Fig. 1

Fig. 2

Fig. 3

William Mearns III  John R. Peet  Ingar T. Tobye
Fred H. Stracke  Inventors

Richard T. Cannaday
Patent Attorney
VESSEL FOR TRANSPORTING LOW TEMPERATURE LIQUIDS

William Means III, Maplewood, John R. Peet, Westfield, Fred H. Stracke, Convent Station, and Ingar T. Toby, Mount Tamal, N.J., assignors to Esso Research and Engineering Company, a corporation of Delaware
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The present invention relates to means for transporting low temperature liquids in bulk. It relates particularly to ship means for bulk transportation of relatively low temperature liquids. It relates particularly to a vessel or tank ship construction suitable for bulk transportation of relatively low temperature liquids at substantially atmospheric pressure, and it relates still more particularly to a vessel or tank ship construction suitable for bulk transportation of substantially atmospheric pressure of liquid materials having normal (atmospheric) boiling points down to about —75° F.

Considerable interest has been shown in recent years in the storage and transportation of low-burning hydrocarbon materials such as propane (—43.7° F. normal boiling point) in the liquid state and at substantially atmospheric pressure. Under these conditions the cold hydrocarbons are placed in thermally insulated containers and are allowed to vaporize or boil off as heat leaks in through the container structure. The vapors thus produced may be either vented directly to the atmosphere, consumed as a gaseous fuel, or recondensed by suitable refrigeration equipment and returned as liquid directly to the insulated container. Obviously the efficiency and economy of such storage and transportation of low-burning liquids is dependent to a large degree upon the effectiveness of the thermal insulation applied to the liquid container.

Another problem besides that of vaporization loss of stored materials which arises in the course of storage and transportation of substantially low-burning liquids is that of embrittlement of metallic structural components of the liquid container. At temperatures as low as —75° F. ordinary ferrous metals such as low carbon steel may suffer at least some loss of energy absorbing capacity at high rates of strain, that is, loss of impact resistance. Storage tanks in general and storage tanks aboard ship in particular may be expected to be exposed to some shock loads during their working lives, even though such loads be applied accidentally. Accordingly, when materials such as propane are liquefied for storage and/or transportation thereupon must be given to the matter of loss of impact resistance of a steel-walled container and the attendant increased susceptibility of this structure to brittle fracture. It will be readily understood that the physical failure of a wall of a tank containing cold liquid hydrocarbons in bulk, liquid propane for example, could be extremely dangerous to both life and property. To minimize the possibility of such failure, proposals have been made for storing liquid propane and other cold liquid materials in steel tanks or container shells provided with internal insulation of appreciable thickness. By placing the insulating material on the inside of the steel container shell rather than on the outside, the steel material is allowed to remain at substantially atmospheric temperature for its entire thickness even though the container be fully charged with cold liquid. In this way low carbon, relatively inexpensive steels may be used in the tank structure instead of resort having to be had to costly alloy steels or other materials retaining significant impact resistance properties at low temperatures.

The insulating materials which have been proposed most frequently for such use according to the teachings of the prior art are balsa wood and cork in the form of rather sizeable blocks or slabs. These materials are reasonably effective as thermal insulators, but in the form applied or proposed to be applied make for a rather expensive construction. This is so not only because balsa wood and cork are not particularly inexpensive on a volume basis, but also because of the carpentry and jointer work necessary for proper fitting of the insulation segments to the metal tank shell and to each other.

Whether the insulation comprise blocks or slabs of the traditional materials or be otherwise constructed, however, direct exposure of the insulating material to the cold liquid being stored or transported has usually not been desired. Accordingly, a liner or inner tank shell is placed within the insulating blocks. One possibility known to the prior art for creation of this inner tank shell is to have it made of aluminum or another metal such as stainless steel retaining a significant impact resistance property at low temperatures. For shipboard containers intended to hold liquids at very low temperatures, for example, containers to hold liquid methane at about —259° F., an inner tank shell of suitable metallic material is the only practical possibility. However, when liquids at temperatures not lower than about —75° F. are to be carried the inner tank shell may be non-metallic and susceptible of easier handling and installation than a metal. Likewise in the temperature range extending down to about —75° F. the insulation material may be other and less expensive than and at least as easily installed as the balsa or cork of the prior art.

