

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
25 January 2001 (25.01.2001)

PCT

(10) International Publication Number  
WO 01/06195 A1

(51) International Patent Classification<sup>7</sup>: F28D 20/02,  
B65B 9/12, B65D 75/48, B01J 2/22

(21) International Application Number: PCT/US00/19168

(22) International Filing Date: 13 July 2000 (13.07.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
09/356,614 19 July 1999 (19.07.1999) US

(71) Applicant: THE UNIVERSITY OF DAYTON [US/US];  
300 College Park, Dayton, OH 45469 (US).

(72) Inventor: HUFF, Lloyd; 439 Walsingham Court, Dayton,  
OH 45429 (US).

(74) Agents: KILLWORTH, Richard, A. et al.; Killworth,  
Gottman, Hagan & Schaeff, L.L.P., One Dayton Centre,  
Suite 500, One South Main Street, Dayton, OH 45402-2023  
(US).

(81) Designated States (*national*): AE, AL, AM, AT, AU, AZ,  
BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE,  
DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID,  
IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT,  
LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ,  
PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT,  
TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,  
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**

- With international search report.
- Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 01/06195 A1

(54) Title: HEAT STORAGE PELLETS OF PHASE CHANGE MATERIAL AND METHOD OF MANUFACTURING SAME

(57) Abstract: Heat storage pellets and a method and apparatus for forming them. The method includes providing a continuous roll of tubing material, filling the tubing material with liquid phase change material, heating the tubing material, compressing the tubing material, crimping the tubing material to form a seal, and cutting the tubing material at the seal to form the pellets. The heat storage pellets can be used in a wide variety of products.

## HEAT STORAGE PELLETS OF PHASE CHANGE MATERIAL AND METHOD OF MANUFACTURING SAME

The present invention relates to heat storage pellets of phase change material and  
5 method of making same.

Phase change materials may be repeatedly converted between solid and liquid phases,  
and utilize their latent heat of fusion to absorb, store and release heat or cool during such phase  
conversions. These latent heats of fusion are greater than the sensible heat capacities of the  
materials. For example, in phase change materials, the amount of energy absorbed upon  
10 melting or released upon freezing is much greater than the amount of energy absorbed or  
released upon increasing or decreasing the temperature of the material over an increment of  
10° C.

Upon melting and freezing, per unit weight, a phase change material absorbs and  
releases substantially more energy than a sensible heat storage material that is heated or cooled  
15 over the same temperature range. In contrast to a sensible heat storage material that absorbs  
and releases energy essentially uniformly over a broad temperature range, a phase change  
material absorbs and releases a large quantity of energy in the vicinity of its melting/freezing  
point.

The problem with such phase change materials is in containing them in an appropriate  
20 matrix. In Salyer U.S. Pat. No. 5,053,446, there is disclosed a polyolefin matrix containment  
system. Salyer U.S. Pat. No. 4,797,160, discloses the use of a cementitious matrix containing  
alkyl hydrocarbon phase change materials neat or in pellets or granules formed by  
incorporating the alkyl hydrocarbon phase change material in polymers or rubbers; Salyer U.S.  
Pat. No. 5,106,520 and 5,282,994 disclose a free flowing, conformable powder-like mix of  
25 silica particles and a phase change material.

Each of these containment means have properties and utilities for specific applications,  
but none is universally best for all applications. For example, pellets of a phase change  
material, such a crystalline alkyl hydrocarbon, and a polyolefin, such as cross-linked high  
density polyethylene (HDPE), have been used in floor panels and elsewhere for moderating  
30 room temperatures and for energy efficiency. But, such pellets are expensive and have a

-2-

problem with some “oozing” (exuding) of the low melting point phase change material during thermocycling of the pellets above and below the melting temperature of the phase change material.

It has also been suggested that thermal energy storage devices may be made in the form of a sealed tube-like container such as a tube-like cylinder or other geometrical configuration partially filled with a phase change material such as calcium chloride hexahydrate. Reference is made to Campbell U.S. Pat. No. 4,388,963, in that regard. But, the cylinders of Campbell are large and unwieldy.

Chen U.S. Patent Nos. 4,504,402, and 4,505,953 disclose thermal energy storage composite pellet-shaped products of about 1/8 to 1 inch in size. In Noppel, U.S. Patent No. 5,069,208, cells of phase change material with a volume of 0.05 to 1 cm<sup>3</sup> are embedded in a heat exchanging agent such as a gel or emulsion, which is contained in a closed, fluid-tight wrapping. The cells can be formed by introducing the phase change material into a continuous tube of material, which is then pinched at intervals, welded to itself, and cut into cells.

All of these methods of providing phase change materials in pellet form have drawbacks. In some, the processing and materials costs are excessive. In others, the containment is not as robust as desired, and some oozing of the low-melting phase change material occurs.

Accordingly, it would be desirable to have ways to make pellets containing phase change materials that might be lower in cost, eliminate oozing, and/or provide properties that would enable the phase change material to be more effectively utilized.

The present invention solves these needs by providing an easy, low cost method of forming heat storage pellets which can be used in a wide variety of products. One aspect the invention is a method for forming heat storage pellets. The method includes providing a continuous roll of tubing material, filling the tubing material with liquid phase change material, heating the tubing material, compressing the tubing material, crimping the tubing material to form a seal, and cutting the tubing material at the seal to form the pellets.

The crimping can be done by heat sealing the tubing material. Optionally, a second seal can be formed by folding the first seal over and crimping the folded first seal.

A coating can be formed on the inside wall of the tubing material. The coating

preferably either increases the sealability of the tubing material or increases the resistance of the tubing material to infiltration by the phase change material or both.

The phase change material can be preheated to liquify it before filling the tubing material. It can also be heated in the tubing material to reliquify it prior to crimping. The  
5 phase change material optionally includes a microwave absorbing material.

The tubing material can be made from any suitable material, such as metals, polymers, or glass.

