	98
204328	vinyl triethoxy silane	6	48 hr/88°C H ₂ O	50	very slight, break apart readily/RT	132	46	98
204328	vinyl triethoxy silane	6	48 hr/88°C H ₂ O	100	very slight, break apart readily/RT	133	46	98
204238	vinyl triethoxy silane	6	48 hr/88°C H ₂ O	400	very slight, break apart readily/RT	133	44	94

(a) On heating touching pellets in air to 200°C, or after melt-freeze cycling in EG.

(b) DSC Conditions Used: 10°C/min heating and cooling rate, range 8, chart speed 20 mm/min, indium calibration standard, ΔH_f = heat of fusion, T_M = melting temperature (peak); ΔH_f values for Alathon 7040 and #20438 are averages of 5 separate DSC samples. T_C - see Section 4.1.1 for discussion of T_M vs T_C.

(c) As compared to ΔH_f of starting Alathon 7040 resin (uncrosslinked).

Long-term stability of this Si-O-Si crosslinked product, as given in Table XV, appeared to be very good also, based on results after 400 melt/freeze cycles in ethylene glycol. These data, comprised of only 2 test samples, are more limited, though, than that obtained for the 5 pound Si-O-Si crosslinked PE sample. Overall then, the objective of achieving a form-stable PE-TES bed material via controlled, limited crosslinking, with high retention of the PE heat of fusion value, appeared to have been met with this Si-O-Si crosslinked PE product. Only actual bed evaluation was needed for confirmation.

4.2.2 One Gallon (4-Liter) TES Unit Evaluation

The three polyethylene prime candidates with demonstrated good form-stability and retained high heat of fusion values were evaluated in a one gallon bed. Five-pound samples of the peroxide-crosslinked/compression molded, TES sample 1, the peroxide-crosslinked/extruded, TES sample 2, and the silane-grafted/crosslinked, TES sample 3, were thermal-cycled between $\sim 75^{\circ}\text{C}$ and $\sim 160^{\circ}\text{C}$ in the 4-liter TES unit. Each of these TES pellet samples underwent from 5 to 20 cycles to determine if the form-stability and high ΔH_f properties would be retained through extended thermal cycling in the lab-scale TES unit under operating pressures (0-5 psig) and temperature conditions.

Both the compression molded/peroxide crosslinked pellets and the silane-grafted/crosslinked pellets were cycled through their melting points more than twenty times. The extruded/peroxide crosslinked pellets (sample 2) underwent only six cycles due to time constraints, but are believed to be similar to TES sample 1 in physical properties.

4.2.2.1 Form-Stability

Each of the three crosslinked HDPE systems demonstrated an adequate form-stability for consideration as a TES material. However, the silane-grafted/crosslinked system (sample 3) was unique in that the pellets showed virtually no adhesion or fusion when exposed in the one gallon (4-liter) unit. The particles were exposed to twenty cycles and examined in detail after the fifth, tenth and twentieth cycles. No changes in performance were indicated through the 20 cycles.

Both peroxide-crosslinked polyethylene systems fused upon thermal cycling. All the compression molded pellets (sample 1) adhered to each other after five thermal cycles, such that when cooled the pellets formed a porous massive cylinder of slightly smaller diameter than the chamber. The pellets then reacted to thermal change by growing or shrinking as an integral

unit. Since the pellets float, they are pushed to the top of the vessel where it is also hottest. However, the adhesion was slight and continued cycling gradually broke up the fused aggregates. After 18 cycles, particle adhesion was very weak, and the maximum aggregate size was ~20 particles (Figure 24).

Based upon limited observations in the one gallon unit, fusion seemed to be somewhat less severe with the peroxide/extruded material. Some agglomerates observed after five cycles (the extent of testing of this polymer) were friable and appeared to be more easily broken than those of TES sample 1, after similar cycling. However, the extruded pellets were more irregular in shape than the compression molded ones, and the lesser adhesion could have resulted from less surface contact between particles.

Both types of peroxide-crosslinked pellets probably possess sufficient form-stability for TES use. The fusing effect apparently diminishes and may disappear with continued cycling, and free flow paths between the pellets are maintained. No shape distortion or melt flow was observed with any of the pellets throughout the tests.

4.2.2.2 Thermal Energy Storage Tests

The mass of the one gallon (4-liter) storage chamber itself was much larger than that of the polymer, about four times as large. Thus, small variations in the experimental determination of the net heat stored by the apparatus, Q_A , were magnified in calculating the heat of fusion (ΔH_f) values for the polymers and caused wide data scatter (see Section 3.3.2.2 for the equations used in these calculations). However, approximate ΔH_f values, based on test cycles with cooling times and temperature ranges closely approximating those used to determine Q_A (as discussed in Section 3.3.2.2) were made and, together with the thermal patterns observed throughout the tests, point up several relative properties of the TES candidate materials.

4.2.2.2.1 Thermal Storage Properties

The approximate thermal storage capacity (ΔH_f) properties found were consistently higher than indicated by DSC by about 10%, while the relative order of efficiency among the TES pellets was the same. The silane-grafted and crosslinked PE had the highest ΔH_f , averaging ~47 cal/gram. The peroxide-crosslinked pellets (TES samples 1 and 2) were essentially the same and had average ΔH_f values of ~43 cal/gram.

(a) Typical pellets of the peroxide/
compression molded PE-TES material
prior to testing

(b) Typical sintered aggregates of the
peroxide/compression molded particles
after 15 thermal cycles

Figure 24. Peroxide/compression molded PE pellets
before and after testing in one gallon
TES unit

Typically, cooling curves for the three TES materials, shown in Figures 25 and 26, followed the pattern of: (1) initial loss of sensible heat and decreasing temperature to the phase change temperature (these higher temperatures were used to assure the entire column was melted); (2) a plateau or period of relatively constant temperature through which heat was removed as the TES pellets changed phase; and (3) a linear temperature decrease as sensible heat was removed after phase change. The plateau region, which demonstrates recovery of the heat of fusion from the recrystallizing TES material, is significant because it allows the maximum heat energy to be withdrawn from the system as a high, useful temperature. The plateau temperatures were consistently 125-130°C for all three TES pellets, i.e., ten to fifteen degrees higher than the peak recrystallization temperatures indicated by the DSC tests (~115°C). The TES unit conditions are expected to more closely approximate actual usage.

4.2.2.2.2 Extended Cycling Stability

Most importantly, the thermal storage properties of crosslinked pellets did not change with extended cycling. Figure 25(a), the cooling profile for cycle 15 of the peroxide-crosslinked/compression-molded PE shows essentially the same energy storage as Figure 25(b), the cooling curve for the twenty-second cycle, differing only in the rate at which heat was removed. Similarly, Figure 26(a) is representative of the data obtained for each of the six test cycles for the extruded/peroxide-crosslinked PE. The silane-grafted/crosslinked PE [Figure 26(b)] had a ΔH_f value about 10% higher than the peroxide-crosslinked TES pellets, a phenomenon consistently observed through more than twenty test cycles.

