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METHOD AND COMPOSITION FOR DETECTING ODORS IN GASEOUS FUELS

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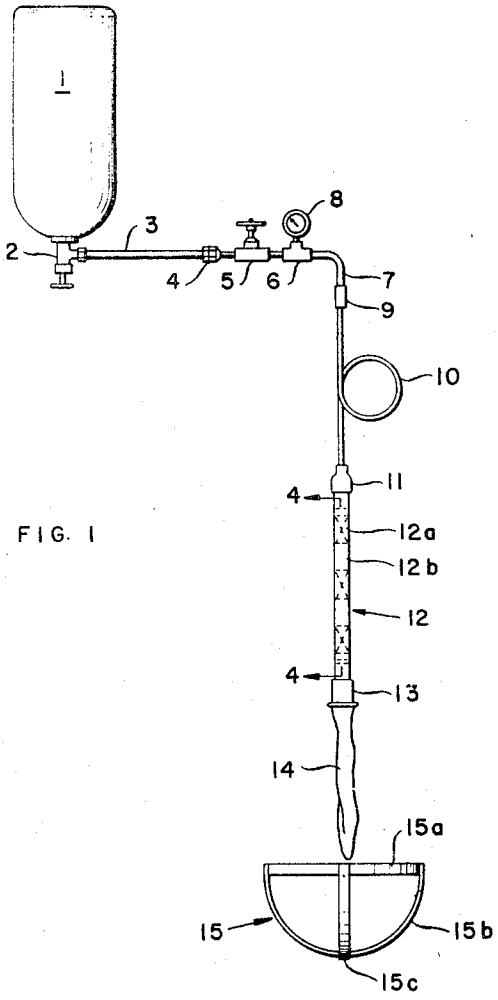


FIG. 1

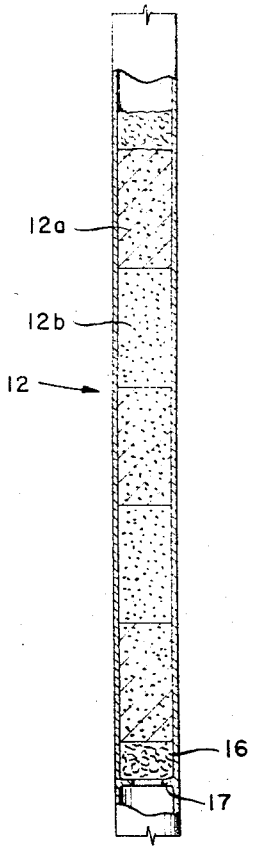


FIG. 4

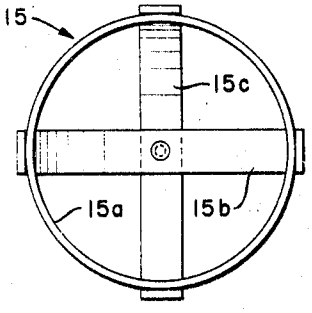


FIG. 3

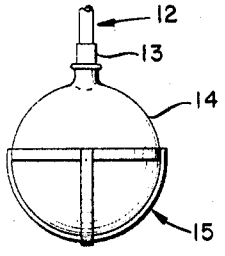


FIG. 2

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METHOD AND COMPOSITION FOR DETECTING ODORS IN GASEOUS FUELS

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U.S. Cl. 23—230 11 Claims

ABSTRACT OF THE DISCLOSURE

A composition of matter and method of detecting odors in hydrocarbon fuels by addition to such fuels an odorous saturated heterocyclic organic sulfide which on contact with an absorbent material impregnated with an acidic solution of an alkali metal iodate, a carbohydrate adsorbent and an organic sulfoxide or sulfone, results in a color change.

This invention relates to an improved odorant detecting composition and device therefor. More particularly, the invention pertains to novel means for detecting odorized light hydrocarbon fuels such as natural gas, liquefied petroleum gases commonly called LPG and various other types of gases and fuels used for homecooking or heating and for industrial uses, odorized with a minor amount of 0.10 part or more per million of a saturated organic heterocyclic sulfide compound containing at least 3 carbon atoms and sulfur as a heteroatom in the molecule.