Another aspect of the invention is an apparatus for forming heat storage pellets. The apparatus includes a feed roll to supply the tubing material containing liquid phase change  
10 material, a heater to heat the tubing material, a compression station having a compression head to compress the tubing material, a crimping station having a crimping head to seal the tubing material, and a cutting station having a cutting head to cut the tubing material into pellets.

The apparatus can include a preheater to liquify the phase change material before filling the tubing material and a filling station to fill the tubing material with the liquid phase change  
15 material. It can also include a heater to liquify the phase change material in the tubing material before crimping.

In one embodiment, the apparatus can include a first pair of opposing cog wheels having a first set of teeth forming the compression head, a second pair of opposing cog wheels having a second set of teeth forming the crimping head, and a third pair of opposing cog  
20 wheels having a third set of teeth forming the cutting head. The first, second, and third pairs of cog wheels are synchronously driven.

In an alternative embodiment, the compression station, the crimping station, and the cutting station form a single station. The single station comprises an assembly comprising two outer sections and an interchangeable inner section between the two outer sections. The  
25 compression head, the crimping head, and the cutting head can be interchanged in the interchangeable inner section.

Alternatively, the crimping station and the cutting station can form a single station, or the compression station and the crimping station can form a single station. Optionally, these single stations can include heaters or ultrasonic welding heads.

30 Another aspect of the invention is the heat storage pellets themselves. They can be used in a wide variety of products. For example, heat storage pellets can be used in a

-4-

temperature-sensitive, non-airtight container. The container is formed from a non-airtight covering and surrounds the heat storage pellets. The non-airtight covering can be made of materials such as breathable fabric or polymeric material.

Another product is a temperature-sensitive composite which includes heat storage  
5 pellets and a matrix material surrounding the heat storage pellets. The matrix material can be materials such as polymeric material, or cementitious material. The composite is preferably rigid.

Still another aspect of the invention involves a method of using heat storage pellets. The method includes placing the heat storage pellets containing phase change material into  
10 void spaces for insulation, and charging the phase change material by heating or cooling. The void space can be the space in a building between a ceiling and floor joists, the core space in cement blocks, the space in a building between wall studs, or the space in a building between two walls. It can also be the space between two walls of a container, such as picnic chests, refrigerated trucks and railroad cars, or shipping containers.

15 Fig. 1 is a view of an apparatus for radially compressing the tubing material.

Fig. 2 shows examples of various crimping tool dies.

Fig. 3 is a diagram of a filling apparatus.

Fig. 4 is diagram of a preferred apparatus for making heat storage pellets.

Fig. 5 is a side view of another preferred apparatus for making heat storage pellets.

20 A long continuous roll of tubing material is needed. The tubing material can be any suitable material, including polymers (e.g., polyethylene, polypropylene, nylon, and polyvinyl chloride), metals (e.g., copper, aluminum, and stainless steel), or glass. The tubing material can have any desired diameter and wall thickness; although, when a low heat conductive material is used, the thinner the wall thickness the better the heat transfer into and out of the  
25 phase change material. The choice of the tubing material (e.g., type, diameter, wall thickness) will depend in part on the specific mechanical requirements of the particular application. Generally, however, the tubing outside the diameter should be .05 in. to 1.0 in. and preferably 0.1 in. to 0.25 in., and the wall thickness should be 1 mil to 40 mil and preferably 3 mil to 10 mil.

Various cross-sectional shapes of the tube material may be used. Some cross-sections may be more advantageous than others in particular applications. For example, maximum heat transfer from and to the phase change material may be obtained with a flattened or oval shaped tube.

5           The tubing material is filled with an appropriate phase change material in the liquid phase. If the phase change material is solid at room temperature, it should be preheated to convert it to the liquid phase. Any desired phase change material can be used.

          The phase change material is preferably in neat form, i.e., without any additives. The use of neat phase change material is desirable because it results in the largest ratio of volume  
10 of phase change material to total volume of the pellet. In many prior art systems, various fillers and other additives were used to prevent oozing of the phase change material. The inclusion of additives in the phase change material reduces the useful phase change material volume ratio, and, that can be avoided with the present invention.

          The chemical, mechanical, thermal, environmental, and biological parameters of the  
15 application will usually suggest particular tubing materials and phase change materials. For example, when the heat storage pellets are used in concrete applications, the tubing material should have good adhesion to the concrete and should not degrade the compressive strength of the concrete. In water heaters, or other applications where the heat storage pellets may be exposed to consumables, a tubing material which is non-toxic, non-corrosive, and, if required,  
20 FDA-approved should be selected.

          As to the PCM's that can be used, crystalline alkyl hydrocarbons having a chain length of C<sub>14</sub> and greater are preferred for most situations. Other PCM's that may be mentioned include water, glycerine, crystalline fatty acids, crystalline fatty acids esters, crystalline alicyclic hydrocarbons, crystalline aromatic compounds, linear crystalline primary alcohols,  
25 hydrated salts (Glauber's Salt preferred), the clathrates, semi-clathrates, gas clathrates, polyethylene glycol, and halogen-terminated alkyl hydrocarbons.

          Suitable clathrates include those which consist of either a noble gas (i.e., the gas clathrates) or a non-polar halocarbon which forms hydrates in as little as 10% concentration. The chlorofluorocarbons clathrates tend to be relatively expensive and are, therefore, not  
30 preferred. Additionally, some specific chlorofluorocarbons (e.g., Freon 11, 12, etc.) are also

suspected to contribute to depletion of the earth's ozone shield and are undesirable for this reason as well.

Promising clathrates also include the quaternary amine salts with halogen or other acids (clathrates or semi-clathrates). These hydrates are pseudo compounds, wherein the crystals of "ice" are able to host organic molecules (of specific composition) in nearly spherical cages of two different sizes. If only the larger of the two cages is occupied by the guest molecules, the pcm may contain 33 or more molecules of water. If both cages are occupied by guest molecules, the PCM will contain about 17 molecules of water. In either case, the water content in these clathrate and semi-clathrate pcms is much higher than in some of the salt hydrates such as sodium sulfate decahydrate.

