United States Patent Office 3,761,232
Patented Sept. 25, 1973

3,761,232

METHOD FOR ODORIZING CRYOGENIC LIQUIDS

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No Drawing. Filed May 10, 1971, Ser. No. 142,069
Int. Cl. C10l 1/24
U.S. Cl. 44—52 11 Claims

ABSTRACT OF THE DISCLOSURE

A method for odorizing cryogenic liquids such as liquefied natural gas with sufficient levels of detectable sulfur containing odorants by the steps of first dissolving said odorant in a liquefied carrier miscible with the cryogenic liquid at concentration levels not attainable in the cryogenic liquid; and then combining said liquefied carrier with odorant and the cryogenic liquid to provide the dissolved odorant in the mixture at the desired detectable levels upon vaporization of the cryogenic liquid.

This invention relates to a method for odorizing cryogenic liquids having inadequate odor levels with sulfur containing odorants now used for odorizing gaseous fuels. The invention particularly relates to an improved method by which sufficient concentrations of odorant are provided in a cryogenic liquid so that gaseous forms of said liquid can be detected.

Conventional odorants are used with gaseous fuels so that escape of the fuel during undetected or catastrophic leakage can be readily detected. Various odorants are used for this, particularly sulfur containing odorants such as mercaptans, sulfides, disulfides, mixtures thereof and the like.

Such odorants have been added to fuel gases used for heating, illuminating and cooking, both in the gaseous and in the liquid forms. The liquid forms usually are liqued petroleum gas or liquefied propane gas, also known as "bottle gas." Various problems may exist with respect to providing means for continually introducing odorant and maintaining odorant levels as gas escapes, but generally there is no problem in any of these forms when initially introducing sufficient levels of odorant so that escaping gas can be detected by smell.

This problem does exist in serious form with the use of cryogenic fuels, for example. Such fuels have received increasing attention in the art because they provide a way for transporting fuels from places of rich natural sources to places remote therefrom. The cryogenic fuels are liquefied gases such as methane or liquefied natural gas or liquefied hydrogen. Such cryogenic fuels are conveniently handled by maintaining very cold temperature environments for enclosures of said gases, say, below —100° F. The cryogenic temperatures permit handling of these fuels without requiring high pressure equipment and materials.

A serious obstacle to the utilization and enjoyment of cryogenic fuels is the inability heretofore of providing such fuels with sufficient levels of odorants. The commercially used and accepted sulfur containing odorants tend to solidfy and precipitate from the fuel prior to reaching adequate and desirable concentration levels. Such conventional sulfur contatining odorants are notorious for solidifying and precipitating at —260° F. and at higher temperatures. Liquified methane boils at about —260° F. at atmospheric pressure, and most liquefied natural gas sources boil generally at about this temperature. Accordingly, the presently most popular sources of cyrogenic fuels are seriuosly handicapped in their utility because of the inability to dissolve adequate levels of sulfur containing odorants therein.

Cryogenic fuels are important types of cryogenic liquids, but others can also be usefully odorized for undetected leakage or the like when vaporized. They include liquefied carbon dioxide, hydrogen, nitrogen, carbon tetrafluoride, and the like. Precipitation of conventional odorants in such liquefied gases remains a problem.

It is accordingly one important object of the present invention to provide a method whereby useful sulfur containing odorants may be incorporated in cryogenic liquids at adequate levels for desired detection, such incorporation resulting from improved steps which lead to the hgher dissolved amounts of odorant in the cryogenic liquids.

Another improtant object of the present invention is to provide an improved method for providing cryogenic liquids with increased amounts of dissolved odorants by utilizing a preliminary carrier for such odorant, which carrier is compatible with the cryogenic liquid and does not detract from the desired properties of such a liquid.

Still yet another important object of the present invention is to provide an improved method for providing cryogenic fuels with increased amounts of dissolved conventional odorants so that levels of odorant introduced into the cryogenic fuel do not separate therefrom through solidification and precipitation which would occur if the odorant were directly introduced in such amounts into the cryogenic fuel.