4.2.2.2.3 Heat Transfer Rate

Heat exchange rates for the three TES pellet systems evaluated were rapid and consistent throughout the tests. The close proximity of the inlet and outlet fluid temperatures with those in the polyethylene particle bed, at the top and bottom of the chamber respectively, indicated very short transfer times, generally less than five minutes. The same effect was seen with the temperature probes near the center of the chamber. These temperatures remained relatively constant during recrystallization of the pellets in this zone. When the phase change energy was exhausted, the temperatures fell rapidly and within about five minutes became asymptotic to the cold inlet temperature. Based upon these observations, fillers, per se, or special particle shapes to improve the heat transfer properties of the pellet bed do not appear necessary.

Figure 25(a). Temperature versus time (mass) data of a typical cooling cycle for peroxide/crosslinked compression molded polyethylene TES material in one gallon test unit

Figure 25(b). Temperature versus time (mass) data of a high flow rate cooling cycle for peroxide/crosslinked compression molded polyethylene TES material in one gallon test unit

Figure 26(a) Temperature versus time (mass) of a typical cooling cycle for peroxide/crosslinked (extruded) polyethylene TES material in one gallon test unit

Figure 26(b). Temperature versus time (mass) data for a typical cooling cycle for silane-grafted/crosslinked polyethylene TES material in one gallon test unit

4.2.2.3 Packing Density

The packing density or packing efficiency, the volume percent of polymer contained by the storage chamber, is a function of the pellet shape and size and thus related to the manufacturing process.

The smooth, regular cylinders of the silane-grafted/crosslinked TES material produced the highest packing density, 58%, in the one gallon (4-liter) unit. This was slightly higher than the 55 volume % packing density of the compression molded/peroxide-crosslinked TES material and significantly higher than the 40% packing density obtained with the extruded/peroxide crosslinked TES material. The packing densities cited are for room temperature conditions. HDPE undergoes ~15 volume % expansion when heated to the maximum operational temperature of the TES unit, and the high temperature packing densities achieved ranged from 67% (silane-grafted/crosslinked) to 46% (peroxide-crosslinked).

4.2.2.4 Selection of the Optimum TES Polymer

Table XVI summarizes the comparative data for the three candidate TES polymers evaluated. On the basis of form-stability and heat of fusion retained after crosslinking and, to a lesser extent, on the packing efficiency, the silane-grafted/crosslinked PE TES material (sample 3) was selected for continued evaluation in the 60 gallon prototype model TES unit.

Table XVI
COMPARATIVE PROPERTIES OF CANDIDATE TES POLYMERS
EVALUATED IN ONE GALLON TES UNIT

	ΔH_f (cal/g)	Form-Stability	Packing Density	
			23°C (%)	130°C (%)
TES Sample 1	43	fair	55 (good)	63
TES Sample 2	43	fair	40 (poor)	46
TES Sample 3	47	excellent	58 (excellent)	67

Based on these results, and previously cited long-term stability and durability results, 250 pounds of the silane-grafted/crosslinked TES material were prepared for the 60 gallon prototype model unit, as described in Section 3.1.2. Analytical characterization data, given in Section 4.2.1, showed it to have a heat of fusion value nearly comparable to the original HDPE polymer, as well as excellent form-stability.

4.2.3 Evaluation of the Prime Candidate PE TES Material in the 60 Gallon Prototype Unit

The 250 pound lot of silane-grafted/crosslinked PE pellets, selected as the prime candidate TES material, was evaluated for energy storage capability and durability in the 60-gallon prototype TES unit, which was described in section 3.3.3. Delays in deliveries of equipment for the 60 gallon unit, the necessity for returning some faulty components to the manufacturers for replacement, and other equipment-related start-up problems resulted in a considerable departure from the anticipated testing schedule.

No delays were experienced due to any difficulty in manufacturing the 250 pounds of form-stable PE pellets; on the contrary, this proceeded smoothly and on schedule. The net result was that fewer melt/freeze test cycles could be attained than had been targeted initially. While it had been planned that 1000 melt/freeze cycles of the form-stable pellets would be obtained in this unit, slightly less than 200 cycles were actually reached by the conclusion of the program. Nevertheless, this was considered sufficient to confirm previous smaller scale results on the TES material's energy storage capability and durability.

Heat of fusion values of 48 cal/g for these form-stable PE pellets were consistently demonstrated, as illustrated below:

TYPICAL HEAT OF FUSION VALUES FOR SILANE-GRAFTED/CROSSLINKED PE PELLETS IN 60 GALLON TES UNIT

<u>Cycle No.</u>	<u>ΔH_f, cal/g^(a)</u>	<u>Ave ΔH_f, cal/g)</u>
69	48.9	48.4
70	47.9	
75	48.3	

(a) See Section 3.3.2.2 for the equations used in the calculations of ΔH_f

The approximate measured output of the 60 gallon TES unit containing 109 kg of the form-stable HDPE pellets and ethylene glycol heat fluid was 7,411,500 calories (29,400 BTU). Thus, about one million BTU's should be available from 1760 gallons, containing 80% PE, in the useful temperature region between 120 and 140°C.

Figures 27(a) and 27(b) show the cooling curves for two of the melt/freezing cycles cited above. These exhibit essentially the same features that were noted previously in the one-gallon (4-liter) TES unit evaluation of these form-stable PE pellets. There was a loss of sensible heat as the temperature decreased to the PE phase change temperature, then a plateau region where the temperature remained constant as the PE pellets changed phase (at $\sim 127-129^{\circ}\text{C}$), followed by a linear decrease as sensible heat was again removed at the conclusion of the phase change. Again, as was the case with the one-gallon TES unit, removal of heat as the PE recrystallized was shown to occur in a high temperature range ($\sim 125-130^{\circ}\text{C}$), particularly useful for absorption air conditioning applications.

An explanation of the reasons behind the selection of these three particular melt/freezing cycles (out of the final total of 170 complete runs) should be given, as all three of these occur in fairly close proximity to one another. The primary difficulty encountered in the testing program in the 60 gallon TES unit was with the variable speed pump used (see Section 3.3.3.1 for a description of the pump). It was found to not function adequately for the test conditions required. At the end of ~ 40 cycles, therefore, the pump was replaced by the manufacturer with another one identical to it.

This first series (which included those with only ethylene glycol in the unit) of 40 runs was used only for determining Q_a , the heat loss (or gain, if run time was less than ~ 40 minutes), versus time. In general, running times/cycle of ~ 2 hours were used, with $\sim 1\frac{1}{2}$ hours, for heat-up from $110-150^{\circ}\text{C}$ and $\sim 1/2$ hour cooling time. Thus, under optimum conditions 11-12 cycles/day could be achieved.