Nearly all hydrated salts can be employed, with various degree of suitability, as PCM. The only such materials which are wholly unsuitable are those which decompose, rather than melt. Marginally suitable hydrated salts are those which melt incongruously, those with low heats of fusion, and those with melting points which lie outside (generally far above) desired temperature ranges. Nevertheless, there are a wide variety of meltable hydrated salts with high heat of fusion and useable melting points; and many of these satisfy stringent cost requirements. The preferred hydrated salts are those which are formed primarily from the combination of positive ions of sodium, potassium, calcium, ammonium and iron with negative ions of acetate, silicate, chloride, nitrate, mono, di, and tri basic phosphate, mono and di basic carbonate and mono and di basic sulphate. Other ions may be added to the above combinations in small quantities, (although they are more expensive) in order to adjust melting point or to obtain other desired properties. Virtually all such combinations will function in the desired manner; and most have melting points in the useful range, for example:

$\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ ,  
 $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Fe}(-\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  
 $\text{K}_3\text{PO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NaHPO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{Na}(\text{CH}_3\text{Coo}) \cdot 3\text{H}_2\text{O}$ . The specific melting point desired is obtained by varying the degree of hydration and by alloying it to form binary or ternary eutectics.

For many uses alkyl hydrocarbons having a carbon chain of about 14°C. atoms or greater are preferred. These waxes are commercially available under a host of trademarks. For instance, these commercially available waxes include : Shellwax ® 100 (MP 42° - 44°C.), ,

-7-

Shellwax ® 120 (MP44-47°), Shellwax 200® (MP52-55°C). Shellwax ® 300 (MP 60°-65°C.) all of which are products of Shell Oil Co.; Boron R-152 (MP 65°C.) a product of B.P. Oil Company; Union SR-143 (MP about 61°C.) a product of Union Oil Co., Witco 128 (MP about 53°C.) Witco LLN, Witco K-18, Witco K-45A, Witco K-61, Witco K-51, and Witco  
5 85010-1, all products of Witco Corporation (Kendall Division); Aristowax ® 143 (MP 34°-61°C.); and Paraffin 150 (MP about 61°C.). These waxes have heats of fusion greater than 30 cal/g and by comparison to other phase change materials, they are inexpensive.

One group of waxes for use are in the present invention includes commercially available mixtures of crystalline alkyl hydrocarbons. These mixtures of alkyl hydrocarbons are  
10 obtained at low cost as by-products of petroleum refining. Typically, these are blends of alkyl hydrocarbons which differ by no more than 4 or 5 carbon atoms. A typical example is Witco 45A which contains about 21% C-18, 33% C-19, 26% C-20, 11% C-21 hydrocarbon, and the balance higher and lower hydrocarbons. Because they are inexpensive, they can be incorporated into the PCM composite at minimal additional expense and, at the same time,  
15 provide high savings in terms of reduced energy costs.

While these waxes are mixtures, they exhibit one melting freezing point which is the average of the melting freezing points of the constituents. Some blends for passive heating and cooling have a melting and freezing point in the range of 24° to 33°C. Some blends for passive cool storage have a melting and a freezing point in the range of 0° to 33°C. In many  
20 applications, the blends will be relied upon for both heating and cooling and will be characterized by having both the melting and a freezing point in the range of 20° to 25°C. For applications requiring a melting point below 0°C. certain primary alcohols, salt water, and a variety of organic solvents such as ethanol and acetone may be used.

Ultra pure alkyl hydrocarbons C-14 to C-22 and higher are also available at a premium  
25 cost. These may have higher heats of fusion and crystallization (e.g., 55-60 cal/g) than the low-cost mixtures described above. These ultra pure alkyl hydrocarbons are also useful in the present invention for critical applications requiring maximum storage capacity in the minimum volume of space.

Another consideration in the selection of waxes used in the present invention is the  
30 difference between the melting and freezing points. The alkyl hydrocarbons are self-nucleating and thus melt and freeze congruently. Thus, when heated or cooled at rates of 2°



C./min. or less the melting and freezing temperatures substantially coincide.

If a microwavable product is desired, a non-polar pcm such as the crystalline long chain ( $C_{14}$  and greater) alkylhydrocarbons, crystalline fatty acids, crystalline fatty acid esters, crystalline primary alcohols, crystalline alicyclic hydrocarbons, crystalline aromatic hydrocarbons can be used provided they are used conjointly with polar compounds such as water, ethylene glycol, glycerine, polyethylene glycol, and ivory liquid, etc. Such polar compounds should be added to the PCM composite in an amount of from .1 to 10 wt.%, preferable 2 to 5 wt.% (based upon the total weight of the PCM/polar compound combination). Alternatively, a microwave absorbing ingredient such as carbon black may be added to any of the above-mentioned PCM's in order to render it microwavable.

In addition, the combination of the tubing material and the phase change material should be chosen so there is not excessive migration of the phase change material through the tube wall over the operating temperature range.

After the coil of tubing material is filled with phase change material, it is placed in an appropriate feeding assembly, such as a feed roll. The feed roll is normally at room temperature during the pellet manufacturing process.

The phase change material may be in a solid or a liquid state after filling, depending on the particular phase change material selected. The tubing material is sealed off at the feed end to prevent the phase change material from flowing out of the tube. The feed end is then introduced into the pellet forming machine using an appropriate feed mechanism.

The tubing material is heated to aid in compressing and crimping it. If the tubing material is a polymer, it can be heated to a temperature which allows plastic flow. The softened polymer can then be compressed and sealed easily. If the tubing material is glass, it should be heated above its melt temperature. In this case, the glass and the phase change material should be chosen so that the melting point of the glass is sufficiently low that heating the glass to the melting point does not decompose the phase change material.

Depending on the properties of the phase change material selected, it may be necessary for the phase change material to be in the liquid state in order to crimp the tubing material. If the phase change material is solid at this point in the process, the phase change material must be heated to liquify it. This should be done prior to crimping the tubing material, and is preferably done before compressing the tubing material.