Still yet another important object of the present invention is to provide an improved method for providing cryogenic fuels with the known sulfur containing odorants at adequate levels through efficient and reliable steps which manipulate small carrier volumes with higher levels of odorant into larger volumes of cryogenic fuel.

A yet another important object is to overcome the disadvantages associated with a slurry mixture of precipitated odorant and cryogenic liquid, such as release of too much or too little odorant upon vaporization, plugging equipment orifices or the like with the separated odorant, and the like.

The above objects are now attained, as well as still other objects which will occur to practitioners from time to time by considering the following disclosure of the invention.

It has been discovered that higher odorant concentrations may be dissolved in particular cryogenic carrier solvents which are miscible with the cryogenic liquids, and which do not detract from the desired properties of such cryogenic liquids. The cryogenic liquids present unique problems associated with extreme low temperatures, and such problems prevent operation of reliable predictability with respect to the use of solutes, solvency and the like. For example, the notorious precipitation of conventional odorants in liquefied natural gas may be due in part to freezing, rather than straightforward solvency in compatibility. Further, conventional odorants are demonstrated to separate when added to a previously mixed cryogenic carrier and cryogenic liquid, even though mixed in the same proportions which operate successfully when following the teachings of the present invention.

The cryogenic carriers are liquefied gases such as nitrogen, hydrogen, fluorinated hydrocarbons and, preferably, liquefied lower alkane hydrocarbons, namely, liquefied butanes, liquefied ethane and, particularly, liquefied propane. The lower alkyl hydrocarbon liquefied carriers also serve as fuels when the cryogenic liquid is a fuel, that is, a liquid with B.t.u. or calorific values. The lower alkane hydrocarbon carriers, therefore, lead to compatible admixture with cryogenic fuels such as liquefied methane, LNG, and liquefied hydrogen. It should be noted that a low or non-calorific carrier could be used with high B.t.u. fuels.

Combining such carrier and odorant with the cryogenic fuels leads to high amounts of the odorant being dissolved in the cryogenic fuel than could be attained by directly introducing such odorant into the cryogenic fuel. By the method of this invention, adequate levels of odorant are dissolved in the fuel without encountering degrees of separation and precipitation which would destroy the odorant function in such fuel carrier.

A wide variety of sulfur containing organic compounds have been used as odorants. These include monomercaptans, acyclic sulfides and cyclic sulfides. Among the sulfur containing odorants known to be successfully used for these purposes are thiophane, ethyl mercaptan, tert-butylmercaptan, dimethyl sulfide, and others. Further reference may be made to U.S. No. 2,625,518 for a variety of odorants and their properties for use with gaseous fuels. The practitioner will recognize that such representative sulfur containing odorants, as well as others, may be usefully adapted in the practice of the present invention to different degrees of success as such practitioner may readily determine.

The practitioner will also select the particular liquefied gas or lower alkane hydrocarbon carrier which meets the particular criteria the practitioner may have set, based on economics, degree of odorization desired, identity of carrier and cryogenic liquid, as well as still other criteria. Improvements will be realized within the scope of the present invention with such various selections, although one preferred embodiment presently contemplated provides utilizing liquefied propane as the carrier for conventional sulfur containing odorants to be used in cryogenic fuels.

The practitioner may find that known or new sulfur containing odorants may operate best alone, or may operate best as one of two or more ingredients in an odorant combination or package. This may depend, in part, on which of the described carriers the practitioner utilizes alone or in various mixtures. In any event, the practitioner will be guided by the goal of incorporating sufficient levels of one or more odorants in a resulting mixture of cryogenic fuel and carrier so that said mixture has a desired detectable level of odorant without substantial change to the B.t.u. or calorific value of the fuel.