While the present invention is applicable, within limits, to use in the storage and transportation of liquefied hydrocarbons generally, it is particularly suitable for use in the handling and shipment of those hydrocarbon materials which exist as liquids at temperatures at least somewhat below normal temperatures, but which have normal boiling points not lower than about —75° F. These materials include but are not limited to the following:

Material: Normal B.P. (° F.)

1-Butene ........................................... 43.3
n-Butane ........................................... 32.9
1,3 Butadiene ...................................... 24.1
Isobutane ......................................... 10.9
Propane ............................................. 45.7
Propene (propylene) .............................. 53.9

Essentially, tank structures of the type with which the present invention is concerned and which are adapted for installation in marine vessels include a first or outer tank shell of rigid and most likely metallic material, and a plastic insulating material lining the interior of this tank shell and preferably sprayed in place with an incorporated expanding or foaming medium of suitable kind. The inner surface of the outer tank shell, whether this shell be of metal, plastic, or other material, may desirably be sprayed with a suitable primer before application of the foam plastic insulation thereonto to prevent oxidation thereof and improve adhesion of the foam.

Preferably the foamed plastic employed as an insulating material should be one which develops a tough surface skin which is relatively impermeable by most hydrocarbons, and may be capable of serving as the second or inner tank shell to contain the cold cargo liquid. The insulating material may also include a fire retardant material or be inherently fire retardant, and if it is desired and may be required to apply to the sprayed foam plastic an extra protective film or coating on its inner surface.
to serve as or at least be a substantial part of the aforementioned second tank shell. For this purpose a plastic or synthetic rubber coating may be used which is of enhanced impermeability by the liquid and vaporous hydrocarbons contained within the tank structure. This exterior film or coating should also be one which provides superior resistance to mechanical damage in comparison with the surface skin of the insulating material alone.

In a modified version of the present invention, the general structure just described may be used with the added element of a layer of balsa wood or cork applied next to the inner surface of the outer tank shell, that is, between this shell and the foamed plastic insulation which will be applied directly or by means of a bonding agent to the inner surface of the added element.

The balsa wood or cork layer will itself serve as insulating material of a relatively rigid nature. Use of this conventional insulating material will also tend to lower the mean temperature of the foamed plastic insulation sprayed or blown upon it. Reduction of temperature of plastic foam materials generally will increase their compression strength faced by given foam A 12 lb. air pressure. Accordingly, use of the aforementioned balsa or cork insulation against the inner surface of the outer tank shell will usually allow a reduction in density of the next-adjacent foam insulation for a desired strength of the latter insulation to resist static and dynamic pressure.

The present invention has several advantages. First the cost of installation of the insulation arrangement provided according to it is substantially less than the cost of fitting block or individually molded segments of insulating material within a tank or vessel shell. Second, a structurally and thermally superior insulation arrangement is obtained in that void spaces, poorly fitted joints, and difficult corner junctures which may occur with traditional block or slab type insulation are avoided. Third, whenever repairs to the insulation are needed they may be effected easily by a spraying operation rather than by resort having to be had to carpentry or joiner work.

These and various other advantages of the present invention as well as its nature and substance will be more clearly perceived and fully understood by referring to the following description and claims taken in connection with the accompanying drawings in which:

FIG. 1 represents a view looking forward in transverse section elevation through a marine vessel having an insulated tank for cold cargo liquids therewithin constructed according to this invention;

FIG. 2 represents a view similar to that of FIG. 1 of a portion of the wall of an insulated tank for cold cargo liquids constructed according to a modification of this invention, and

FIG. 3 represents a graphic portrayal of compressive strength properties at 70° F. and 120° F. of two foamed plastic materials suitable for use as thermal insulation at least at some applications.

Referring now to the drawings in detail, especially to FIG. 1 thereof, a marine vessel configured more or less similarly to a conventional tank ship is designated 10. Ship 10 is provided with a deck 12 and side or transverse bulkheads 29 and 22. Extending fore and aft within the ship are longitudinal bulkheads 20 and 22. These will go to or through transverse bulkheads which will be located at suitable intervals along the length of the ship. The structural items of the deck or inner shell plate, and bottom plating 32 so far designated will serve to define at least two port and starboard wing tank spaces such as 24 and 26. These wing tanks may be used for storage of materials which are ordinarily liquids at atmospheric conditions of temperature and pressure. Such liquids would include various crude petroleums and petroleum distillates.