Various odoriferous materials such as liquid mercaptan or aliphatic or aromatic sulfides or unsaturated cyclic sulfides, e.g., thiophenes, are used as odorants for gaseous fuels as warning means of leaks and possible consequent existence of toxic and explosive hazards. Such materials particularly the mercaptan, e.g., ethyl mercaptan, are normally susceptible to oxidation resulting in products lacking in desired odor intensity and they are generally corrosive to various metals such as copper and iron with which such odorized gases are in contact. However, these materials particularly the mercaptans are used as odorants for gaseous fuels such as liquid petroleum gas (LPG) and various reagents and tests have been devised for their detection as evidenced by reference to Anal. Chem., vol. 26, No. 3, March 1954, pages 528–536, and to U.S. Patent 3,208,828.

A class of odoriferous materials useful for this purpose are saturated heterocyclic organic sulfides which are more stable than the odorants mentioned above and inhibit corrosion. These materials occur naturally in petroleum oils and can be recovered from acid sludge formed during the acid treatment of light liquid hydrocarbons such as cracked gasoline, kerosene and the like by suitable means such as by distillation. Thus, the acid sludge on distillation produces an oily condensate which is rich in saturated heterocyclic sulfides known as petroleum thiophanes, which materials possess excellent stability and are useful noncorrosive odorants for gaseous fuels. The acid sludge from which the thiophanes are recovered can be first hydrolyzed to remove weak acids and the tars formed are subjected to distillation to recover petroleum thiophanes from the condensate. Pure thiophane or tetrahydrothiophene can also be used as an odorant.

While various tests, reagents and detector devices are known for detecting odorous sulfur-containing compounds such as the mercaptans or certain sulfides in light hydrocarbons as pointed out above, effective means for detecting the presence of petroleum thiophane or pure thiophane, e.g., tetrahydrothiophene, in gaseous fuels are unknown thus making it under various circumstances inadvisable to use, particularly with personnel who are insensitive to the odor and for various other reasons.

It has now been discovered that an excellent reagent or composition for detecting small amounts of even less than 10 p.p.m. of odorous saturated heterocyclic organic sulfides such as thiophanes in gaseous fuels such as natural gas, liquid petroleum gas and the like can be readily accomplished by contacting said odorous fuel with a sorptive granular material, e.g., alumina or silica gel impregnated with an acidic solution of an alkali metal iodate, a finely divided carbohydrate adsorbate and an organic sulfoxide and/or sulfone and noting change in color such as from white to yellow or if a dye is added to the silica impregnated composition such as a blue dye, the color change due to the presence of the saturated heterocyclic organic sulfides would be from blue to green. The device or apparatus for detecting odorous compounds mentioned can be essentially the same as described in U.S. Patent 3,208,828 provided the detecting reagent or composition is the one described in the present invention.

Specifically, the chemical composition used to impregnate the sorptive granular materials such as silica impregnating material include a mixture in specific proportions so as to produce the desired color change of (1) an alkali metal iodate such as potassium iodate or mixtures of potassium iodate and palladium chloride; (2) a carbohydrate adsorbent such as starch or other suitable materials capable of forming a colored complex with iodine; and (3) an organic sulfoxide and/or organic sulfones which functions as a sensitivity agent and due to its presence increases the sensitivity of the chemical reagent compositions several fold. Materials of this type include aliphatic, aromatic, cyclic and heterocyclic sulfoxides or sulfones and mixtures thereof, such as dimethyl, diethyl, dibutyl, dioctyl, methyl phenyl, ethyl phenyl, diphenyl, dicyclohexyl sulfoxides and/or sulfones of which preferred are dimethyl sulfoxide, diethyl sulfoxide, dimethyl sulfone and diethyl sulfone and mixtures thereof.

The odor detecting apparatus or device can be essentially the same as described in U.S. Patent 3,208,828 provided the detector tube for determining the odorants in gases or liquid fuel compositions contains silica gel or other suitable material impregnated with an acidic solution of potassium iodate, starch and dimethyl sulfoxide. To conduct a test using the device described in U.S. Patent 3,208,828, the fuel, e.g., LPG or natural gas, is allowed to vaporize and pass through the detector into a rubber balloon which is used to measure the gas volume. When the balloon reaches a predetermined size, the sampling is stopped. The natural color change of the treated silica gel is white to yellow; however, if a small quantity of blue dye is added to the reagent solution used to treat the silica gel, the color change is from blue to green.