In general, the carrier with odorant comprises a very small volume relative to the volume of cryogenic fuel. Such carrier with odorant thereby comprises a minor volume relative to a major volume of the fuel, say, less than about 10% by volume of the cryogenic fuel. Many embodiments may find this minor volume to comprise from about 1% to about 5% by volume. It is preferred that agitation be provided during addition for better mixing. Such agitation can be performed with a mechanical stirrer, or by flashing cryogenic liquid, or by other means.

It is generally desirable to add the minor volume of carrier with odorant to the cryogenic liquid, rather than vice versa. It is believed that introduction of such small small volumes to the larger fuel volume contributes to higher incorporation of the odorant as a solute without inducing loss by precipitation. For generally the same purposes, it is also believed desirable to add the minor volume of carrier with odorant in successive small increments to the major volume of cryogenic liquid. These increments may be delivered in various ways to the volume of cryogenic liquid, such as above-the-surface, or the preferred below-the-surface introduction. It is believed that the below-the-surface feed contributes to better miscibility without inducing separation which might result from splashing or otherwise hard contact between the two liquids. Such below-surface feed may also provide desired agitation.

It is intended that the liquefied hydrocarbon carrier with odorant may be pressurized in a cylinder or the like to provide another form for handling and introducing the carrier with solvent to the cryogenic fuel. Some pressurization will reduce the temperature requirements for liquefaction, depending upon the properties of the carrier-odorant.

The boiling point of liquefied methane at atmospheric pressure is —258.9° F., and it is recognized that LNG may have this very same boiling point or some departure therefrom. It is recognized that LNG may consist of from about 75% to close to 100% of methane, therefore, the boiling point will come closer to the —260° F. level as the content approaches 100%, and accordingly depart therefrom proportionately as the content approaches the lower range of about 75%. When either liquefied methane or LNG is employed as a cryogenic fuel, then, in general, a hydrocarbon carrier should have a freezing point less than —260° F., or below the boiling point of the particular batch of LNG which is used. It is generally required that a carrier freezing point should be lower than the cryogenic liquid boiling point, and be miscible therewith. The practitioner will recognize that in some embodiments cryogenic carriers can be successfully used, even though the freezing point may be somewhat higher than the cryogenic liquid. It is a requirement, however, that the liquefied hydrocarbon carrier should have a boiling point higher than —260° F., or higher than the boiling point of the particular batch of LNG which is used. Such a range will assure that the carrier will retain its liquid form when it is combined with liquefied methane or LNG.

Some liquefied hydrocarbon carriers may require precooling to about —260° F., or to the boiling point of the particular LNG batch which is selected to minimize flashing of the cryogenic fuel. For example, the pressurized forms of the carrier previously described might very well require such precooling prior to combination with liquefied methane or LGN.

The following specific example is presented as a representative embodiment of the practice of the invention.

Chemically pure methane is passed through activated charcoal and then liquefied under lowered temperature at atmospheric pressure. The liquefied methane is essentially clear. Into a Dewar flask is placed about 300 ml. of liquid methane. Ethanethiol is then added in increments of three microliters below the surface of the liquid methane. This first increment results in the formation of a white immiscible precipitate which sinks to the bottom of the flask. Additional increments of three microliters also assume the appearance of white, solidified odorant which slowly precipitated, but did not otherwise render the methane turbid.

A solution is formed of liquid propane carrier and 10% by volume of ethanethiol. The solution of carrier and solvent is added under the level of the liquid methane present in an amount of 300 ml. in the open Dewar flask. The carrier with odorant solution is added in increments under the surface until a total of about 20–25 ml. of the carrier-odorant solution is added. A final amount of about 3–5 ml. of the carrier with odorant is then added above the surface of the liquid methane. No precipitation is observed.

A 50% by volume solution of ethanethiol liquid propane is next added to the above clear liquid methane in an amount of 5–10 ml. of the solution. The addition results in a slight turbidity, but no observable precipitation. A second aliquot of 5–10 ml. of the 50% by volume solution is added, whereupon a dense white cloud forms in the liquid methane.