Runs 40-60 were next made, using the second pump, at varying pump rates to confirm that pump performance was reliable. The data obtained from runs 60 to 85 were considered the most satisfactory, and it is from these that the cited calculations of ΔH_f were made. Beyond this point, difficulties with the second pump began to be encountered, and actual flow rates became questionable (preliminary estimations of ΔH_f from runs 96 and 163 indicated ΔH_f values of >50 cal/g, probably due to uncertain pump flow rates).

While no problems were encountered with the PE-TES pellets themselves in cycling through the phase change, during the 170 completed runs, data beyond the 90th run was not considered totally reliable. Therefore, the cycling was discontinued. A new, larger, more durable, mechanically sealed pump has since been supplied by the manufacturer, and in any continuation of this testing, would be utilized in place of those pumps which had failed.

Figure 27(a). Temperature versus time (mass) data for the 68th cooling cycle of the 250 lb prime candidate PE pellets in the 60 gallon prototype TES unit

Figure 27(b). Temperature versus time (mass) data for the 75th cooling cycle of the 250 lb prime candidate PE pellets in the 60 gallon prototype TES unit

Nonetheless, it is felt that sufficient confirming evidence was obtained from the 60 gallon TES unit runs which, when combined with other smaller-scale results, demonstrates quite well the potential usefulness of these form-stable PE pellets for thermal energy storage, particularly for absorption air conditioning applications.

4.2.4 Economic Analysis of the Proposed TES Systems

With the demonstrated technical feasibility of the crosslinked PE-TES system, as shown by the results cited in this report, the economic aspects of such a system become of paramount importance. A brief discussion of the cost situation for the best candidate HDPE-TES pellets is therefore included here.

Using a highly conservative approach to costing of the silane-grafted and crosslinked HDPE, an estimate of 42¢/lb was reached, based on the following: (1) use of a finished, premium grade HDPE (such as the Alathon 7040 employed here); (2) payment of a licensing fee, as well as purchase of the silane-grafting material; and (3) processing of the HDPE to its form-stable state as a separate and independent operation.

However, this projected cost of 42¢/lb would certainly make this PE-TES system less attractive, and therefore an alternate best foreseeable cost projection was made. This projection was based on the following: (1) removing numerous polyethylene specifications, such as color, etc., which would have no bearing on its thermal energy storage properties; (2) starting with a polyethylene intermediate, rather than a finished molding compound; and (3) compounding and crosslinking the polyethylene in the same plant where it is manufactured. Based on the above criteria, a selling price of 25-27¢/lb was projected for form-stable polyethylene pellets, manufactured in multi-million pound per year quantities. Of this, raw material costs were estimated at 21¢/lb and conversion to the crosslinked PE at 4-6¢/lb.

Using the above best foreseeable cost projection of 26¢/lb for the form-stable HDPE and a reasonable value of 50 cal/g for ΔH_f , a comparison of the cost/BTU was then derived for both liquid (ethylene glycol) and air heat transfer systems. This is shown in Table VII. Included for comparative purposes is the projected cost of a liquid only (ethylene glycol) TES system, operating in the temperature range (120-140°C) which is most suited for absorption air conditioning applications. As shown, the projected cost (¢/BTU) for the HDPE/EG system of 0.4¢ versus 1.0¢ for EG alone represents a 2.5-fold savings. The projected cost for an air heat transfer system using HDPE is 0.2¢/BTU, or approximately half that for the liquid heat transfer system. No capital equipment costs are included, but these could be expected

Table XVII

COMPARISON OF COSTS FOR FORM-STABLE HDPE USING LIQUID OR AIR
HEAT TRANSFER AT 130°C^(a)

Storage Material	Ethylene Glycol Liquid Heat Transfer		Air Heat Transfer
	HDPE	EG (alone)	HDPE
Output, BTU	1 million	1 million	1 million
Volume, gallons	1760	4410	1920
Weight, lb	14,000	35,000	8940
Expected Life, years	30 (min)	6 (max)	30 (min)
Cost			
\$/gallon	2.31	2.42	1.21
Total \$	4070	10,670	2320
¢/BTU, initial	0.407	1.07	0.232
¢/BTU, lifetime	0.00004	0.0005	0.00002

(a) Basis for calculations:

Temperature Range: 120-140°C
 ΔT : 200°C
 HDPE(50) : Best reasonable projection - 50 cal/g and 26¢ lb,
 80% hot volume
 Ethylene glycol : 25¢/lb, $C_p = 0.71$ @135°C
 Volume and Weight: Includes media and heat transfer fluid or gas.
 Costs : Includes only original storage and heat transfer
 media costs. No capital equipment.

to be less for the air heat transfer system than for the liquid heat transfer system, also.

Overall then, the projected costs/BTU stored of 0.4¢ lb and 0.2¢/lb, for liquid and air transfer systems respectively, do not appear unreasonable, particularly if projected over an expected 30 year (or longer) useful lifetime of the HDPE-TES material. At an estimated 333 cycles/year, the cost/BTU stored would then drop to only 0.00004¢ and 0.00002¢, respectively, for the liquid and air transfer systems. Thus, the economic, as well as the technical, feasibility of the use of form-stable crystalline polymer pellets for thermal energy storage can be demonstrated.

5. RECOMMENDATIONS FOR FUTURE WORK

Recommendations for future work (Phase II) to further develop the form-stable crystalline polymer pellets for thermal energy storage are suggested.

Envisioned for Phase II are four major tasks. These tasks have been selected to take the thermal energy storage material through the development state and into a full-scale residential demonstration. The four tasks include:

1. Demonstration of the long-term durability of the form-stable crystalline polyethylene TES materials using the laboratory prototype test system.
2. Development of an optimized process for manufacture of the higher performance form-stable polyethylene TES materials.
3. Design, fabrication and delivery of a full-scale residential thermal energy storage unit compatible with ERDA recommended auxiliary systems.
4. Development of alternative latent-heat TES polymers with advantageous operating parameters.

5.1 TASK 1 - LONG-TERM DURABILITY DEMONSTRATION

The durability of the crystalline TES materials will play a dominant role in the final evaluation of cost effectiveness of this type storage system. Accordingly, proposed is an extended cycling of the prototype (60 gallon) unit with the best TES material to at least 1500 accelerated cycles. It is recommended that cycling of a more realistic nature also be conducted on the unit over a period of at least one month to confirm the accelerated data. This additional cycling would be done since the time-temperature characteristics of the accelerated cycle could be considered by some to be unrealistic in practice and could prevent annealing, which would be beneficial.

The polyethylene TES material evaluated in the laboratory prototype would consist of the one material considered best in Phase I, i.e., the Si-O-Si grafted/crosslinked PE product. However, two strong TES material candidates have evolved that consist of a single polyethylene crosslinked by one of two methods, resulting in either C-C or Si-O-Si crosslinked PE. The two TES materials appear to be nearly equal in their ability to repeatedly store energy over a period of time. The costs of manufacturing, and

the nature of the resultant pellet (especially with respect to ability to pack) of these two, however, do differ. The prime candidate TES (i.e., the Si-O-Si grafted/crosslinked PE) material tested in Phase I, has a slightly higher heat of fusion but requires a more involved manufacturing process. Other things being equal, a more efficient process would add considerably to minimizing the cost of a TES system. It is therefore recommended that this secondary TES system (i.e., the C-C crosslinked PE) be evaluated and its durability be determined over at least 500 accelerated cycles.

