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TESTING LIQUEFIED PETROLEUM GAS

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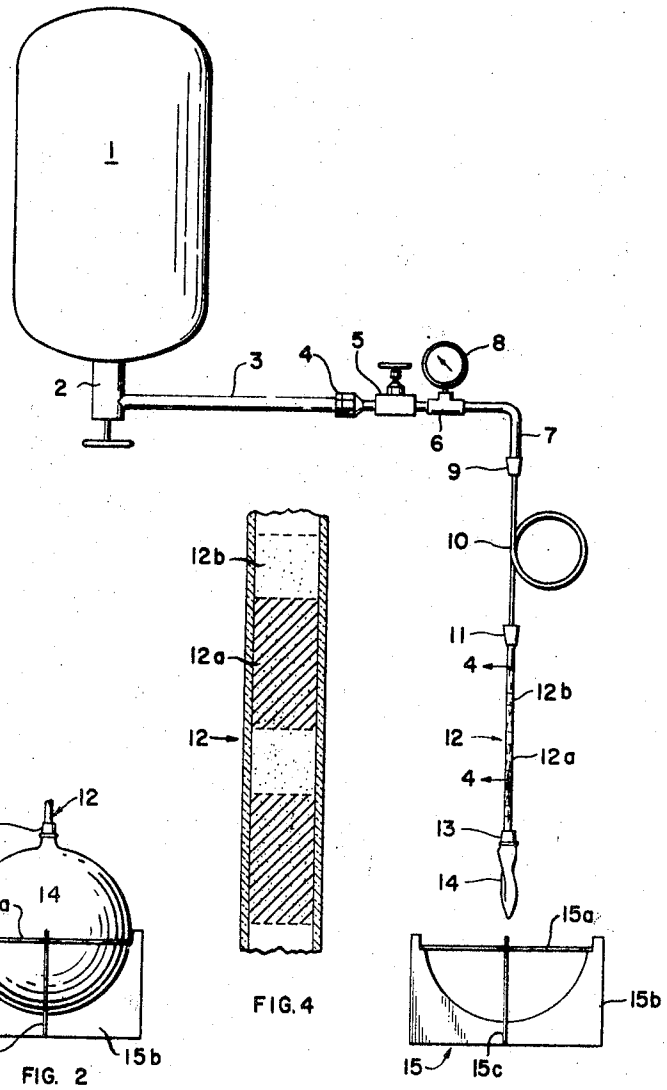


FIG. 1

FIG. 2

FIG. 4

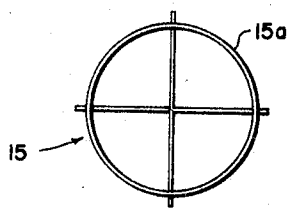


FIG. 3

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TESTING LIQUEFIED PETROLEUM GAS

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This invention relates to a method and a device for testing liquefied petroleum gases for determining whether an indicator such as an odorant has been added to the liquefied gas and is present in a required concentration.

Liquefied petroleum gases commonly called LPG are generally butane or propane, or mixtures thereof, which are comparatively readily liquefiable. Propane has a boiling point of —42.2° C. at atmospheric (760 mm.) pressure and n-butane a boiling point of —0.5° C. at atmospheric pressure. These hydrocarbon gases separated from natural gas or refinery gas are liquefied by compression and are stored in vessels under pressure at atmospheric temperature or alternately at atmospheric pressure under refrigerated or reduced temperature conditions. Generally, small amounts of LPG are stored and transported in cylinders and other pressure vessels and turned into gases at or near the point of utilization by releasing the pressure. They thus provide a portable source of gaseous fuel and are most useful for areas wherea normal piped gas distribution system does not exist.

In recent years, there has been a rapid increase in the use of LPG for both industrial and domestic purposes. One of the problems met with is that the gas has very little odor so that its presence in the atmosphere is not readily noticeable. As will be apparent, an undetected leak or escape of the gas, which is under pressure, can lead to the formation of a combustible or highly explosive air-hydrocarbon mixture so that the slightest spark can result in loss of life and property.

In order to more readily detect an escape of the gas it is a practice to add a strong smelling additive to the liquefied gas which has a boiling point close to that of the LPG so that an escape of gas can be readily and quickly noticed by the characteristic odor. A commonly used odorant is ethyl mercaptan.

For some industrial and chemical uses, the presence of an odorant in the LPG is not desirable. Consequently, it is sometimes a practice to ship LPG from oil refineries and other plants where LPG is produced without the odorant being present in the liquid. The odorant is then only added at the distribution or bottling plant for those fields of use where the odorant is desirable or necessary.

While it is possible by careful control methods and appropriate cylinder markings to be reasonably certain that only odorized LPG is used domestically, such as in cooking stoves, heaters, etc., there is always the danger that a mistake may be made. Field checks are therefore most desirable. Odor checks commonly used, however, are sometimes not sufficiently positive due to the presence of other odors, due to the non-sensitivity of personnel to the odor, or for other reasons are not acceptable. It is therefore an object of this invention to provide a simple, fast and positive method of detecting the presence and amount of odorant in LPG containers such as cylinders and other pressure vessels.