Compression of the tubing material in the area of crimping helps to force the phase change material out of the seal area so that an effective seal can be formed. The compression can be accomplished by tooling that results in a flat compressed region. For some applications, it may be advantageous to perform the compression so that the tubing material is  
5 compressed radially, comparable to the end of a sausage casing. This radial compression can be accomplished using a compression tool having an appropriate design, such as is shown in Fig. 1. Radial compression has the advantage of forming a seal area which is physically smaller than will result from flat compression, which allows tighter compaction of the pellets.

Crimping the tubing material can be accomplished in many ways. In some cases,  
10 simple mechanical crimping may suffice, while in others, some form of welding or thermal sealing may be desired. Examples of crimping dies which could be used are shown in Fig. 2. The crimping die surfaces can be designed to form a variety of surfaces and configurations. For example, the crimp area can be a single flat area, an area with a series of ridges and valleys, or a cross-hatched pattern.

15 In the case of metal tubing material, crimping can be accomplished by mechanically crimping the tubing material with an appropriate crimping die. With polymeric tubing material, crimping is preferably accomplished by thermal welding or heat sealing. Heat sealing can be performed, for example, by direct thermal conduction from a mechanical heat sealing tool, ultrasonic heat sealing, microwave heat sealing, or optical radiation heat sealing  
20 using focused conventional light or a laser.

After the tubing material is crimped, it is fed to the cutting station where the tubing is cut in the middle of the crimp area, forming individual pellets. The tubing material can be cut using any suitable cutting device. The heat storage pellets can be made in various lengths and sizes, preferably from less than a millimeter to several centimeters in length.

25 The crimping and cutting operations can be combined into one step, if desired. Alternatively, the compression and crimping can be performed in a single step. For example, when glass is used as the tubing material, the compression and crimping steps are preferably performed in a single operation, with the seal being formed by the compression of the molten glass in the seal area. For polymer materials the compression and crimping can be performed  
30 in a single step with an appropriate ultrasonic tube sealer unit.

-10-

Optionally, after the pellet is cut, the crimp area can be folded over and crimped again to obtain a more durable and reliable seal. This second seal is preferably used with metal tubing material.

In one embodiment of the process, the inner wall of the tubing material is coated before  
5 the tubing material is filled with the phase change material. The tubing material can be coated with a substance which will, for example, enhance the sealing operation, or make the tubing material more impervious to the phase change material, or both. The inner wall of metallic tubing might be coated with an epoxy material to enhance the seal reliability of a mechanical crimp seal. The inner wall of a polymeric material, such as polyethylene or polypropylene,  
10 might be coated with a material, a rubber compound for example, to make the tubing wall more impervious to the phase change material and prevent migration of the phase change material through the wall. And, the inner wall of a high barrier polymeric material, such as polyvinylidene chloride or polytetrafluoroethylene, might be coated with a better heat sealable material such as polyethylene or polypropylene.

15 One way to coat the inner wall is to pump the coating material through the tubing. After the tubing is coated, any excess coating material can be blown out of the tubing. A thin layer of coating material remains on the inner wall of the tubing. The coating material is allowed to dry or cure prior to filling the tubing material with the phase change material.

Fig. 3 shows an example of a filling operation for the tubing material. The phase  
20 change material 2 is transported to a heater 4, which heats the phase change material 2 to liquify it, if necessary. The liquified phase change material is then transferred to a filling station 6 which fills a roll of tubing material 8 with phase change material. The filled tubing material is placed on a feed roll.

In a preferred embodiment, compression, crimping, and cutting can be performed by a  
25 sequential set of cog wheels, as shown in Fig.4. There is a feed roll 10 of tubing material filled with phase change material. The tubing material 12 is fed into a series of three pairs of opposing cog wheels. The tubing material is heated with a heater 14. A second heater 16 may be included to heat the phase change material in the tubing material 12 to liquify it. The two heaters 14 and 16 may be combined into a single heater.

30 The first pair of opposing cog wheels 18 compresses the tubing material 12. The cog wheels 18 have teeth 20 which are compression heads. Typically, the compression heads are

flat. However, they could be radial compression heads, as shown in Fig. 1. The teeth 20 of the compression cog wheels 18 may be at a sufficiently low temperature so that after the tubing passes through the compression cog wheels 18, the temperature of the tubing material 12 drops below the plastic flow temperature and the tubing material 12 remains in the compressed state until it reaches the crimping assembly.

The tubing material 12 is then crimped by a second pair of opposing cog wheels 22 which have teeth 24 which are crimping heads. The crimping heads can have many designs, including those shown in Fig. 2. The crimping heads can be heated to perform the sealing operation using direct thermal conduction. The tubing material 12 is cut by a third pair of opposing cog wheels 26. The cog wheels 26 have teeth 28 which are cutting heads. After the tubing material has been cut by the cutting heads, the heat storage pellets 30 are collected.

The three pairs of cog wheels 18, 22, and 26 are driven synchronously so that the opposing teeth make the proper contact at the proper distance. The size of the pellets can be altered by changing the distance between the teeth, the diameter of the cog wheels, or the speed of the tubing material and the cog wheels for example. The teeth 20, 24, and 28 of the cogwheels are appropriately shaped to perform the desired compression, crimping, and cutting.

In another preferred embodiment, the compression station, the crimping station, and the cutting station can be combined into a single station as shown in Figs. 5A, 5B, and 5C. The single station 40 includes an upper assembly 42 and a lower assembly 44. The upper assembly 42 has a pair of outer sections 46A, 46A, and interchangeable inner sections 48A, 50A, 52A. The lower assembly has corresponding outer sections 46B, 46B, and interchangeable inner sections 48B, 50B, 52B. The upper and lower assemblies 42, 44 move from an unengaged position to an engaged position. In the compression step, Fig. 5A, the compression heads 48A, 48B together with the outer sections 46A, 46A, 46B, 46B, compress the tubing and force the liquid phase change material out of the compression region. After the tubing is compressed, the upper and lower assemblies 42, 44 remain in the unengaged position. The compression heads 48A, 48B are withdrawn and replaced with crimping heads 50A, 50B which then move together to crimp the tube, forming a seal. The crimping heads 50A, 50B are then withdrawn and replaced with cutting heads 52A, 52B which are brought together to cut the tubing in the middle of the crimped area, forming the heat storage pellet. The upper and lower assemblies 42,44 are then moved to the unengaged position, the cutting heads 52A, 52B are withdrawn

and replaced by compression heads 48A, 48B, the tubing is advanced, and the process is repeated.