Emphasis has been on liquid heat transfer systems, specifically ethylene glycol. At this stage it is suggested that gas transfer systems also be considered and evaluated on a polyethylene bed of at least 50 kg (~100 lb).

5.2 TASK 2 - OPTIMIZATION OF PROCESS FOR MANUFACTURE OF THE HIGHER PERFORMANCE FORM-STABLE POLYETHYLENE TES MATERIALS

For any TES material to be cost effective, it must be low in cost and require only low cost modifications and/or processes. It is therefore proposed that manufacturing processes for the higher performance TES materials be developed. It is important that the processing be developed and conducted on a scale adequate to estimate future production costs. The process used to make the presently more effective TES material requires separate compounding, extrusion, and post-conditioning treatments, whereas the secondary material requires only a once-through extrusion to provide a suitable product (silane-grafting plus crosslinking versus direct peroxide crosslinking). Attempted will be the definition of a single melt stage process to produce the desired form-stable pellets (or other desired configuration as may be defined in Task 3).

As a final part of the process development, a quantity of form-stable polyethylene pellets should be manufactured to fill a full-scale residential thermal energy storage unit. This is estimated to be in the range of 2000 to 5000 kilograms (up to ~10,000 lb) depending on the selected storage criteria. Manufacture of a quantity of this size will assure that practical large scale processes will be used, as it would be impractical to use laboratory facilities for such a volume. Based on throughput and yields, then, an estimate of the conversion costs could be made.

5.3 TASK 3 - DESIGN, FABRICATION AND DELIVERY OF A FULL-SCALE RESIDENTIAL THERMAL ENERGY STORAGE UNIT COMPATIBLE WITH ERDA RECOMMENDED AUXILIARY SYSTEMS

The final practicality and utility of the crystalline polyethylene TES materials can best be determined by evaluation of a

full-scale residential thermal energy storage unit in conjunction with auxiliary systems, such as solar collectors and heat transfer systems. Accordingly, proposed is the design, fabrication, laboratory evaluation and delivery of a full-scale thermal energy storage unit for use in residential heating and cooling.

This task would first involve the design of a practical unit which would maximize the effectiveness of the TES material, and the cost effectiveness of the system. Considered would be TES material size and shape, i.e., pellets (used up until now), versus other configurations such as rods, tubes, etc. that may pack more efficiently and/or easily. The design would maximize the use of the polyethylene material itself for baffling and provide the proper flow of thermal transfer fluids. In some cases, it is expected however, that additional baffling, diversion, etc. may be highly desirable. Both the polyethylene and the heat transfer fluid will expand upon heating. The design must therefore accomodate this expansion and change in physical arrangement of the heat transfer bed. The design would incorporate overall size and shape characteristics that would make the system practical for use in a residence and facilitate its shipment. Finally, it would be made physically compatible with ERDA selected collector and heat transfer systems.

Following design of a full-scale unit it should be fabricated, evaluated and delivered to ERDA for installation. It is expected that ERDA would monitor this system. However, observation and evaluation would be conducted by the MRC project team to facilitate a proper analysis of the unit and materials performance.

5.4 TASK 4 - DEVELOPMENT OF ALTERNATIVE LATENT-HEAT TES POLYMERS WITH ADVANTAGEOUS OPERATING PARAMETERS

The operating parameters of thermal energy storage units need to be controllable, especially with respect to temperature and total storage requirements. The program up to this point has been dedicated to the use of crystalline polyethylene as the thermal energy storage medium. This is logical since it has a relatively high degree of crystallinity (high heat of fusion) and melts at a rather attractive temperature (approximately 135°C).

Thermal energy storage materials that are usable at other temperatures (either lower or higher) and have utility over a broader temperature range are needed. Thus it is proposed that a study be conducted to include other candidate crystalline polymers, polyblends of mixed polymers and mixtures of polymer pellets that melt at various temperatures.

Suggested first is that polyethylene with lower crystallinity (because of branching and/or crosslinking) be examined to provide a potentially more desirable melting point (100°C), even though it is expected that the thermal storage capacity would be reduced. It is then suggested that other polymers be examined to provide thermal storage at other temperatures.

It is recognized that as well as the definite advantages, other polymers may have individual problems involving thermal and hydrolytic stability. It is suggested that these candidates be examined in a lab-scale test unit (1 gallon) for storage ability and practicality. Subsequent evaluation and development then would be conducted when sufficient evidence proves their worth. Foremost, ability to introduce form-stability will need to be considered up through their melting points in appropriate heat transfer fluids and/or gases.

6. REFERENCES

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2. F. W. Billmeyer, Text Book of Polymer Science, 2nd edition, Wiley-Interscience, New York, 1971, p. 169.
3. D. H. Kaelble, et. al., Polymer Eng. and Sci., 15(9), 673 (1975).
4. H. G. Scott, U.S. Patent 3,646,155, February 29, 1972.

7. PATENT STATUS

Patent applications have been filed on the form-stable crystalline polymer pellets for thermal energy storage described in this report. Copies were submitted to:

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APPENDIX A

PHILLIP'S PETROLEUM COMPANY

PROCEDURE FOR DETERMINATION OF GEL CONTENT IN CROSSLINKED PE

APPENDIX A

PHILLIP'S PETROLEUM COMPANY

PROCEDURE FOR DETERMINATION OF GEL CONTENT IN CROSSLINKED PE

1. Weigh a 0.2 - g sample cut from molded part to ± 0.002 g. Record the sample weight as W_1 .

Note: Eight samples can be measured in one run.

2. Cut a 1.5 x 3 inch piece of 100-mesh stainless steel screen for each sample. Clean the screen with ethyl benzene, rinse with acetone, and dry in a stream of air.
3. Fold the screen to form a 1.5 by 1.5 inch square. Make a fold about 1/4-inch along each of the two open edges to form a pouch, and staple each fold.
4. Staple the sample into the screen envelope and wire it. Mark each sample with a metal tag. Weigh the sample plus screen to ± 0.002 g and record this weight as W_2 .
5. Place 1500 ml of ethyl benzene and 10 g of Plastanox 2246 in the resin kettle and heat to reflux.

Note: The Plastanox 2246 is added to prevent further cure of the polymer during the extraction.

6. Place the samples in the refluxing solvent for 16 hours. An overnight run is convenient.
7. Remove the samples while hot, and dry to constant weight (W_3) in a forced draft oven at 338°F (170°C) (usually about two hours) or to const. wt. in 150°C vacuum oven.

APPENDIX A (cont'd)

8. Calculations

$$\text{Gel wt. \%} = \frac{W_1 - (W_2 - W_3)}{W_1} \times 100\%$$

Where W_1 = weight of sample, g.