Another object of this invention is to supply an odorant test means which can be readily operated by non-technical personnel.

Briefly the invention comprises the provision of a method and means for readily determining and measuring the ethyl mercaptan content of LPG by contacting the material with a supported chemical indicator which

changes to a bright color in the presence of mercaptan and is so arranged that with the passage of a definitely readily ascertained volume of gas, the indicator will show the concentration of ethyl mercaptan in the LPG.

The following is a description of a specific embodiment of the invention throughout which description reference is made to the accompanying drawing showing further details of the invention.

In the drawing,

FIG. 1 is an elevation of the assembled apparatus partially in section and connected to an LPG container, prior to test.

FIG. 2 shows an elevation of the lower part of the apparatus after the test.

FIG. 3 is a plan of the standard volume ring shown in the FIGS. 1 and 2.

FIG. 4 is an enlarged sectional view taken along the lines 4—4 of FIG. 1.

Referring to the FIG. 1, a filled pressure cylinder of LPG **1** having its regular shutoff valve **2** is inverted and connected by a high pressure flexible conduit **3** to an adapter or reducer **4** to one side of a needle valve **5**. The other side of the needle valve **5** is connected by means of a T piece **6** to tubular elbow **7**. A pressure gauge **8** is attached to the third arm of the T piece **6**. The end of the elbow **7** is connected by a rubber connector **9** to a coiled metal vaporizer tube **10**. The other end of the vaporizer tube **10** is connected by a rubber connector **11** to a detector tube **12**. The detector tube is made of transparent material such as glass and is provided with uniform sections of impregnated silica gel **12***a* having a buff color and unimpregnated sections of silica gel **12***b* having a white color. The lower end of the detector tube is connected by a suitable rubber connector **13** to the neck of a completely deflated rubber sac or balloon **14**.

The rubber balloon **14** is encompassed by a standard volume ring gauge **15** which consists of an upper horizontal ring element **15***a* and two base-forming plates **15***b* and **15***c* which are fitted together at right angles by being suitably slotted as will be seen from FIG. 3 of the drawing.

The length of the treated sections of silica gel **12***a* is adjusted so that a color change of each section or zone corresponds to a level of 10 p.p.m. mercaptan in a prescribed volume of vaporized LPG. LPG without mercaptan odorant produces no color change. More specifically, the silica gel forming the treated buff colored zones is impregnated with a solution of palladium chloride and this material can be prepared by the following steps:

(a) Place 0.500 g. $PdCl_2$ in a 50-ml. beaker and add 10-ml. distilled water, 5-ml. 6 N HCl and 5-ml. 6 N H_2SO_4.
(b) Warm solution gently and stir until solid is dissolved.
(c) Transfer solution to a 25-ml. volumetric flask and dilute to the mark with distilled water.
(d) Weigh out 5.00 g. of 60–80 mesh silica gel (Davison Grade 950) in a 50-ml. beaker.
(e) With a pipette, add slowly, with stirring 4-ml. of $PdCl_2$ solution to the silica gel.
(f) Stir mixture until uniform.
(g) Place wetted gel in a vacuum oven and heat at 50–55° C. for 5 hours to dry and activate. Stir occasionally to prevent darkening of the outer layer of gel.
(h) Place treated gel in sealed tubes or store under dry conditions.

Variations of the above procedure may be used. The concentration of the palladium chloride stock solution can be varied between wide limits; e.g., between saturation and 1.5 g./l. Either one or both acids may be omitted in the procedure. However, the presence of acid increases the

distinctness of the color change upon exposure to the ethyl mercaptan. The amount of palladium chloride stock solution applied may vary from 1 to 10-ml./5 g. silica gel. Drying and activation of the treated silica gel may be carried out in an ordinary oven or in a vacuum oven, and the activation time may vary from 3 to 24 hours.

To load the detector tubes the following procedure can be used:

(1) Cut a 6-inch length of 4-mm. O.D. glass tubing and place a 0.10–0.15-inch cotton plug about 1.5 inches from one end.
(2) Fill the tube with alternate layers of treated silica gel (0.0400 g.) and pure silica gel (30–60 mesh) (0.0200 g.).
(3) Vibrate the tube during the filling process with a mechanical vibrator. A completed tube consists of 3 layers of treated silica gel and 2 layers of pure silica gel.
(4) Place another cotton plug in the tube and pack down cotton from both ends.
(5) Seal both ends of the tube with a flame.

As will be appreciated, considerable variation is permissible in the manner of packing and in the physical dimensions of a completed mercaptan detector tube.

Calibration of the detector tubes was established with an LPG sample analyzed for ethyl mercaptan by a standard analytical method employing caustic scrubbing and potentiometric titration with silver nitrate. According to this method the mercaptan is removed from the gaseous sample by passing it through a scrubber containing aqueous sodium hydroxide solution. The separate solution is titrated electrometrically with silver nitrate solution using as an indicator the potential between a glass or acetate reference electrode and a silver-silver sulfide indicating electrode.