The foregoing example illustrates that substantially no ethanethiol is soluble in the liquid methane when added directly; in any event, substantially less than 0.001% by volume. Such solubility is increased up to 0.6% by volume when the ethanethiol is added as a 10% by volume solution with liquefied propane; and when the 50% by volume of ethanethiol and liquid propane carrier was subsequently added, the total concentration of the odorant and the resulting mixture was from about 1½% by volume to more than 2% by volume. This represents more than a 2000 fold increase in the solubility of the odorant when follow-

ing the steps of the invention. The volume percent of 1% to 2% in the cryogenic fuel is far in excess of the amounts required for efficient odorization.

The claims of the invention are now presented.

What is claimed is:

1. A method for providing cryogenic liquefied gases with sufficient soluble levels of organic sulfur containing odorants selected from the class consisting of thiophane, an acyclic sulfide, a cyclic sulfide and a mercaptan, including

dissolving said odorant in a liquefied hydrocarbon gas carrier said carrier being miscible with the cryogenic liquefied gas, said carrier having a boiling point which is higher than that of the cryogenic liquefied gas, said odorant being dissolved in said carried at concentrations greater than could be dissolved in the cryogenic liquefied gas, and

combining said cryogenic liquefied gas and minor volumes of said carrier with dissolved odorant so that said cryogenic liquefied gas component of said mixture contains detectable concentrations of odorants.

2. A method which includes the steps of claim 1 above wherein said cryogenic liquefied gas is a cryogenic fuel.

3. A method which includes the steps of claim 2 above wherein said cryogenic fuel is liquid methane.

4. A method which includes the steps of claim 2 above wherein said cryogenic fuel is liquefied natural gas.

5. A method which includes the steps of claim 2 above wherein said carrier is a liquefied lower alkane hydrocarbon.

6. A method which includes the steps of claim 5 above wherein said liquefied lower alkane hydrocarbon carrier has said odorant dissolved therein from about 10% to about 50% by volume, and wherein said carrier with dissolved odorant is added to liquefied natural gas to attain dissolved odorant levels in the mixture up to 2% by volume.

7. A method which includes the steps of claim 6 above, and which further includes adding said carrier with dissolved odorant to said cryogenic fuel in successive increments until the desired level of odorant is attained in the cryogenic fuel mixture.

8. A method which includes the steps of claim 7 above wherein a minor volume of carrier with odorant is added to a major volume of cryogenic fuel.

9. A method which includes the steps of claim 8 above wherein the odorant with carrier is pressurized, and wherein said carrier with odorant is precooled prior to being combined with said cryogenic fuel to thereby enhance the miscibility of the components.

10. A method which includes the steps of claim 2 above wherein said cryogenic fuel is liquefied natural gas boiling at substantially —260° F. at atmospheric pressure, and wherein said carrier with odorant is precooled to substantially —260° F. at atmospheric pressure prior to combination with said cryogenic fuel.

11. A cryogenic fuel composition with detectable odorant levels, including

a cryogenic liquefied gas component,

a miscible liquefied hydrocarbon gas carrier component, said carrier component having dissolved therein from about 10% to about 50% by volume of an organic sulfur containing odorant selected from the class consisting of thiophane, a mercaptan, an acyclic sulfide and a cyclic sulfide, and

said components in admixture retaining said odorant substantially in solution so that the resulting composition is substantially free from precipitated odorant and retains such odorant in sufficient levels to detect the fuel following vaporization.

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U.S. Cl. X.R.

44—59; 48—195, 196 FM, 197 FM

Notice of Adverse Decision in Interference

In Interference No. 98,750, involving Patent No. 3,761,232, D. L. Klass and C. D. Landahl, METHOD FOR ODORIZING CRYOGENIC LIQUIDS, final judgment adverse to the patentees was rendered Aug. 25, 1976, as to claims 4 and 5.

[*Official Gazette November 30, 1976.*]