A typical preparation of a detecting reagent is as follows.

Potassium iodate solution:
- 1 part (by volume) 6 N H_2SO_4
- 3 parts (by volume) glacial acetic acid
- 1 part (by volume) 0.3 M KIO_3

Reagent solution (mix in order shown):
- (1) 0.005 g. $PdCl_2$
- (2) 0.67 ml. KIO_3 solution (see above)
- (3) 0.33 ml. 0.2% w. starch solution (containing 0.001% HgI_2)
- (4) 1.85 ml. distilled water
- (5) 1.15 ml. dimethyl sulfoxide (Spectro grade)
- (6) 0.10 ml. methylene blue, 4.0 g./l.

This combined solution is added to 5.0 g. of 60–80 mesh Davison grade 950 silica gel, stirred well and heated in a vacuum oven at 50° C. for 30 minutes. The gel should be stirred at 10 minute intervals to prevent formation of a crust. The dried gel is packed into 2 mm. ID glass tubes

in 1 cm. sections separated by fine glass beads or sand. The packed tubes are sealed with a flame.

Essentially, the invention comprises the provision of a method and means for readily determining and measuring the saturated organic heterocyclic sulfides, e.g., petroleum thiophane or pure thiophane content of gaseous fuels, e.g., natural gas or LPG, by contacting the material with a supported chemical indicator as described above which changes color in the presence of petroleum thiophane or pure thiophane and is so arranged that with the passage of a definitely readily ascertained volume of gas, the indicator will show the concentration of the thiophane in the fuel, e.g., LPG or natural gas or the like.

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

In the drawing,

FIGURE 1 is an elevation of the assembled apparatus connected to a gaseous fuel, e.g., a LPG container, prior to test;

FIGURE 2 shows an elevation of the lower part of the apparatus after the test;

FIGURE 3 is a plan of the standard volume ring shown in the FIGURES 1 and 2; and,

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

Referring to FIGURE 1, a filled pressure cylinder of gaseous or liquid fuel, e.g., natural gas or 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 or plastic and is provided with uniform sections of impregnated sorptive material, e.g., silica gel **12*a***, having a white (or blue if dye is added) color and unimpregnated sections of purified sand **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 straps **15*b*** and **15*c*** which are fitted together at right angles by being suitably fastened as will be seen from FIGURE 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. thiophane in a prescribed volume of vaporized fuel, e.g., LPG. The fuel without the odorant produces no color change. Above and below the silica gel strata is packed a plug of cotton **16** held in place by wedge **17**.

Variations of the above procedure may be used. One of the acids or the starch may be omitted in the procedure. However, the presence of acid and starch increases the distinctness of the color change upon exposure to the odorant. The palladium chloride may be omitted, but its presence helps to retain the reacted colors for a longer period of time. The concentration of the reagent composition can be varied between wide limits in order to adjust the sensitivity; e.g., the amount of potassium iodate stock solution applied may vary from 0.1 to 10 ml./5 g. silica gel. Since dimethyl sulfoxide affects the sensitivity, its volume may be varied, e.g., between 0.1 and 2.0 ml., to achieve the desired response. 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 0.5 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 (0.047 g.) and purified sand (0.041 g.).

(3) Vibrate the tube after the filling process with a mechanical vibrator. A completed tube consists of 3 or 4 layers of treated silica gel and 2 or 3 layers of purified sand.

(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 odorant detector tube.

Calibration of the detector tubes was established with LPG samples prepared by adding a known weight of saturated heterocyclic organic sulfide, e.g., thiophane, to a known weight of liquefied propane.