W_2 = weight of sample + screen, g.

W_3 = weight of sample + screen after extraction, g.

APPENDIX B

SUPPLEMENTARY DATA TABLES

Table B-1

EFFECT OF CROSSLINKING AGENTS AND CONCENTRATIONS USED IN CROSSLINKING DUFONT'S ALATHON 7040 HDPE

NBP Ref. No.	Crosslinking Agent		Compression Molded*	Observations on Thermal Form-Stability**			DSC Results***				Average ΔH_f (cal/g)	ΔH_f Retained on Crosslinking (%)
	Name	Concentration (phr)		Flows on Melting	Pellets stick together on Melting	Pellets stick to hot plate on Melting	Cycle	T_m °C	T_c °C	ΔH_f (cal/g)		
197507 and 197510	none	-	no	yes	yes (fused)	yes (tenacious- ly)	1 2 3	130 133 133	109 110 109	41.6 42.7 42.7	{ 42.7	-
198402 -5	none	-	yes	yes	yes (fused)	yes (slight)	-	-	-	-	-	-
198402 -4	dicumyl peroxide	0.25	yes	yes (very slight)	yes (slight)	yes (slight)	1 2	130 131	109 109	34.4 36.8	{ 35.6	83
198402 -3	dicumyl peroxide	0.50	yes	no	no	yes (slight)	1 2	129 129	109 109	33.4 32.5	{ 33.0	77
198402 -2	dicumyl peroxide	0.75	yes	no	yes (slight)	yes (slight)	1 2	130 129	108 109	34.2 34.2	{ 34.2	80
197507	dicumyl peroxide	1.0	yes	no	no	no	1 2	128 129	107 107	31.9 31.0	{ 31.5	74
198403 -1	di- <i>t</i> -butyl peroxide	0.5	yes	yes (slight)	yes (firmly)	yes (firmly)	-	-	-	-	-	-
198402 -6	2,5 di- methyl- 2,5-bis (<i>t</i> -butyl- peroxy, hexane	0.5	yes	no	yes (slight)	yes (slight)	1 2	134 132	111 110	40.9 38.8	{ 39.9	93

*Crosslinking and Molding Conditions Used: Peroxide incorporated into HDPE on mill roll, then sample compression molded 30 min/350°F, cooled slowly (in air) to RT, removed from mold and pelletized.

**Observations made on heating to 200°C on Fisher-John's m.p. apparatus.

***DSC Conditions Used: 10°C/min heating and cooling rate, range 8, 0.75 in./min. chart speed, indium calibration standard
 T_m = melting temperature (peak)
 T_c = recrystallization temperature (peak)
 ΔH_f = heat of fusion

Table B-II

USI CHEMICAL COMPANY'S LS-606 HDPE RESIN - EFFECTS OF CROSSLINKING ON THERMAL PERFORMANCE

NBP Ref. No.	Crosslinking Conditions ^(a)		Thermal Form Stability ^(b)		DSC Results ^(c)			Ave. ΔH_f (cal/g)	% ΔH_f ^(e) Retained
	Agent	Conc. (phr)	Flows on Melting	Pellets Stick Together	Cycle	T_M (°C)	T_C (°C)	ΔH_f (cal/g)	
LS-606 HDPE Resin (as received)	none	-	yes	yes (fused)	1	131	111	38.8	45.7
					2	132	111	45.3	
					3	133	112	45.6	
					4	132	-	46.2	
LS-606 HDPE Resin (as received)	none	-	yes	yes (fused)	1	129	111	39.5	47.2
					2	132	110	47.7	
					3	133	110	46.7	
197537-1	none	-	yes	yes (fused)	1	132	110	49.0	47.5
					2	131	111	45.9	
197538-1	Dicumyl Peroxide (DCP)	0.3	yes (slightly)	yes (firmly)	1	130	110	42.4	41.7
					2	130	110	41.0	
198068-2	DCP	0.5	no	yes (slightly)	1	131	110	41.4	40.7
					2	131	110	39.9	
198063-1	DCP	0.5	no	yes (slightly)	1	130	110	41.1	40.4
					2	129	110	39.6	
197538-2	DCP	0.7	no	yes (very slightly)	1	130	110	41.2	40.7
					2	130	110	40.2	
198063-2	Lupersol 101 ^(d)	0.3	yes (slightly)	yes	1	130	111	43.5	43.8
					2	130	111	44.0	
198068-1	Lupersol 101	0.5	no	yes (firmly)	1	132	111	44.5	43.8
					2	131	111	43.0	
197538-5	Lupersol 101	0.6	yes (very slightly)	yes	1	132	110	45.5	44.3
					2	131	110	42.6	
					3	131	110	44.9	
197538-4	Lupersol 101	1.0	no	yes (very slightly)	1	131	110	44.1	42.9
					2	129	110	41.6	
197538-3	Lupersol 101	1.24	no	yes (very slightly)	1	130	110	46.4	47.0
					2	130	110	47.5	

(a) Peroxide crosslinking agent (if used) incorporated into PE on steam-heated mill roll, then sample compression molded 30 min/350°F, cooled slowly in air to RT, and pelletized.

(b) As determined by heating pellets (touching) in air to 200°C on Fisher-Johns m.p. apparatus.

(c) DSC Conditions: 10°C/min heating and cooling rate, 0.75 in./min chart speed, indium calibration standard.

T_M = Melting temperature (peak)

T_C = Recrystallization temperature (peak)

ΔH_f = Heat of fusion (crystalline melting)

(d) 2,5 dimethyl-2,5-bis(*t*-butyl peroxy) hexane

(e) As compared to #197537-1, a compression molded (but not crosslinked) sample of LS-606 HDPE