The central part of the vessel includes at least one compartment such as 28 which is bounded fore and aft by the aforementioned transverse bulkheads, and laterally by longitudinal bulkheads 29 and 22. Within compartment 28 there is located at least one tank structure for the storage of cold liquid cargo materials. This tank structure includes a first or outer metal shell member 30, a second or inner nonmetallic shell 32 in non-contacting relation to the outer shell, and thermal insulation material 34 substantially filling the region between the two shells. A cold liquid storage volume 36 is defined within the inner shell 32.

The centerline vertical keel of tank ship 10 is designated 38. This is surmounted by a platform structure 40 which is otherwise suitably supported and braced, and which provides immediate support for the tank structure of which shell member 30 defines the outer boundary. The tank structure may be secured on said platform by any appropriate and customary means, proper allowance being made for dimensional changes due to thermal effects.

Primary location of outer shell member 30 with respect to the hull structure of ship 10 is, of course, effected by its seating and securing on platform structure 40. To prevent wash away of this shell, however, with rolling of the ship it is held transversely centered by such means as buffer brackets 42 and 44 secured to longitudinal bulkheads 20 and 22 near the top of the tank shell. These brackets have no effect of restricting movement of the tank structure due to temperature change as they are not actually fastened to outer tank shell 30 but simply bear relatively lightly against it. Each of these brackets may be a composite structure including a facing member of relatively soft buffering material such as rubber or wood wherein actual contact with outer shell member 30 is intended to be effected. Facing members 46 and 48 of this nature are designated as parts of the structures of brackets 42 and 44 respectively.

Now considering particularly the structure of the cold liquid storage tank and its internal and external attachments, outer shell 30 will be of steel. Being internally insulated, this steel may be of a low carbon, relatively inexpensive grade. It may of course be of a stainless or other high alloy grade, but the particularly beneficial properties of these considerably more expensive steels will not have significant opportunity of development in the course of such use. On its interior bottom surface, outer tank shell 30 is fitted with a series of structural elements such as inverted T-beams 50 which support a steel plate 52, and this in turn supports the bottom layer of thermal insulation material 34 with which outer shell 30 is filled.

The heat path from bottom plating 14 of ship 10 to any cold liquid cargo in tank space 36 will be a difficult one, not only because of the bottom layer of insulation material 34 but also because of the limited cross sectional area of the webs of T-beams 50 normal to the direction of heat flow.

As shown in FIG. 1, the sprayed foam plastic insulating material 34 substantially completely lines the inner surface of outer tank shell 30 and/or plate 52 if this plate is in fact used to provide an inner bottom for the tank shell. In view of the large surface area within a tank 10, it is seen from FIG. 2, shown in FIG. 1, it may be expected to be constructed and in view also of the motion which may be expected to be imposed upon this structure, it will be desirable that insulating material 34 be capable of withstanding substantial static and dynamic pressures over a fairly wide range of temperatures.

As an example of the foregoing, for the storage and transportation of liquid propane the insulating material should be capable of withstand static pressure of at least 10 and preferably 14 pounds per square inch from the stored liquid without significant crushing, even in the face of a superimposed dynamic pressure of equal amount. In general, insulating material 34 should be capable of withstanding a total pressure in the range of 20-28 p.s.i. Moreover, the insulating material should be capable of withstanding such pressure throughout a
range of temperatures extending from at least as high as \(120\,^\circ\text{F.}\) to at least as low as \(-75\,^\circ\text{F.}\).

In addition to possessing a definite mechanical strength, especially in compression, insulating material 34 must of course offer a great degree of resistance to the flow of heat therethrough. Preferably, in keeping with working regulations of the United States Coast Guard, insulating material 34 in the thickness applied should not permit a heat flux in excess of 0.075 B.t.u. per hour per square foot per degree Fahrenheit temperature differential (0.075 B.t.u.-hr.\(^{-1}\)-ft.\(^{-2}\)-°F.\(^{-1}\)).