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 a fuel, e.g., LPG, will pass through to metal vaporizer tube **10**. Upon the release in pressure through the needle valve, the fuel will expand and change to the gaseous state with the withdrawal of heat from the metal walls on the conduits. The gas next passes through detector tube **12** containing the silica gel and sand 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 fuel flow is then turned off and the detector tube disconnected. The detector tube is observed to note the number of bright yellow zones (or green) formed from the white (or blue) impregnated silica gel. If, for example, the device is used for measuring the concentration of thiophane 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, thiophane in the concentration of 10 p.p.m. by weight is reacted entirely in one zone. This reaction with the potassium iodate-sulfoxide mixture turns the color from white to a bright yellow (or blue to green). By counting the number of zones or fractions thereof colored yellow (or green), a rapid determination of the concentration of thiophane in the fuel can be made. When testing natural gas, the balloon is filled three times to take into account the difference in molecular weight between methane and LPG.

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 fuel, e.g., 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 fuel 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 thiophane 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 purified sand. The needle valve **5** was opened slowly until 15 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 16.6 cm. A balloon when filling the standard volume ring had a content of 2.4 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 white color had turned to a bright yellow and that approximately ⅕ of the third zone was yellow. The complete yellow zones formed each corresponded to 10 p.p.m. of thiophane in the volume of LPG passed, namely 2.4 liters. It was estimated that the LPG contained approximately 22 p.p.m. of thiophane. This was confirmed by accurate laboratory analysis with a coulometric titrator.

One of the advantages of our invention it should be noted, is that the yellow or green colored zones retain these colors for long periods of time and the detector tubes can be filed for later reference.

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. 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. A composition of matter for detecting odor in light hydrocarbon fuel compositions containing a thiophane odorant consisting essentially of a sorptive granular material selected from the group consisting of alumina and silica gel impregnated with an acidic solution of alkali metal iodate in an amount of 0.1 to 5 ml. per 5 grams of the sorptive material, a carbohydrate adsorbant capable of forming a color complex with iodine and an organic sulfur-oxygen-containing compound selected from the group consisting of organic sulfoxide and organic sulfone and mixtures thereof in an amount sufficient to function on a sensitivity agent.

2. The composition of claim 1 wherein the iodate compound is potassium iodate, the carbohydrate is starch, the organic sulfur-oxygen-containing compound is dialkyl sulfoxide and the sorptive granular material is silica gel.

3. The composition of claim 2 wherein the dialkyl sulfoxide is dimethyl sulfoxide.

4. The composition of claim 1 wherein the odorous saturated heterocyclic organic sulfide is petroleum thiophane and is present in the fuel, the fuel is liquid petroleum gas and the solution impregnated in the silica gel is a mixture of potassium iodate, starch and dimethyl sulfoxide.

5. The composition of claim 4 wherein the fuel is natural gas.

6. The composition of claim 4 wherein the odorant is thiophane.

7. The composition of claim 6 wherein the fuel is liquid petroleum gas.

8. The method of detecting and determining the presence of a thiophane odorant in a light hydrocarbon fuel under pressure which comprises the step of:

(a) reducing the pressure on the fuel by metering restrictive means to a predetermined lower pressure;

(b) vaporizing the liquefied gas;

(c) flowing a predetermined volume of the vaporized liquefied gas through successive separate elongated beds of sorptive granular material of a solution of an alkali metal iodate and mixtures thereof, the iodate being present in from 0.1 to 5 ml. per 5 grams of adsorptive material, a carbohydrate capable of forming a color complex with iodine and an organic sulfur-oxygen-containing compound which upon contact with thiophane odorant changes color over a length which is dependent upon the concentration of the thiophane in the fuel, a complete color change of each of said alternate beds thereby indicating a predetermined concentration of thiophane; and, therefore,

(d) determining the number of separate elongated beds which have changed color as an indication of the total concentration of thiophane in the vaporized fuel.

9. The method of detecting and determining the concentration of odorant in liquefied petroleum gases under pressure as defined in claim 8 in which the alkali salt reagent is potassium iodate, the carbohydrate is starch and the odorant is petroleum thiophane.

10. The method of detecting and determining the presence and concentration of thiophane as in claim 9 in which the liquefied petroleum gas is propane.

11. The method of detecting and determining the presence and concentration of thiophane as in claim 9 in which the fuel is natural gas.

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MAYER WEINBLATT, Primary Examiner

U.S. Cl. X.R.

23—232, 254; 48—195, 196, 197; 252—408