The heat storage pellets of the present invention have many uses. For example, heat storage pellets can be used in temperature-sensitive, non-airtight containers. The containers  
5 are formed from a non-airtight covering surrounding the heat storage pellets. The covering can be made of materials such as breathable fabric or polymeric material. These containers can be used for such things as hot and cold packs for thermal medical therapy, personal comfort products including ear muffs, hand warmers, and seat cushions, building insulation (e.g., placed into the space between the ceiling and floor joists or suspended between vertical wall  
10 studs), and temperature-sensitive product storage and transport. Non-airtight bags are more flexible than airtight bags, and they are flexible right out of the freezer. The presence and amount of air in the bags is not a concern in manufacture. The bags are also easier to seal. In addition, it is not necessary to fill the bag with a precise amount of product. As a result, making bags with the desired amount of conformability is much easier with a non-airtight bag  
15 than with an airtight bag.

The heat storage pellets can also be used in temperature-sensitive composites. The heat storage pellets can be incorporated into a matrix material, such as a polymeric material, or a cementitious material, to make a variety of rigid forms, including blocks, sheets, rods, tubes, and vessels. The polymeric matrix material may be a foam such as polystyrene or  
20 polyisocyanurate form. The composite can be used to make products such as drywall, poured concrete and concrete blocks, heat storage panels for greenhouses, insulation and heat storage panels for buildings, heat storage disks for pizza heaters, and food serving and storage containers.

The pellets can also be used in non-contained free form. In this form, they can be used  
25 as insulation which has not only an insulating ability but also a thermal storage capacity. They can be poured into void spaces in buildings, such as between a ceiling and floor joists, the core space in cement blocks, the space between wall studs, or the space between two walls. They can also be poured into the void space between two walls of a container, in products such as picnic chests, refrigerated trucks and railroad cars, or shipping containers.

30 The free form pellets can also be used in pellet bed heat exchangers. Heat exchangers containing the pellets could be used in hot water heaters to increase the amount of hot water

available, or to decrease the size of the hot water heater unit. The heat exchangers could also be used in waste heat storage systems, for example, in systems for storing waste heat from vehicle engines. In addition, the heat exchangers could be used as non-central thermal storage (heat or cold) in buildings for heating and cooling.

- 5           Having described the invention in detail and by reference to preferred embodiments thereof, it will be apparent that modifications and variations are possible without departing from the scope of the invention defined in the appended claims.

**CLAIMS**

1. A method for forming heat storage pellets comprising:
  - providing a continuous roll of tubing material;
  - filling the tubing material with a phase change material in liquid form;
  - 5 heating the tubing material;
  - compressing the tubing material;
  - crimping the tubing material to form a first seal; and
  - cutting the tubing material at the first seal to form the pellets.
- 10 2. The method of claim 1 wherein the tubing material is radially compressed.
3. The method of claim 1 further comprising forming a coating on an inside wall of the tubing material.
4. The method of claim 3 wherein the coating increases the sealability of the tubing material.
5. The method of claim 3 wherein the coating increases the resistance of the tubing material to  
15 infiltration by the phase change material.
6. The method of claim 1 wherein the phase change material is heated to liquify it before filling the tubing material.
7. The method of claim 1 wherein the phase change material is heated in the tubing material to liquify the phase change material before compressing the tubing material.
- 20 8. The method of claim 1 wherein the crimping comprises heat sealing.
9. The method of claim 1 wherein the phase change material further comprises a microwave absorbing material.

-15-

10. The method of claim 1 further comprising folding the first seal over and crimping the folded first seal to form a second seal.
11. The method of claim 1 wherein the tubing material comprises a metal.
12. The method of claim 1 wherein the tubing material comprises a polymer.
- 5 13. The method of claim 1 wherein the tubing material comprises glass.
14. An apparatus for forming heat storage pellets comprising:  
a feed roll to supply tubing material containing phase change material;  
a heater to heat the tubing material;  
a compression station having a compression head to compress the tubing material;  
10 a crimping station having a crimping head to seal the tubing material; and  
a cutting station having a cutting head to cut the tubing material into pellets.
15. The apparatus of claim 14 wherein the heater also heats the phase change material in the tubing material to liquify the phase change material.
16. The apparatus of claim 14 further comprising a preheater to liquify the phase change  
15 material before filling the tubing material and a filling station to fill the tubing material with the liquid phase change material.
17. The apparatus of claim 14 wherein the crimping head is heated.
18. The apparatus of claim 14 wherein the compression head radially compresses the tubing material.



19. The apparatus of claim 14 wherein the compression station comprises a first pair of opposing cog wheels having a first set of teeth, the first set of teeth forming the compression head, wherein the crimping station comprises a second pair of opposing cog wheels having a second set of teeth, the second set of teeth forming the crimping head, and wherein the cutting station comprises a third pair of opposing cog wheels having a third set of teeth, the third set of teeth forming the cutting head, and wherein the first, second, and third pairs of cog wheels are synchronously driven.
20. The apparatus of claim 19 wherein the first pair of opposing cog wheels is cooled.
21. The apparatus of claim 19 wherein the second pair of opposing cog wheels is heated.
22. The apparatus of claim 14 wherein the compression station, the crimping station, and the cutting station form a single station.
23. The apparatus of claim 22 wherein the single station comprises an assembly comprising a pair of outer sections and an interchangeable inner section between the pair of outer sections, and wherein the interchangeable inner section comprises the compression head, the crimping head, and the cutting head alternately.
24. The apparatus of claim 14 wherein the crimping station and the cutting station form a single station.
25. The apparatus of claim 24 wherein the single station includes a heater.
26. The apparatus of claim 14 wherein the compression station and the crimping station form a single station.
27. The apparatus of claim 26 wherein the single station includes a heater.
28. The apparatus of claim 26 wherein the single station comprises an ultrasonic welding head.