The aforesaid properties of fairly high thermal strength and relatively low thermal conductivity are not easily to find in combination among foamed plastic materials. This is because the lighter foams have improved insulating properties but decreased strength in compression. Accordingly, considerable care is required in the choice of insulating material 34 for use of the nature indicated in Fig. 1.

Although this invention is not limited to the employment of any particular foamed plastic insulating material so long as the material selected satisfies at least the stated basic requirements, an insulating material particularly desirable for use will be a polyurethane foam prepared by reacting a suitable resin, usually a polyester or a polyether, with a diisocyanate and an appropriate catalyst, and an expanding agent or a reactant from which an expanding agent may be generated. For example, if a polyester resin, toluene-2,4-diisocyanate, and a catalyst such as trimethylamine are mixed with water there will be a release of carbon dioxide gas as a reaction by-product, and this gas will serve as the expanding agent to foam the plastic material as it is deposited on the interior surface of outer tank shell 30. Further information on chemistry and processes relevant to the operation just described may be obtained by reference to the following booklet publications:

1. "Rigid Urethane Foams—II Chemistry and Formulation" (HR-26, April, 1958) by C. M. Barringer, Elastomer Chemicals Dept., E. I. du Pont de Nemours & Co., Wilmington, Del.


Alternatively to a mixing and reactive process wherein the expanding agent is generated as a by-product, the expanding agent may be added as a mixture ingredient and carried through the mixing steps and any associated reactions with itself being changed only in physical rather than chemical condition. Specifically what is contemplated is that the expanding agent will be changed from the liquid to the gaseous or gaseous state in this connection a halogenated hydrocarbons such as one of the "Freons" marketed by E. I. du Pont de Nemours & Co. will be suitable as an expanding agent, and is specifically preferred for purposes of this invention. The reason for this preference is that of the significantly lower coefficient of thermal conductivity or "K" factor of a Freon-expanded polyurethane foam in respect of that of the same material expanded by carbon dioxide to the same density.

The halogenated hydrocarbon known technically as trichlorofluoromethane and known and sold commercially as Freon-11 is especially satisfactory for use as an expanding of foaming agent, this material in liquid from being substituted as a mixture ingredient for the water mentioned above. The polyester, the diisocyanate, and the catalyst will react exothermically as they are mixed, and the heat so released will vaporize the liquid Freon-11 which has a boiling point of 22°F. at a pressure of 1 atm. Upon this vaporization of the Freon-11, the plastic material will be expanded rapidly into foamed form, and it will cure quickly at room or normal atmospheric temperatures to provide a good insulating structure having a dense and relatively impermeable surface film or skin. This skin will define the inner boundary of insulating material 34 as this material is applied to the inner surface of outer tank shell 30, assuming that a polyurethane material is in fact used. Plastic foams of the kind described adhere quite tenaciously to steel surfaces. Insulating material 34 may, accordingly, simply be blown onto the interior surface of outer tank shell 30 to build up on this surface and on itself to the desired thickness, about 2 1/4 to 3 1/2 inches, without the erection of any forms or molds. For truly durable adhesion of the insulation to tank shell 30, the interior surface of this shell should be cleaned of at least mill scale, oil, and paint prior to the blowing on of insulating material 34, this material expanding to a foamed condition as and after it strikes the tank surface. Suitable cleaning of the interior surface of the tank may be effected by sand blasting. After such cleaning, an adhesive primer of any appropriate nature may be applied to the inner surface of outer tank shell 30 if desired.

Density of the plastic material constituting the thermal insulation of the tank structure shown in Fig. 1 may be controlled by changes in formulation, and may range from less than 2 to more than 50 pounds per cubic foot in the expanded or foamed condition. The problem of crushing of insulating material 34 has been mentioned already. Such crushing, if it takes place, may be not only of a sudden nature upon application to the insulating material of a breaking compressive load, but also of a quite gradual nature as in the case of compressive creep. In order to hold creep deformation of the insulating material within tolerable limits, that is, hold it short of crushing to eventual failure, a minimum compressive strength of 90 p.s.i. will often be desired for the thermal insulation of tanks in the sizes contemplated to be constructed according to this invention. Corresponding to such a creep resistance requirement, the minimum practical density for insulating material 34 in the foamed condition will be about 5 lbs./ft.\(^3\). In the smaller sizes of tanks with accompanying lower compressive loads imposed on the insulation it may, of course, be permissible to use plastic foams having densities less than 5 lbs./ft.\(^3\) and correspondingly reduced compressive strengths.

