May 14, 1974 L. F. CREASER 3,810,839

FLEXIBLE INSULANTS FOR CONTAINERS AND CONDUITS

Original Filed May 13, 1970

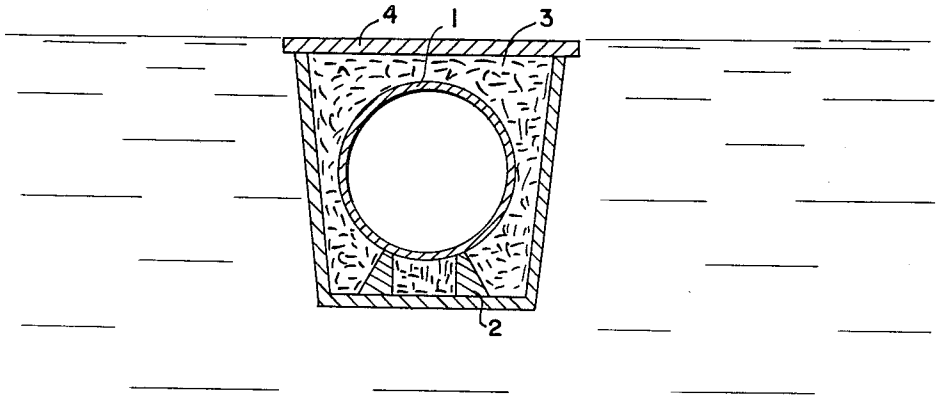



FIG. 1

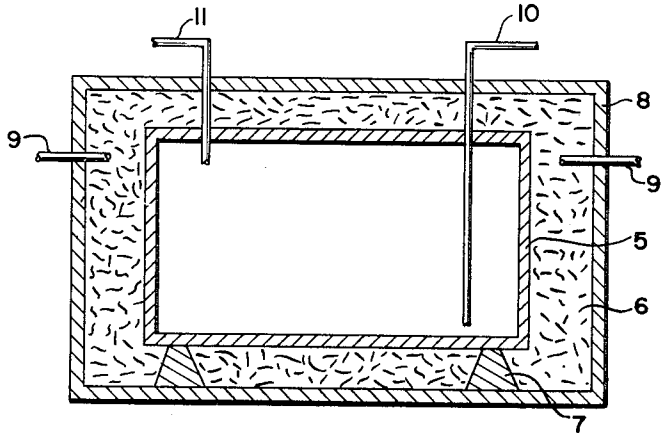



FIG. 2

United States Patent Office

3,810,839
Patented May 14, 1974



3,810,839

# FLEXIBLE INSULANTS FOR CONTAINERS AND CONDUITS

Leonard F. Creaser, Wirral, England, assignor to Shell Oil Company, New York, N.Y.

Original application May 13, 1970, Ser. No. 36,828, now Patent No. 3,682,824. Divided and this application Dec. 2, 1971, Ser. No. 204,380
Claims priority, application Great Britain, Nov. 11, 1969, 55,096/69
Int. Cl. C04b *43/00*
U.S. Cl. 252—62 5 Claims

## ABSTRACT OF THE DISCLOSURE

An improved thermal insulating material for systems containing liquefied gases at low temperatures, said insulant being a hydrocarbon-based foam having a freezing temperature lower or slightly higher than the liquefied gases.

This is a division, of application Ser. No. 36,828, filed May 13, 1970, now U.S. Pat. No. 3,682,824.

This invention relates to thermal insulating materials, and particularly to thermal insulating materials for use in connection with the transport and storage of liquefied gases.

## BACKGROUND OF THE INVENTION

Many thermal insulating materials, hereinafter referred to as "insulants" are known in the art for the insulation of vessels, conduits and the like for the storage or transport of substances as described in U.S. Pats. 2,330,966; 3,045,709; 2,940,631; 2,947,438; 2,947,780 or 3,101,861. However, in the storage and transportation of liquefied gases at low temperatures, the problem becomes complex and in this field of technology, no satisfactory insulants have been found. Contraction of the insulant on cooling from ambient temperature, for example, may cause cracking, resulting in the breakdown of the internal structure of the insulant and/or in the separation of the insulant from the wall of the vessel or conduit, with consequent reduction in insulating efficiency. The use of conventional insulants, such as normally solid cellular materials, sometimes complicates the examination and repair of the insulated vessel or conduit in that, should it be necessary, removal of the insulant may prove difficult.

In the transport of liquefied gases, particularly liquefied natural gas (LNG), at low temperatures in insulated container ships, the loading and unloading points for such ships is generally done with the aid of insulated flexible conduit, joints, loading arms, etc. Insulated flexible conduit may also be used for the transport of such liquefied gases between storage tanks. It will be apparent that in such devices, where a degree of movement must be expected, the tendency of conventional brittle insulants to crack, and possibly fragment, will be greater than when they are used as insulating material for rigid containers.