29. Heat storage pellets made by the method of claim 1.
30. A temperature-sensitive, non-airtight container comprising:  
heat storage pellets made by the method of claim 1; and  
a container formed from a non-airtight covering surrounding the pellets.
- 5 31. The container of claim 30 wherein the non-airtight covering comprises a breathable fabric.
32. The container of claim 30 wherein the non-airtight covering comprises a polymeric material.
33. A temperature-sensitive composite comprising:  
heat storage pellets made by the method of claim 1; and  
10 a matrix material surrounding the heat storage pellets.
34. The composite of claim 33 wherein the matrix material comprises a polymeric material.
35. The composite of claim 33 wherein the matrix material comprises a cementitious material.
36. The composite of claim 33 wherein the matrix material comprises a polymeric foam.
37. The composite of claim 33 wherein the matrix material is rigid.
- 15 38. A method of using heat storage pellets comprising:  
placing heat storage pellets made by the method of claim 1 into a void space for  
insulation; and  
charging the phase change material by heating or cooling.
39. The method of claim 38 wherein the void space comprises a space in a building between a  
20 ceiling and floor joists.

40. The method of claim 38 wherein the void space comprises a core space in cement blocks. .
41. The method of claim 38 wherein the void space comprises a space in a building between wall studs.
42. The method of claim 38 wherein the void space comprises a space in a building between  
5 two walls.
43. The method of claim 38 wherein the void space comprises a space between two walls of a container.
44. The method of claim 43 wherein the container comprises a picnic chest.
45. The method of claim 43 wherein the container comprises a refrigerated truck.
- 10 46. The method of claim 43 wherein the container comprises a refrigerated railroad car.
47. The method of claim 43 wherein the container comprises a shipping container.
48. The method of claim 43 wherein the container comprises a tank for storing or transporting liquid.
49. A heat exchange comprising a pellet bed heat exchange comprising heat storage pellets  
15 made by the method of claim 1.
50. A hot water heater comprising the heat exchange of claim 49.

FIG. 1

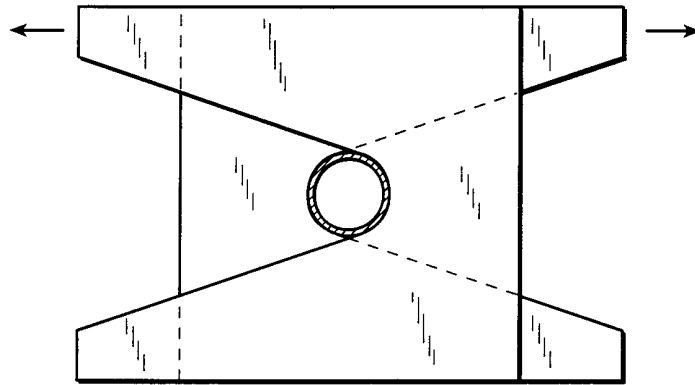


FIG. 2(C)

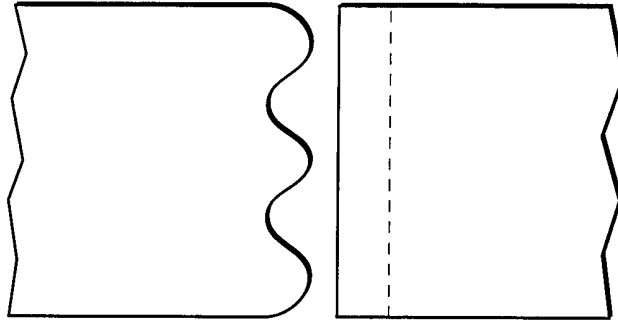


FIG. 2(B)

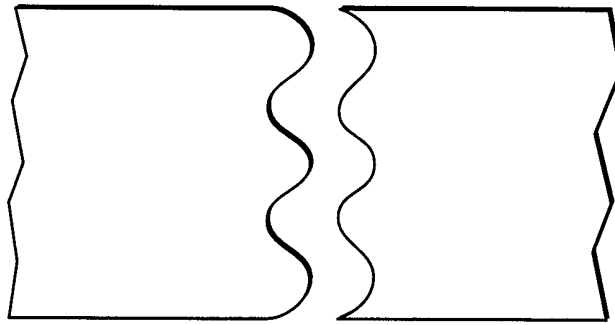


FIG. 2(A)

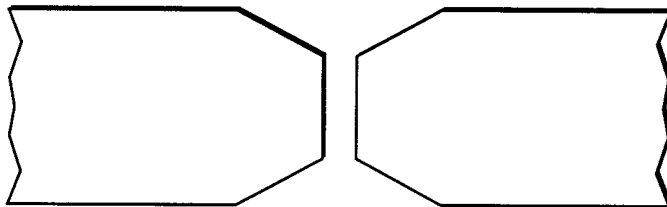
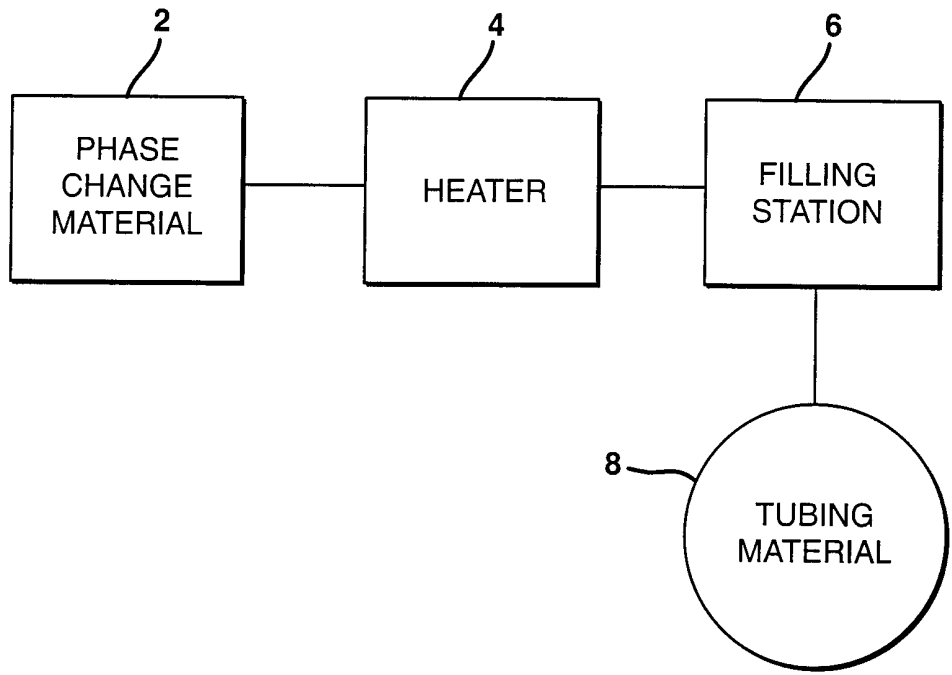