Although a tough skin and one relatively impermeable by most hydrocarbons will be formed on the inner surface of plastic insulating material 34 as this materialcures in place on outer tank shell 30, this skin will not be any great thickness and may be subject to mechanical puncture. Should it be so punctured, low boiling hydrocarbon liquids and their vapors in contact with it might effect considerable permeation of the cellular structure of the main body of insulating material 34. Such permeation would reduce the thermal insulation property of this material to a great extent, as well as cause loss of cargo liquids and create at least some hazard of fire. In order to substantially eliminate the possibility of such mechanical puncture of the insulating skin and subsequent hydrocarbon permeation of the insulating material body, a second or inner tank shell 32 is formed or fitted onto the interior surface or tough inner skin of insulating material 34 to define the cold liquid storage volume 36. According to the present invention it is contemplated that shell member 32 will be fabricated of non-metallic material.

An eminently suitable material for inner tank shell 32 is a polyester film known commercially as "Mylar," and manufactured by E. I. du Pont de Nemours & co. This film is essentially a highly durable, transparent, water and hydrocarbon impervious polyethylene terephthalate resin. It is characterized by outstanding strength and chemical inertness. It is characterized further by a high degree of flexibility even at temperatures well below
Mylar is available in thicknesses up to about ten mils (0.010"), and in strip widths up to about 54 inches. Strips of this material may be joined to each other by heat-sealing or welding without coating them with benzyl alcohol and subsequently making application of heat as from a hot iron, or by lamping and the use of a suitable adhesive material.

In effecting the installation of inner tank shell 32, assuming the material of it to be Mylar it will of course be necessary to obtain a firm edge joint between abutting strips of the polyester film to insure the creation of a tank shell that is both gas and liquid tight, and it will be at least highly desirable to obtain a bond between the Mylar strips and the interior surface of the inner tank shell 32 once it has been fabricated. Such a bond may be obtained by applying a light coating of a cementing agent such as a thiol-epoxy adhesive compound to the tough skin or inner surface of the inner tank shell 34 before the polyester film strips are set in place thereupon and joined to each other.

It is to be understood that when inner tank shell 32 is made of polyester film it may be given any desired wall thickness by cementing together in superimposed relation a plurality of film sheets. Such cementing may be carried out by an epoxy cement compound or other suitable adhesive. Likewise, any convenient degree of prefabrication of the polyester film inner tank shell 32 may be carried out depending upon the construction sequence chosen for erection of the cold cargo liquid storage tank. Such prefabrication would be in contrast to laying up individual shell panels of polyester or Mylar film after the cold cargo liquid storage tank had been substantially completed otherwise.

A number of elements and systems make connection to and penetration of the tank structure of this invention from and through main deck 12 of marine vessel 10. These include cargo vent conduit 54 extending from cargo liquid space 36, cargo liquid filling conduit 56 extending into cargo liquid space 36, and steam turbine or other prime mover 58 wherefrom steam 60 extends downwardly to a deep well pump 62 near the bottom of cargo liquid space 36, this sleeve containing the turbine power transmitting means such as shafting of conventional nature for pump 62, and also containing the discharge line of pump 62 wherethrough cargo liquid is removed from tank space 36. Cargo vent conduit 54 intended to carry cold gases or vapors, and cargo liquid filling conduit 56 intended to carry cold liquids are provided with thermal insulation coverings 64 and 66 respectively.

It is contemplated that the several conduit and sleeve elements passing through main deck 12 will each have a fixed point at the deck level. Consistent with this, it will be desirable that each such element be flexibly connected to the tank structure of this invention to allow for dimensional changes in connected parts owing to changes in their temperatures, for example. Flexible connections of the kind desired may be effected through bellows joints, and have been so made for purposes of illustration. The bellows joint structure associated with pump sleeve 60 will be identified and discussed in particular as being representative of all such joint structures shown in FIG. 1.