Table B-III
SYNOPSIS OF FIBRINATE CROSSLINKED HDPE MATERIALS FOR MACRO SCALE TESTING

NDP Ref. No.	HDPE Resin	Crosslinking (a) Peroxide (b)	Observations on Thermal Form-Stability (c)		DSC Results, Initial (d)				Ave. ΔH_f	ΔH_f (e) Retained (%)	Results Obtained After Three Melting Cycles in Ethylene Glycol (f)						Percent Change in ΔH_f (g)
					Flows on Melting	Pellets Stick Together	Cycle	T_m (°C)			T_c (°C)	ΔH_f (cal/g)	Observation on Pellets	DSC Results			
			Cycle	T_m (°C)										T_c (°C)	ΔH_f (cal/g)	Ave. ΔH_f	
198402-5	Alathon 7040	-	yes	yes (firmly)	1 131 108 43.2 2 132 109 44.4	43.8	102				-	-	-	-	-	-	
198403-2	Alathon 7040	dicumyl peroxide	no	yes (slightly)	1 131 109 35.4 2 130 109 35.7 3 130 109 33.8						Pellets are stuck together, but break apart easily, have some void spaces between them	1 130 108 40.1 2 130 108 37.9	39.0	+11.4			
198402-3	Alathon 7040	dicumyl peroxide	no	yes (slightly)	1 129 109 33.4 2 139 109 32.9	33.0	77				-	-	-	-	-	-	
198402-6	Alathon 7040	Lupersol 101 [2,6 dimethyl- 2,5 bis(c- butyl peroxy) hexane]	no	yes (slightly)	1 134 111 40.9 2 132 110 38.8	39.9	93				Pellets are firmly stuck together but do have con- siderable void spaces between them	1 132 110 44.7 2 131 110 42.6 3 130 110 41.3	42.9	+7.5			
107407-2	Alathon 7040	Lupersol 101	no	yes (slightly)	1 131 110 35.0 2 131 110 35.7	35.7	83				-	-	-	-	-	-	
198403-4	Marlex 6030	dicumyl peroxide	no	no	1 129 110 35.5 2 128 110 35.5 3 128 110 34.1	35.0	77				Pellets are firmly fused into a tight mass (very little void spaces)	1 129 110 34.5 2 127 109 33.9	34.2	-2.2			
z																	
197407-1	Marlex 6030	Lupersol 101	no	yes (firmly)	1 130 109 32.4 2 129 109 31.6	32.0	72				-	-	-	-	-	-	
Second DSC sample:																	
					1 129 110 31.7 2 128 109 33.7	31.7	76										

(a) Crosslinking Conditions:

All samples compression molded 30 min/350°F, cooled slowly in air to RT, and pelletized (peroxide crosslinking agent, if used, first incorporated into PE on steam-heated mill roll)

(b) Peroxide Concentration, 0.5 phr.

(c) Samples (~3-4 pellets) heated in air on Fisher-John's m.p. apparatus to 200°C.

(d) DSC Conditions:

10°C/minute heating and cooling rate, range 8, 0.75 in./minute chart speed, indium calibration std.,

T_m = melting temperature (peak);

T_c = recrystallization temperature (peak);

ΔH_f = heat of fusion (melting).

(e) Original ΔH_f values used for comparison:

Alathon 7040 = 42.7 cal/g.

Marlex 6030 = 45.7 cal/g.

(f) Small test tubes (1.5 cm x 10 cm) half-filled with crosslinked HDPE pellets plus ethylene glycol. Heated in ethylene glycol bath above PE melting point, cooled to RT, and remelted (3 times).

(g) As compared to initial ΔH_f values.

Table B-IV
CROSSLINKING OF ALATHON 7040 HDPE VIA EXTRUSION

NBP Ref. No.	Crosslinking Conditions		Conditions of Extrusion(a)	Appearance of Extruded Rod	Observations on Form Stability (Pellets)		Cycle	T _m (°C)	T _c (°C)	ΔH _f (cal/g)	Ave. % ΔH _f (e)	
	Crosslinking Agent and Conc. (phr)	Method of Incorporation of Crosslinking Agent			In air/200°C(b)	E. Glycol/above MP(c)					ΔH _f	Retained
197548	Lupersol 101, 0.5	Via hot mill roll/ 140°C (2-3 min), resulting sheet granulated prior to extrusion	Screw speed 45 rpm 1 - 165°C 2 - 170°C 3 - 175°C 4 - 175°C	"spiralled"	No flow - slight flattening of pellets - stick together slightly in melt/not at RT	Pellets do stick together somewhat in melt, but break apart at RT	1 2	131 132	115 115	37.7 39.6	38.7	84
after 6 melting cycles in e. glycol												
							1 2	132 132	114 114	40.1 39.2	39.7	87
198427-4	Lupersol 101, 0.5 (diluted with 2.5 phr paraffin oil)	Pellets tumble- blended 2-1/2 hr at RT, then extruded	(a) 50 rpm 1 - 140°C 2 - 170°C 3 - 145°C 4 - 145°C (b) 50 rpm 1 - 145°C 2 - 180°C 3 - 165°C 4 - 165°C (c) 50 rpm 1 - 145°C 2 - 190°C 3 - 165°C 4 - 165°C	smooth rod smooth rod slightly "spiral" rod	Pellets flow somewhat on melting-fused into one mass at RT Pellets flow slightly on melting and flatten out- stick together and can't break apart at RT No flow but slight flat- tening of pel- lets; stick slightly in melt but break apart at RT	- - -	- - 1 2	- - 130 130	- - 116 116	- - 35.8 36.8	- - 36.3	- - 78
198427	Lupersol 130, 0.5	Via hot mill roll/ 140°C (2-3 min), sheet granulated prior to extrusion	(2) 45 rpm 1 - 165°C 2 - 180°C 3 - 180°C 4 - 180°C (3) 22 rpm 1 - 165°C 2 - 200°C 3 - 200°C 4 - 200°C	smooth rod slightly "rough" appearance	Pellets flow slightly at edges and flat- ten some; stick in melt but can break apart at RT No flow, but slight "flat- tening" of pellets; stick slightly in melt but break apart at RT	- Many of the pellets fused together after melting in ethylene glycol	1 2 1 2	133 134 132 132	113 113 115 115	44.3 46.0 39.5 39.8	44.7	97 87
198429-1	Lupersol 130, 0.5 (diluted with 2.5 phr paraffin oil)	Pellets tumble- blended/RT for 2 hr, then ex- truded	50 rpm 1 - 160°C 2 - 215°C 3 - 190°C 4 - 175°C	very "spiralled" rods	No flow at all; pellets stick only very slightly in melt and break apart readily at RT	-	1 2	129 130	115 115	33.7 35.3	34.5	75
198429-2	Lupersol 130, 0.25 (diluted with 1.25 phr paraffin oil)	Pellets tumble- blended/RT for 1 hr, then ex- truded	(a) 35 rpm 1 - 160°C 2 - 195°C 3 - 180°C 4 - 180°C (b) 50 rpm 1 - 160°C 2 - 215°C 3 - 190°C 4 - 175°C	slightly "rough" appearance very "spiralled" rods and very regu- lar pattern (chopped into small pellets)	Pellets "flatten" considerably on melting; stick together slightly No flow or change in shape on melt- ing; stick together very slightly in melt but break apart readily at RT	- Small pellets - most break apart on cool- ing to RT, but some stick together permanently	1 2 1 2	130 132 133 132	114 114 114 114	37.4 39.1 42.3 40.1	38.3 41.2	84 90
198429-28 (5 lb batch)	Lupersol 130, 0.25 phr (diluted with 1.25 phr paraffin oil)	Pellets tumble- blended ~1/2 hr/ RT then extruded	50 rpm 1-160-145°C 2-175-223°C 3-180-215°C 4-180-178°C (tapp. ranges during run)	"spiralled" rods (chop- ped into ~1/4 in. pellets)	No flow or change in shape of pel- lets; no sticking in melt and none at RT	Large (~1/4 in.) pellets - do not stick together at RT - break apart easily - same results after cycled 6 times around m.p. in ethylene glycol						