FIG. 3



4/5

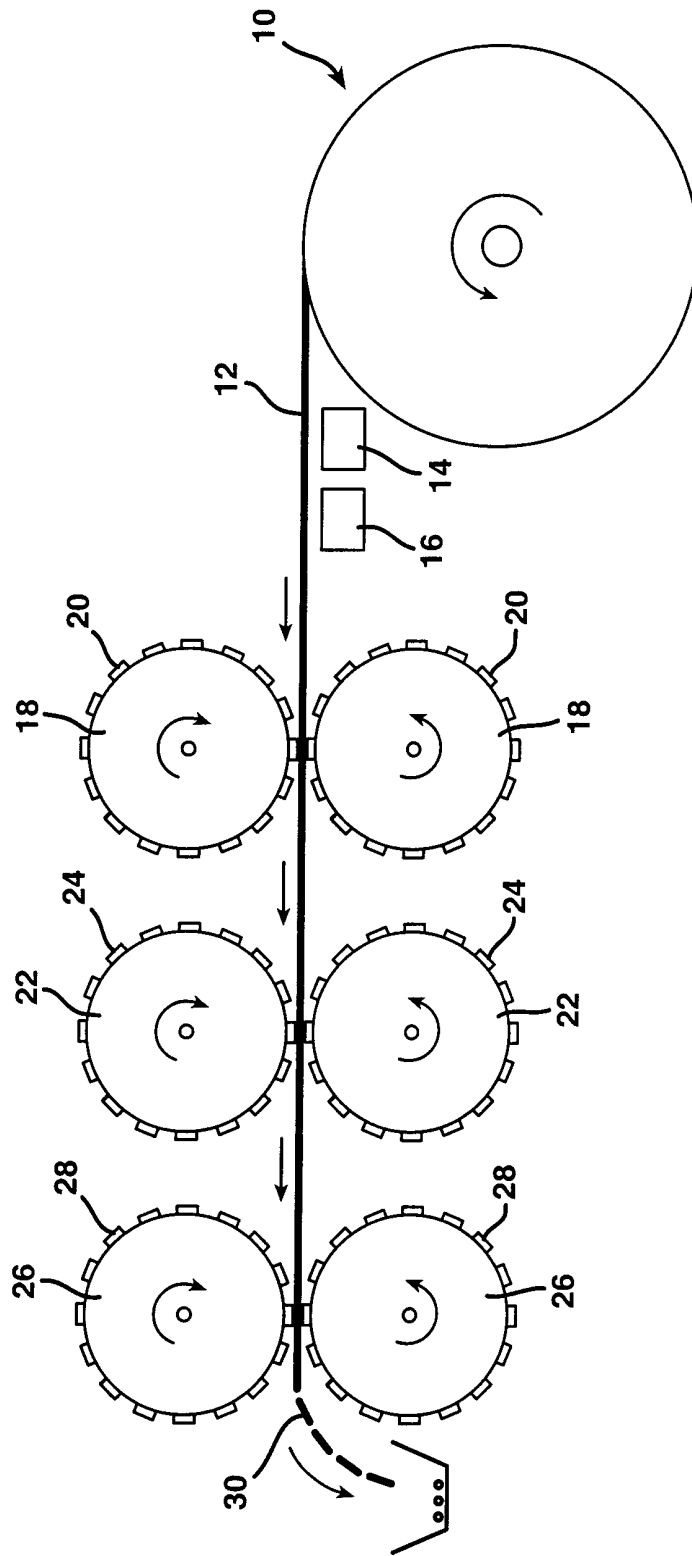


FIG. 4

FIG. 5(A)

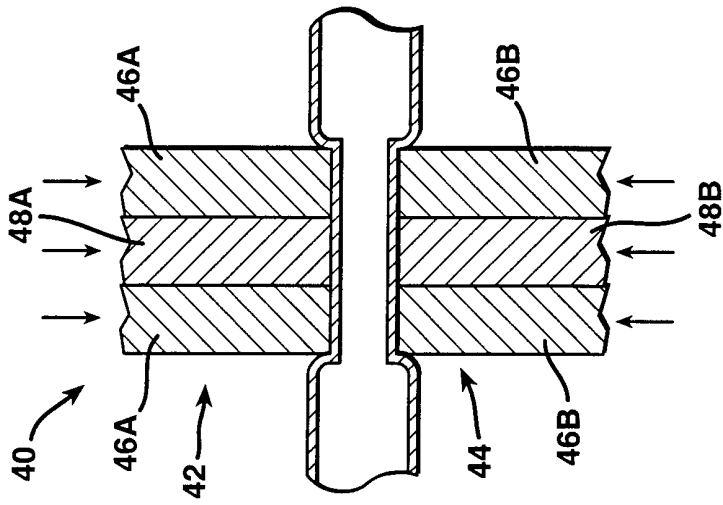


FIG. 5(B)