Sleeve 60 passes through the material of the outer and inner tank shells 30 and 32 with ample clearance, but is joined to these two shell members by bellows elements 68 and 70 respectively. Bellows 68 will preferably be of metal for attachment in any suitable manner to the outer tank shell 30 and pump sleeve 60 which will both be fabricated of metal. Bellows 70 will preferably be of polyester film for separate attachment to inner tank shell 32 as shown by a suitable cement, or for integral formation with the inner tank shell. Securing of bellows 70 to pump sleeve 60 is shown as effected by a clamping ring 72.

It may be seen that by use of the illustrated bellows arrangement a two-shell barrier is maintained all around the cold cargo liquid space 36. It is expected that the above mentioned material may be further detailed that by use of this arrangement the cold liquid storage tank structure of this invention may flex quite freely due to temperature variations, working of vessel 10, or any other reason without there being danger of rupture of either tank shell surrounding the cold cargo liquid or of any undue stresses being developed or structural parts.

As pointed out earlier, the polyester film Mylar is an eminently suitable material for inner tank shell 32. This tank shell may, however, be formed of other non-metallic materials if desired. One other material suitable for fabrication of the inner tank shell is a plastic coating composition known as "Plastine No. 9120" which is sold commercially by Wisconsin Protective Coating Corp. of Green Bay, Wis. This composition is formulated of epoxy resin, asphalt, phenolic resin, polyamide, and a suitable curing agent. It has been demonstrated to be impervious to any liquid propane under pressure for extended periods of time.

Plastine No. 9120 may be spread by any convenient apparatus onto the tough skin or inner surface of polyurethane insulating material 34 to a finite thickness, a thickness of 60 mils (0.060") for example, and allowed to set and cure to form a tank shell, or coating compound or other suitable adhesive. For completion of this structure a separate Mylar bellows and clamping ring such as 70 and 72 discussed already can be used to make the final joint to pump sleeve 60, the bellows being cemented to the Plastine inner tank shell by any suitable adhesive agent.

Referring next to FIG. 2, the cold cargo liquid tank wall structure shown therein is identical to that shown in FIG. 1 except that a relatively thin layer of blocks or slabs of balsa wood or cork or other at least semi-rigid insulation 74 has been applied next to the inner surface of outer tank shell 30 with the polyurethane foam material 34 being sprayed upon it in turn. When such an insulating layer as 74 is used for the reason given earlier in this specification, the blocks or slabs which it comprises should be rather carefully fitted and secured by appropriate means to the inner surface of outer tank shell 30. This fitting, although it should be careful, will be much easier and less expensive for thin layer 74 than it would be for a full balsa wood or cork insulation system.

Referring next to FIG. 3, the two fumed plastic materials tested for determination of their compressive strength properties were Freon-expanded polyurethanes. As noted by the legends expanded to a wall thickness of 4.5 lbs./ft.\(^2\) while the other, with less expansion, had a density of 5.1 lbs./ft.\(^2\). Compressive tests were carried out in a standard laboratory testing machine which strained the test specimens at the rate of approximately 0.05 in./min. As noted further in the legends, tests on material of each density were carried out at about 70°F and about 120°F. The latter and somewhat elevated temperature was achieved and maintained by a heating chamber enclosing the test specimens in place in the testing machine.

Material specimens of each density tested at about 70°F were rectangular blocks having dimensions of approximately 3 in. x 3 in. x 1 in. Those of each density tested at about 120°F were likewise rectangular blocks but with the somewhat different dimensions of approximately 2 in. x 2 in. x 1 in. In all tests the specimens were strained, with bellows elements in place. Load readings taken from the machine were converted to stress values on the basis of loaded areas of the specimens, and strain or deflection readings in absolute values were converted to proportional values on the basis of the original values of the strained dimensions of the specimens.

For all tests the data show the existence of a substantially linear stress-strain relation up to a rather definite
yield point, especially for the lower temperature and the more dense material. Qualitatively the data indicate that for a given material density there is a tendency for compressive strength to increase with decreasing temperature, at least over the temperature range explored. Quantitatively they indicate that polyurethane foam having a density of 4.5 lbs./ft.\(^2\) will not develop the aforementioned compressive strength value of 90 p.s.i., at least not at normal temperatures, but that this value will be developed by the 5.1 lbs./ft.\(^2\) density material at temperatures at least up to 120° F. It may be concluded that the latter material will be of general application as thermal insulation in tanks of substantially all the sizes contemplated to be constructed according to this invention, whereas the former will be limited in application to tanks of the smaller sizes.