(a) Extruder Used - C. W. Brabender, 3/4 in. screw size, 4 heated zones (zone 1 - hopper, zone 4 - die)

(b) Pellets (touching) heated in air to 200°C on Fisher-Johns m.p. block

(c) Pellets heated in ethylene glycol (with agitation) above m.p., then cooled to RT

(d) DSC Conditions: 10°C/min heating and cooling rate, 0.75 in./min chart speed, indum calibration standard

T_m = Melting temperature (peak)

T_c = Recrystallization temperature (peak)

ΔH_f = Heat of fusion (crystalline melting)

(e) As compared to a value of ΔH_f = 45.8 cal/g for Alathon 7040 pellets (not crosslinked)

Table B-V

"SURFACE" CROSSLINKING OF ALATHON 7040 HIGH DENSITY POLYETHYLENE RESIN WITH BENZOYL PEROXIDE

NBP Ref. No.	HDPE Resin	Crosslinking Conditions ^(a)		Thermal Form Stability ^(b)		DSC Results ^(c)			Ave. ΔH_f (cal/g)	% of ΔH_f Retained
		Benzoyl Peroxide (phr)	Time, Hr., in Boiling H ₂ O	Pellets Flow on Melting	Pellets Stick Together	Cycle	T _M (°C)	T _C (°C)	ΔH_f (cal/g)	
197533	Alathon 7040	-	-	yes, pellets flow together	yes, fused into one mass	1	132	108	43.9	45.8
						2	132	109	45.8	
						3	133	109	45.7	
						4	134	109	45.8	
197531-1	Alathon 7040	1.0	2	yes, definite change in shape of pel- lets occurs	yes	1	129	109	42.5	42.9
						2	130	109	42.9	
						3	131	109	42.8	
						4	132	109	43.5	
197531-3	Alathon 7040	1.0	6	a slight change in shape occurs	yes	1	130	108	44.6	45.0
						2	132	108	45.1	
						3	131	109	45.3	
197531-5	Alathon 7040	1.0	26	a slight change in shape occurs	yes	1	130	109	43.3	42.7
						2	132	109	42.8	
						3	132	109	42.1	
198073-1	Alathon 7040	2.0	1	yes, flow together	yes, fused into one mass	1	129	108	44.2	44.8
						2	130	108	45.3	
						3	131	108	44.8	
198073-2	Alathon 7040	2.0	2	yes, slight change in shape occurs	yes (slightly)	1	130	109	44.5	45.2
						2	131	109	45.7	
						3	131	109	45.3	
198073-3	Alathon 7040	2.0	24	very slight change in shape	yes, slightly (also have turned yellow in color)	1	130	108	43.9	44.3
						2	132	108	45.0	
						3	131	108	44.1	

(a) Refluxed in H₂O containing 10 phr Pluronic F-68 (80/20 ethylene oxide/propylene oxide block copolymer) [4:1 (V/W) H₂O/polymer] for indicated time].

(b) As determined by heating pellets (touching) in air to 200°C on Fiske-Johns m.p. apparatus.

(c) DSC Conditions 10°C/min heating and cooling rate, 0.75 in./min chart speed, indium calibration standard.

T_M = Melting temperature (peak)

T_C = Recrystallization temperature (peak)

ΔH_f = Heat of fusion (crystalline melting)

Table B-VI
EVALUATION OF SILANE-CONTAINING POLYETHYLENES

NBP Ref. No.	Description of Silane-Containing PE	Crosslinking Conditions Used	Observations on Thermal Form-Stability (a)		DSC Results (b)				
			Flows on Melting	Pellets Stick Together	Cycle	T _m (°C)	T _c (°C)	ΔH _f (cal/g)	Ave. ΔH _f (cal/g)
198404-2	Norchem XLM (silane-containing PE) + Norchem Master Batch (catalyst-containing PE)-coextruded in 95/5 ratio	none	yes	yes (firmly)	1 2	101 99	86 86	9.9 11.4	10.7
198404-2 and 197513-1	Norchem XLM (silane-containing PE) + Norchem Master Batch (catalyst-containing PE)-coextruded in 95/5 ratio	30 min/boiling H ₂ O	no	yes (slightly)	1 2	100 100	86 86	14.5 14.3	14.4
198404-2 and 197513-1	Norchem XLM (silane-containing PE) + Norchem Master Batch (catalyst-containing PE)-coextruded in 95/5 ratio	1 hr/boiling H ₂ O	no	no	1 2	100 100	85 85	13.5 14.8	14.2
198404-2 and 197513-1	Norchem XLM (silane-containing PE) + Norchem Master Batch (catalyst-containing PE)-coextruded in 95/5 ratio	2 hr/boiling H ₂ O	no	no	1 2	101 101	85 84	12.7 14.8	13.8
198404-2 and 197513-2	Norchem XLM (silane-containing PE) + Norchem Master Batch (catalyst-containing PE)-coextruded in 95/5 ratio	2 hr/RT/H ₂ O	no	yes (slightly)	1 2	101 102	84 84	14.6 14.6	14.6
198060	Alathon 7040 HDPE containing 3 phr vinyltriethoxy silane + Alathon 7040 containing 1 phr di-butyl tin dilaurate catalyst - co-extruded in 95/5 ratio	none	yes	yes	1 2	132 132	114 114	41.8 46.7	44.3
198062-1	Alathon 7040 HDPE containing 3 phr vinyltriethoxy silane + Alathon 7040 containing 1 phr di-butyl tin dilaurate catalyst - co-extruded in 95/5 ratio	16 hr/boiling H ₂ O	yes (slightly)	yes	1 2	131 132	114 114	46.1 44.6	45.4
198062-2	Alathon 7040 HDPE containing 3 phr vinyltriethoxy silane + Alathon 7040 containing 1 phr di-butyl tin dilaurate catalyst - co-extruded in 95/5 ratio	26 hr/boiling H ₂ O	yes (very slightly)	yes (slightly)	1 2	133 133	113 114	45.6 43.8	44.7
198062-3	Alathon 7040 HDPE containing 3 phr vinyltriethoxy silane + Alathon 7040 containing 1 phr di-butyl tin dilaurate catalyst - co-extruded in 95/5 ratio	48 hr/boiling H ₂ O	yes (very slightly)	yes (slightly)	1 2	133 133	113 113	48.1 46.8	47.5
198062-4	Alathon 7040 HDPE containing 3 phr vinyltriethoxy silane + Alathon 7040 containing 1 phr di-butyl tin dilaurate catalyst - co-extruded in 95/5 ratio	72 hr/boiling H ₂ O	yes (very slightly)	yes (slightly)	1 2	132 131	114 114	47.1 44.1	45.6

(a) As determined by heating 3 or 4 pellets side-by-side in air to 200°C on Fisher-John's m.p. apparatus.

(b) DSC Conditions:

10°C/minute heating and cooling rates, range 8, 0.75 in./minute chart speed, indium calibration standard.