The testing apparatus is operated as follows. With the valve **2** on cylinder **1** open, the needle valve **5** is gently and carefully opened to a small extent so that LPG will pass through to metal vaporizer tube **10**. Upon the release in pressure through the needle valve, the LPG will expand and change to the gaseous state with the withdrawal of heat from the metal walls of the conduits. The gas next passes through detector tube **12** containing the silica gel units **12***a* and **12***b*. Gas from the lower end of the detector tube **12** is conducted into the empty balloon placed inside the gauge ring stand **15**. The gas flow is continued at a slow rate until the balloon makes a snug fit inside the ring **15**. The LPG flow is then turned off and the detector tube disconnected. The detector tube is observed to note the number of bright yellow zones formed from the buff color impregnated silica gel. If, for example, the device is used for measuring the concentration of ethyl mercaptan in the 0–30 parts per million range, three zones of impregnated silica gel in the detector are provided. These zones are of such concentration of reagent that with the passage of the volume of gas received in the balloon, ethyl mercaptan in the concentration of 10 p.p.m. by weight is reacted entirely in one zone. This reaction with the palladium chloride turns the color from buff to a bright yellow. By counting the number of zones or fractions thereof colored yellow, a rapid determination of the concentration of ethyl mercaptan in the LPG can be made.

Care must be taken to ensure that the needle valve is not opened rapidly or opened to a fast rate of flow. With a rapid opening or fast rate of flow the rubber connections are liable to be blown off and the test necessarily will have to be started over again. If too rapid a flow is used, the LPG will not be completely vaporized in the vaporizer tube **10**, consequently an inaccurate test can result. Observation will indicate whether or not liquid is entering the detector tube. If the ambient temperature is low the vaporizing of the LPG in the metal vaporizer tube **10** can be aided by slightly warming the tube by contact with the operator's hand. In case of very low ambient temperature the vaporizer tube can be positioned so that it can be inserted into a container of hot water.

Example

A test was made on a propane cylinder to determine the ethyl mercaptan content. A glass detector tube having sealed ends was, after the tips had been broken off, inserted into the system. The detector tube had three equal length zones of impregnated silica gel separated by zones of unimpregnated silica gel. The impregnated zones had a light buff color while the unimpregnated zones were white. The needle valve **5** was opened slowly until 25 lbs. pressure reading was obtained on the pressure gauge **8**. The LPG was allowed to flow until the balloon was filled to a snug fit in the ring which had an internal diameter of 6$\frac{9}{32}$ inches. A balloon when filling the standard volume ring had a content of 2 liters of gas. The needle valve was then turned off and the detector tube carefully removed from the system. It was noted that two impregnated zones of buff color had turned to a bright yellow and that approximately $\frac{1}{5}$ of the third zone was yellow. The complete yellow zones formed each corresponded to 10 p.p.m. of ethyl mercaptan in the volume of LPG passed, namely, 2 liters. It was estimated that the LPG contained approximately 22 p.p.m. of ethyl mercaptan. This was confirmed by accurate laboratory analysis.

One of the advantages of our invention it should be noted, is that the yellow color zones are permanent and the detector tubes can be filed for later reference. The yellow color intensifies to a certain degree with age but the demarkation of the zones does not change.

The material we prefer for the granular sorptive carrier or support for the indicator is silica gel, although other materials such as alumina could be used. If alumina is employed as a support, the unreacted area remains whiter, but the reacted area is a much lighter yellow than that obtained with a silica gel support. The size of the support granules is governed in part by the cross-sectional area of the detector tubes used. Instead of glass tubes, tubes of suitable clear plastic material could be employed, or glass tubes covered with a transparent plastic material could be used. Various other modifications may be made. For example, instead of rubber connectors of the type shown in the drawing, pipe fittings of molded plastic could be substituted, although this will require the further use of hand tools to effect an assembly of the apparatus, which would somewhat detract from the simplicity of the method and apparatus set forth herein.

We claim as our invention:

1. The method of detecting and determining the presence of ethyl mercaptan in liquefied petroleum gases under pressure which comprises: reducing the pressure on the liquefied gas by metering restrictive means to a predetermined lower pressure; vaporizing the liquefied gas; flowing a predetermined volume of the vaporized liquefied gas through successive separate elongated beds of sorptive granular material alternate ones of which are of equal length and carry a metallic salt reagent which upon contact with ethyl mercaptan changes color over a length which is dependent upon the concentration of the ethyl mercaptan in the vaporized liquefied petroleum gas, a complete color change of each of said alternate beds thereby indicating a predetermined concentration of ethyl mercaptan; and, thereafter determining the number of separate elongated beds which have changed color as an indication of the total concentration of ethyl mercaptan in the vaporized liquefied gas.

2. The method of detecting and determining the concentration of ethyl mercaptan iin liquefied petroleum gases under pressure as defined in claim **1** in which the metallic salt reagent is palladium chloride.

3. The method of detecting and determining the presence and concentration of ethyl mercaptan as in claim **2** in which the liquefied petroleum gas is propane.

4. The method of detecting and determining the presence and concentration of ethyl mercaptan as in claim 2 in which the liquefied gas is n-butane.

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