The tank structure of this invention is considered to be highly useful for the storage and transportation of hydrocarbon liquids which are at least moderately cold. Its utility is not, however, restricted to employment with hydrocarbons only, but rather extends to employment with at least somewhat refrigerated liquids generally. For example, it is contemplated that the tank structure of this invention will be suitable for the storage and transportation of ammonia, chlorine, some Freons, etc., in liquid state.

It will be understood that in any of its particular apparatus embodiments various modifications may be made in this invention without departing from the spirit thereof. Specifically the use of foamed plastics other than polyurethane as insulating materials and the use of materials other than Mylar or a Plastie compound for the inner tank shell are contemplated as being within the scope of this invention, these other materials having in each case properties appropriate to their intended use. It is proposed to secure protection by Letters Patent of all these embodiments and modifications within the broadest interpretation of the following claims that the relevant prior art permits.

What is claimed is:

1. A thermally insulated tank structure for containing low temperature liquids, said tank structure being adapted for insulation in marine vessels and comprising (1) a first shell member of a material which is subject to at least some reduction in its impact resistance property at the normal low temperature of said liquid, (2) a relatively thin layer of a first thermal insulation material in substantially continuous contact with the inner surface of said first shell member, said first thermal insulation material being at least semi-rigid and applied to said inner surface of said first shell member in block form, (3) a layer of substantially thickness of a second thermal insulation material in substantially continuous contact with the inner surface of said first shell member, said second thermal insulation material consisting essentially of polyurethane applied to said inner surface of said first insulating material in sprayed form and expanded to a foamed condition by the vapor of a halogenated hydrocarbon, and (4) a second shell member of a plastic, nonmetallic material in substantially continuous contact with the inner surface of said second insulation material, said second shell member defining a low temperature liquid storage volume within its own inner surface.

2. A thermally insulated tank structure according to claim 1 in which said first shell member consists essentially of a low carbon steel and said first thermal insulation material consists essentially of balsa wood.

3. A thermally insulated tank structure according to claim 1 in which said first shell member consists essentially of a low carbon steel and said first thermal insulation material consists essentially of cork.

4. A thermally insulated tank structure according to claim 1 in which said first shell member consists essentially of a low carbon steel and said second shell member consists essentially of a polyester film.

5. A thermally insulated tank structure according to claim 1 in which said first shell member consists essentially of a low carbon steel and said second shell member consists essentially of a formulation of epoxy resin, asphalt, phenolic resin, polyamide, and a curing agent therefor.

6. A thermally insulated tank structure according to claim 1 in which said layers of first and second insulation materials taken together are of a thickness sufficient to permit a heat flux therethrough not in excess of 0.075 B.t.u.-hr.\(^{-1}\)-ft.\(^{-2}\)-°F.\(^{-1}\).

7. A thermally insulated tank structure according to claim 1 in which said second thermal insulation material has a compressive strength of at least 20 p.s.i.

8. A thermally insulated tank structure according to claim 1 in which said halogenated hydrocarbon consists essentially of trichloromonomfluoromethane.

9. A marine vessel for bulk transportation of low temperature liquids, said vessel comprising a basic structural hull and at least one tank structure mounted in said hull and occupying a substantial portion of the interior volume thereof, said tank structure including (1) a shell member of a metallic material, (2) a relatively thin layer of a first thermal insulation material in substantially continuous contact with the inner surface of said shell member, said first thermal insulation material being at least semi-rigid and applied to said inner surface of said first shell member in block form, and (3) a layer of substantially thickness of a second thermal insulation material in substantially continuous contact with the inner surface of said first shell member, said second thermal insulation material consisting essentially of polyurethane applied to said inner surface of said first insulation material in sprayed form and expanded to a foamed condition by the vapor of a halogenated hydrocarbon, and characterized by a tough skin at its own inner surface which is relatively impermeable by liquid and vaporous hydrocarbon materials.

10. A marine vessel according to claim 9 in which said metallic material is a low carbon steel.

11. A marine vessel according to claim 9 in which said second thermal insulation material has a compressive strength of at least 20 p.s.i.

No references cited.