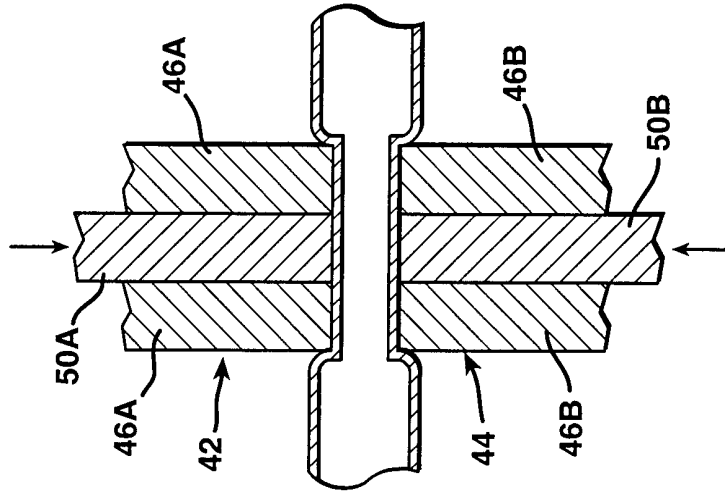
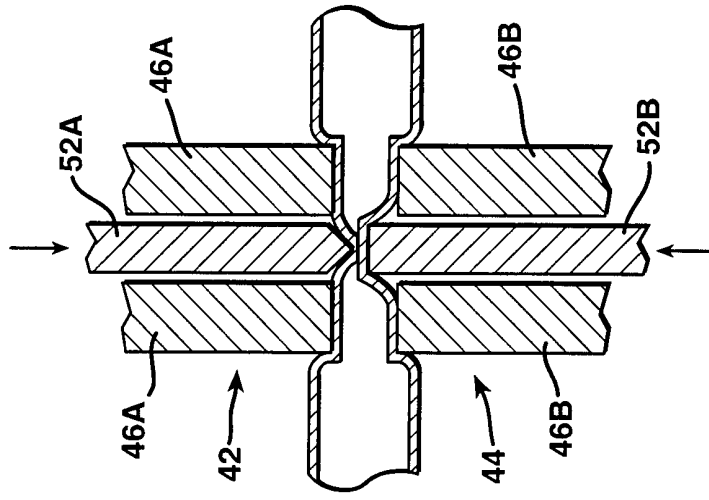


FIG. 5(C)





# INTERNATIONAL SEARCH REPORT

Int. Application No  
PCT/US 00/19168

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7 F28D20/02 B65B9/12 B65D75/48 B01J2/22		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 7 F28D B01J B65B B65D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 076 897 A (STIFFLER MARIO) 20 April 1983 (1983-04-20)  page 1, line 3 - line 5 page 2, line 29 -page 3, line 8 page 4, line 18 - line 28 page 5, line 18 - line 32 page 7, line 12 -page 8, line 5; figure 1 --- -/--	1,2,8, 10,12, 14,24, 26,29, 33-37,40
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		
<input checked="" type="checkbox"/> Patent family members are listed in annex.		
° Special categories of cited documents :		
*A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family	
Date of the actual completion of the international search  <p style="text-align: center;">9 November 2000</p>	Date of mailing of the international search report  <p style="text-align: center;">16/11/2000</p>	
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer  <p style="text-align: center;">Cubas Alcaraz, J</p>	

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/19168

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SE 509 372 C (WILHO ERIKSSON) 18 January 1999 (1999-01-18)	3-5,14, 17,18, 22-28
P,X	-& WO 99 39979 A (VILHO ERIKSSON) 12 August 1999 (1999-08-12)  page 1, line 26 -page 3, line 24 page 5, line 21 -page 8, line 2; figures 1-3	3-5,14, 17,18, 22-28
X	US 4 504 402 A (CHEN JOHNSON C H ET AL) 12 March 1985 (1985-03-12) cited in the application column 3, line 21 - line 61 column 4, line 7 - line 14 column 4, line 27 -column 6, line 16	29-42, 49,50
X	GB 2 084 311 A (STEINMUELLER GMBH L & C) 7 April 1982 (1982-04-07) page 1, line 28 - line 33 page 1, line 77 - line 83; claims 1-4	29,38, 43,49,50
X	US 4 720 980 A (HOWLAND LELAND L) 26 January 1988 (1988-01-26) claim 1	30,38, 43,45-47
X	US 5 159 973 A (STORY RAY A ET AL) 3 November 1992 (1992-11-03) claims 1,2; figure 3	30,38, 43,44

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/19168

Patent document cited in search report		Publication date	Patent family member(s)	Publication date			
EP 0076897	A	20-04-1983	AT 19646	T 15-05-1986			
			AU 559354	B 05-03-1987			
			BR 8204808	A 02-08-1983			
			DE 3270995	D 12-06-1986			
			NZ 201549	A 14-03-1986			
			ZA 8205765	A 31-08-1983			
			SE 509372	C	18-01-1999	AU 3281699	A 23-08-1999
			SE 9800382	A 18-01-1999			
			WO 9939979	A 12-08-1999			
US 4504402	A	12-03-1985	US 4505953	A 19-03-1985			
			CA 1207139	A 08-07-1986			
			DE 3338009	A 13-12-1984			
			FR 2547334	A 14-12-1984			
			GB 2142135	A, B 09-01-1985			
			IL 69390	A 30-01-1987			
			IT 1170460	B 03-06-1987			
			JP 1801126	C 12-11-1993			
			JP 5006117	B 25-01-1993			
			JP 60004792	A 11-01-1985			
			US 4513053	A 23-04-1985			
			GB 2084311	A	07-04-1982	DE 3035386	A 08-04-1982
						FI 812670	A 20-03-1982
			FR 2490801	A 26-03-1982			
			JP 57055397	A 02-04-1982			
			NL 8103261	A 16-04-1982			
			SE 8104777	A 20-03-1982			
			ZA 8106327	A 24-11-1982			
US 4720980	A	26-01-1988	DE 3805988	A 15-09-1988			
			FR 2611871	A 09-09-1988			
			GB 2202038	A, B 14-09-1988			
			IT 1220652	B 15-06-1990			
			JP 63226576	A 21-09-1988			
			US 5159973	A	03-11-1992	NONE	