Table B-VII

RESULTS OF GRAFTING VINYL TRIETHOXSILANE ONTO ALATHON 7040 HDPE AND SUBSEQUENT CROSSLINKING/BOILING H₂O

NBP Ref. No.	Grafting Conditions (a)			Crosslinking Time, Hr. (Boiling H ₂ O)	Gel (b) Content	Thermal Form Stability (c)		DSC Results (d)					Ave. ΔH _f	% ΔH _f (e) Retained
	Silane (phr)	Benzoyl Peroxide (phr)	Method of Mixing			Pellets Flow on Melting	Pellets Stick Together on Melting	Cycle	T _M (°C)	T _C (°C)	ΔH _f (cal/g)			
198065-1	6	0.2	hot mill roll only	none	-	yes (but re- main as individual pellets)	yes, very firmly	1 2	131 130	114 115	44.7 45.3	45.0	98.5	
198065-3	6	0.2	hot mill roll only	2	-	yes, pellets "flatten" out on melt- ing	yes	1 2	132 133	113 114	45.3 45.1	45.2	99	
198065-4	6	0.2	hot mill roll only	5	-	yes, some "flattening" of pellets	yes	1 2	131 132	115 115	46.5 46.3	46.4	100	
198065-5	6	0.2	hot mill roll only	24	-	yes	yes	1 2	132 133	115 115	46.1 44.4	45.3	99	
198065-2	6	0.2	hot mill roll only	64	-	no, but slight shape change noted	yes, firmly	1 2	131 131	115 114	47.4 44.6	46.0	100	
198072	6	0.15	pellets tumble blended 2 hr RT then hot milled	none	-	yes	yes, firmly	1 2 3	131 132 132	115 115 115	45.1 45.6 44.4	45.0	98	
198072-1	6	0.15	pellets tumble blended 2 hr RT then hot milled	1	-	yes, pellets "flatten"	yes, firmly	1 2	132 132	115 115	46.3 44.7	45.5	99	
198072-4	6	0.15	flakes of 7040 resin tumble blended 2 hr/ RT then hot milled	24	39%	yes, flow together	yes, fused	1 2	132 132	114 114	46.1 45.3	45.7	100	
198075	10	0.15	flakes of 7040 resin tumble blended 2 hr/ RT then hot milled	none	-	yes, flow together	yes, fused	1 2 3	132 133 132	114 114 114	45.7 44.2 45.2	45.0	98	
198075-2	10	0.15	flakes of 7040 resin tumble blended 2 hr/ RT then hot milled	2	48%	yes, slight "flattening"	yes, slight	1 2	132 133	114 114	45.2 43.8	44.5	97	
198075-1	10	0.15	flakes of 7040 resin tumble blended 2 hr/ RT then hot milled	18	-	yes, slight "flattening"	yes, slight	1 2	132 132	114 114	46.0 48.4	45.7	100	
198075-4	10	0.15	flakes of 7040 resin tumble blended 2 hr/ RT then hot milled	48	45%	yes, slight "flattening"	yes, slight	1 2	132 132	114 114	46.7 44.3	45.5	99	

(a) General Procedure: The vinyl triethoxysilane (containing the benzoyl peroxide) was mixed into the Alathon 7040 resin as indicated above, then the mixture granulated and co-extruded in 95:5 w/w ratio at 165°C with Alathon 7040 HDPE catalyst batch containing 1 phr dibutyltin dilaurate and 0.1 phr benzoyl peroxide (mixed separately on hot mill roll and granulated). Co-extruded mixture pelletized, and portions crosslinked for various lengths of time (given above) in boiling H₂O.

(b) Extracted 16 hr in refluxing ethyl benzene and dried 1-1/2 hr/140°C/vacuum oven.

(c) As determined by heating pellets (touching) in air to 200°C on Fisher-Johns m.p. apparatus

(d) DSC Conditions: 10°C/min heating and cooling rate, 0.75 in./min chart speed, indium calibration standard.

T_M = melting temperature (peak)

T_C = Recrystallization temperature (peak)

ΔH_f = Heat of fusion (crystalline melting)

(e) As compared to ΔH_f of 45.8 for Alathon 7040 resin (untreated).

Table B-VIII
PROCESSING CONDITIONS AND THERMAL FUSION CHARACTERISTICS OF SILANE-GRAFTING AND CROSSLINKING OF HDPE
USING LARGE BANBURY MIXER

NBP Ref. No.	Silane Charge (a) Concentrations Used		Processing Conditions Employed			Form Stability (c)			DSC Data (d)		
	VTES (phr)	Bz ₂ O ₂ (phr)	Banbury Mixing and Grafting Conditions	Extrusion Conditions	Crosslinking Conditions	Pellets Flow on Melting in Air	Pellets Stick Together on Melting in Air	After 10 Cycles in Ethylene/Glycol	T _M (°C)	T _C (°C)	ΔH _f (cal/g)
204315-R1	8	0.2	Flux PE 4 min/RT, mix in silane charge 1 min cold, 5 min with steam, cool 2 min (cold H ₂ O) and remove grafted PE.	Co-extrude 95 pts. grafted, granulated PE with 5 pts of PE Catalyst Batch (b)	16 hr/boiling H ₂ O	v. slightly	v. slightly	-	-	-	-
				- 3 passes through 1 inch extruder/165°C.	40 hr/boiling H ₂ O	no	no	no	133	116	45
204315-R2	8	0.2	Flux PE ~4 min/RT, mix silane charge 10 min with steam, cool 10 min and remove grafted PE.	Co-extrude as above, - 2 passes/165°C.	16 hr/boiling H ₂ O	no	yes, firmly at RT	-	-	-	-
					40 hr/boiling H ₂ O	no	v. slightly	no	134	116	46
204315-R3	6	0.2	Flux, PE ~4 min/RT, mix silane charge 5 min with steam, cool 5 min, reheat 2 min to remove grafted PE.	Co-extrude as above, - 2 passes/165°C.	16 hr/boiling H ₂ O	no	v. slightly	-	-	-	-
					40 hr/boiling H ₂ O	no	no	no	133	116	47

(a) VTES = Vinyl Triethoxy Silane (Union Carbide A-151); Bz₂O₂ = Benzoyl Peroxide. Resin - Alathon 7040 HDPE, Banbury batch size - 5 lb.

(b) Catalyst Batch: 100 parts Alathon 7040 PE, 1 phr dibutyltindilaurate, 0.15 phr benzoyl peroxide, hot milled and granulated.

(c) In Air: heat to 200°C on Fisher-John's m.p. apparatus; in ethylene glycol - cycle around m.p. in open beaker.

(d) DSC Data: 10°C/min heating and cooling rate, range 8, ch. sp. - 20 mm/min, indium standard.

T_M(°C) - melting temp. (peak)

T_C(°C) - recrystallization temp. (peak)

ΔH_f (cal/g) - heat of fusion. Values given are averages of 2nd and 3rd melting cycles only.