Due to the importance of liquefied gases in domestic and commercial applications, the invention will be described with particular reference to these materials. However, the invention is applicable to the insulation of vessels and conduit for other low temperature materials, and where the expression "liquefied gases" is used hereinafter it is to be understood as referring not only to liquefied



natural gas (LNG), but to other materials such as LPG, $CO_2$, $N_2$, which may be stored or transported at low temperatures i.e. of the order of 210° K. to 75° K.

## SUMMARY OF THE INVENTION

It has been found that the reduction or even complete elimination of insulant cracking due to cooling can be accomplished by employing as the insulant a hydrocarbon-based foam which freezes at a temperature lower than, or only slightly higher than that at which the liquefied gas is to be stored or transported. According to one aspect of the invention, therefore, there is provided a method of thermally insulating a vessel or conduit adapted to transport and/or store liquefied gas, by means of an insulant which is flexible at ambient temperature and which solidifies at a temperature lower than or slightly above the temperature of the liquefied gas.

Preferably the insulant is one which remains flexible at the storage or transport temperature.

The insulants of the invention are gelled hydrocarbon-forms which can be prepared by judicious choice of certain components so that the foam does not solidify at a temperature so high that further cooling to the temperature of the liquefied gas produces serious cracking. Suitably the foam solidifies at a temperature below or up to 40°, preferably 20° K., above that of the liquefied gas.

The selection of the insulant to be employed according to the invention can be made with regard to the temperature of the liquefied gas which is to be transported or stored. Such liquefied gases have a wide range of temperatures (they are usually stored and carried at a temperature about their boiling point at ambient pressure). For example LNG has a temperature of about 110° K.

The insulants of the invention comprise a hydrocarbon component preferably of a lower molecular weight, preferably a gasoline fraction, hydrocarbon having a freezing or setting point approximating to the temperature of the liquefied gas, a gelling agent, and optionally a foaming agent or emulsifier.

The hydrocarbon component can be a mixture of hydrocarbons or substituted hydrocarbons, and due regard should be given in their selection, to the fact that their freezing or setting temperature could be influenced by the presence of other components, for example, the gelling agent, or, if present, the emulsifier.

Generally, the hydrocarbon component comprises one or more normally liquid low molecular weight hydrocarbons having a hydrocarbon chain length of from about 8 to about 16 carbon atoms such as gasoline, about 8 or 9, or kerosene fractions being typical examples of such materials, and containing hydrocarbon components having an average chain length within the stated range. Substituted hydrocarbons, such as hydrocarbons containing substituted halo atoms, or other substituents, may be employed either as the sole hydrocarbon constituent, or part of it, for example to control the freezing point of the insulant or to influence some other characteristic, such as the degree of inflammability.

Gasoline is the preferred hydrocarbon for use as an insulant for LNG according to the invention, since foams made from it maintain their flexibility to LNG temperatures. Kerosene foams solidify at about 190° K. so that they are more suitable for the insulation of materials about that temperature.

The foams used according to the invention are of relatively small cell size, less than 2 mm., and preferably less than 1 mm., in average diameter and contain from 30 to 90% of gas by volume.

The foams are gelled to assist in the maintenance of their foamed state. Gelling of the foam may be brought about by any suitable gelling agent, any of which are now known from extensive research in connection with the preparation of safety fuels. As a preferred example we may mention aluminum soaps, particularly aluminum octoate. The gelling agent may be employed in any convenient proportion, but we have found that from 2 to 10%, preferably 3 to 7% by weight of the hydrocarbon component is generally satisfactory.

Selection of the gelling agent will of course be made with regard to the nature of the hydrocarbon component of the insulant, in the light of known requirements for gelling agents for hydrocarbon materials.

Gellation may commence before foaming takes place and this is usually preferable so that the mixture when foamed rapidly acquires a degree of gellation at which it does not readily collapse.

The emulsifier, when used, is employed to facilitate the production of a foam. Emulsifiers are usually unnecessary for the preparation of gasoline and kerosene foams which are subjected to a gelling step before foaming, or which are foamed by expulsion of the hydrocarbon through a nozzle with a pressurized gas, but where they are employed they should be soluble in the hydrocarbon. Silicone based emulsifiers and condensates of an alkylphenol and an alkylene oxide such as Triton X–100 (Robin and Haas) Triton X–45, etc., are generally effective but the range of known emulsifiers is wide.

The "blowing agent" a term which includes gas such as inert gases, e.g., nitrogen, $CO_2$, methane, fluoro-hydrocarbons, etc., are incorporated in the mixture by agitation, under pressure or by evolution within the mixture (for example, by chemical reaction) may remain as a gas, or it may be converted to the liquid or solid state at the temperature of the liquefied gas which is to be insulated. Permanent gases, that is, gases which remain in the gaseous state at the temperature of the liquefied gas to be insulated are preferred. For reasons both of safety and convenience, we prefer to employ an inert gas, particularly nitrogen, as the blowing agent.

Other blowing agents which may be employed according to the invention include fluoro-hydrocarbons such as fluorinated olefins, e.g., "Arcton" or "Freon" range of materials having low boiling points and low surface tension and made by DuPont under the quoted trade name. Monobromofluoromethane, for example, can be used for this purpose. However, such materials are not generally so satisfactory as are the permanent gases, as blowing agents since if they are cooled below their boiling point the condensation of the gas to the liquid state, with the consequent very considerable drop in pressure inside the foam, tends to cause collapse of the foam unless it has sufficient rigidity, either due to freezing or gellation to resist collapse.

The invention provides, therefore, a foamed insulant comprising a low molecular weight liquid hydrocarbon, preferably gasoline or kerosene, a gelling agent, optionally an emulsifying agent, and a blowing agent which preferably is a permanent gas.

The insulant, because of its non-rigid nature at ambient temperature, can be confined within an enclosure surrounding the vessel or conduit to be insulated. The insulant is conveniently introduced into the said enclosure by pouring (where this is feasible), or by pumping it through suitably disposed nozzles to effect its satisfactory distribution within the enclosure.

The insulant may be introduced into the enclosure by pouring before or after foaming, whichever method is most convenient.



The enclosure within which the foam is contained may comprise a cavity bounded on the one side by the wall of the vessel or conduit and on the other by an outer wall, so that a double walled structure is obtained. Alternatively, the enclosure may comprise a trough or hole in which the vessel or conduit is suspended or placed, the insulant then being poured into the trough or hole to surround the vessel or conduit.

According to a further aspect of the invention therefore there is provided a vessel or conduit adapted to contain or transport liquefied gas insulated by a foamed insulant which remains flexible at the temperature of the liquefied gas or freezes to a rigid foam at a temperature slightly above the temperature of the liquefied gas.

## DESCRIPTION OF THE DRAWINGS

In the accompanying drawings, which illustrate the invention,

FIG. 1 is a section of a conduit **1**, supported by supports **2** and lying within a trough or trench and surrounded by a foamed insulant composition **3** according to the invention. A cover **4** is shown in position covering the trough.

FIG. 2 is a section of a storage vessel **5** surrounded by a foamed insulant **6** according to the invention and supported by supports **7**, the whole being bounded by an outer casing **8** through which pass tubes **9** for injecting or removal of the insulant foam.

## PREFERRED EMBODIMENT OF THE INVENTION

The invention is illustrated by the following examples.

### Example 1

An insulant suitable for the insulation of LNG storage vessels and conduits (LNG has a temperature of about −160° C.) was prepared by mixing together 100 gm. gasoline and 50 gm. of aluminum octoate in a pressure vessel and injecting nitrogen gas into the mixture at a pressure of about 35 atmospheres, and agitating the mixture vigorously. The pressure vessel was opened, with ejection of a gelled foam which was used to insulate a vessel containing LNG. The foam, which was flexible at 113° K. had a thermal conductivity of 0.053 B.t.u./ft. ° F./hr.

### Example 2

Example 1 was repeated using kerosene instead of gasoline. The container was heated to 60° C. to promote gellation of the kerosene before the foam was released.

The resulting foam was flexible to about 190° K., and had a thermal conductivity similar to that of the gasoline foam of Example 1.

### Example 3

A storage vessel as shown in FIG. 2, was supported in an outer casing **8** and inner casing **5** having support **7** and a gasoline foam **6** and **9** prepared as described in Example 1 was introduced into the space between the vessel and outer wall via conduit **9**. LNG was poured into the storage vessel via conduits **10** and **11** and as the foam cooled to the temperature of the LNG it showed some shrinkage, due mainly to contraction of the gas within the foam.

More foam was then introduced into the space between the outer casing and the storage vessel to occupy the space left by the cooled foam.

I claim as my invention:

**1.** An improved insulating material comprising an inert gas blown mixture of a hydrocarbon containing from 6 to 18 carbon atoms and a gelling agent.

**2.** The insulating material of claim **1** wherein the hydrocarbon is kerosene and the gelling agent is an aluminum soap.

**3.** The insulating material of claim **1** wherein the hydrocarbon is gasoline and the gelling agent is aluminum soap.

4. The composition of claim 2 wherein the aluminum soap is aluminum octoate.

5. An insulating material for vessels and conduits utilized in the storage and transportation of liquefied gases at low temperatures comprising an inert gas blown mixture if a hydrocarbon containing from 6 to 18 carbon atoms and a gelling agent.


**References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,860,103 | 11/1958 | Buehanan et al. | 252—8.55 |
| 3,158,459 | 11/1964 | Guilhem | 220—15 X |
| 3,280,868 | 10/1966 | Poettmann | 138—145 |
| 3,642,624 | 2/1972 | Howland et al. | 252—62 X |
| 3,682,824 | 8/1972 | Creaser | 252—62 |
| 2,448,280 | 8/1948 | Sargent et al. | 252—62 |
| 2,751,283 | 6/1956 | Van Strien et al. | 252—316 X |
| 2,866,754 | 12/1958 | Cardwell et al. | 252—316 X |
| 3,041,190 | 6/1962 | Griffith et al. | 252—62 X |
| 3,334,052 | 8/1967 | Kurz et al. | 252—316 |
| 3,480,545 | 11/1969 | Dale | 252—316 X |





EDWARD G. WHITBY, Primary Examiner

U.S. Cl. X.R.

156—78; 220—10; 252—316