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ODORANT COMPOSITION FOR LIQUEFIED PETROLEUM GASES

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ABSTRACT OF THE DISCLOSURE

Improved odorant composition for liquefied petroleum gases includes an azeotropic mixture of an organic sulfur compound selected from the group consisting of ethyl mercaptan and dimethyl sulfide and at least one relatively non-odorous, chemically inert material, such as methyl formate, n-pentane, isopentane, amylene, isoamylene, chloropropane and the like, capable of forming a minimum boiling point azeotrope with the organic sulfur odorant compound present.

This application is a continuation-in-part of my prior application, Ser. No. 153,853, filed June 16, 1971, now abandoned.

This invention relates to odorants that are incorporated with combustible fuel gases in order to serve as a warning agent by means of which leaks or open gas cocks can be detected and immediately brought to the attention of one in the vicinity. More particularly, this invention relates to a novel and improved composition containing ethyl mercaptan and/or dimethyl sulfide as an odorant for liquefied petroleum gases, such as propane or butane.

Commercial liquefied petroleum gas (LPG) is customarily odorized with either ethyl mercaptan or thiophane at a rate of about one pound of odorant per 10,000 gallons of LPG. However, both ethyl mercaptan and thiophane have the serious disadvantage of being higher-boiling than propane or butane so that the odorant concentration is not uniform in the vapors evolving from the odorized liquid. That is, the gas is always much leaner than the liquid with respect to odorant concentration, and the odorant concentration may vary over a 20 to 50 fold range as evaporation continues.

Although ethyl mercaptan is the leading commercial odorant in terms of unit weight consumed, it is subject to an inherent objection as the LPG containers or vessels are successively exhausted, refilled and reused. Not only does the accumulation of ethyl mercaptan in the spent cylinder residues produce a progressively increasing atrocious stench in the expended cylinder, but also a ferrous mercaptide/sulfide complex builds up as a result of a reaction with the container walls. This ferrous mercaptide/sulfide residue is frequently susceptible to spontaneous ignition upon exposure to air.

While attempts have been made to locate and test candidate odorants which form an azeotrope with propane and butane in order to yield a uniform odorant concentration in the vapor, to date no azeotrope has been found having the desired composition and odor intensity. Furthermore, reference to Horsely, "Azeotropic Data," Am. Chem. Soc., Advances in Chemistry, Series No. 6, 1952 and No. 35, 1962, would lead to the conclusion that LPG azeotrope formation is impropable when considering the difference in boiling point between propane (—42.1° C.) or butane (—0.6° C.) and the most likely compounds having the requisite odor intensity (ethyl mercaptan B.P. 35.0° C. or dimethyl sulfide B.P. 37.8° C.).

In addition, yet still another problem exists in the art of odorizing LPG and natural gas—that of selective anosmia in which certain people are completely insensitive to odors that are readily perceptible to most persons in the general population. In this regard, it is considered that current LPG odorants, especially ethyl mercaptan, are less than ideal in effect upon some people. That is, even though the smell is readily perceived, such odor is not always identifiable by the observer as one characterisic of "gas."

It is therefore an object of this invention to provide an improved odorant composition in which the foregoing problems are substantially eliminated or reduced.

Other objects of this invention are to provide an improved odorant of the character described which is easily and economically produced, effective in application and highly efficient in operation.

In essence, the odorant composition of the instant invention comprises in combination with LPG an azeotropic mixture of (1) ethyl mercaptan and/or dimethyl sulfide and (2) a chemically inert, relatively non-odorous organic material which is capable of forming a minimum boiling point azeotrope with which ever organic sulfur compound of (1) is present. The group (2) compounds are hereinafter referred to as "azeotrope-formers" and should be present in an amount in excess of that which is required to form the azeotrope itself.

The azeotropes may either be binary or ternary. The binary compositions are a mixture of either ethyl mercaptan or dimethyl sulfide with the azeotrope-former, the latter constituent acting as an "azeotroping agent" with the sulfur-containing organic odorant. The ternary compositions comprise both ethyl mercaptan and dimethyl sulfide in combination with the azeotrope-former.

The azeotrope-former itself may either be a single compound or a mixture of compounds, typically having a boiling point ranging between 22° C. to about 37° C., and capable of forming an azeotrope with either ethyl mercaptan, dimethyl sulfide, or both. By virtue of economy and their compatibility with both the active organic sulfur odorant compounds and the propane-butane system itself, hydrocarbons in the C_5 range which satisfy the boiling point range requirements are suitable azeotrope-formers for the purpose of this invention. The hydrocarbons may be straight chain, branched chain, saturated or unsaturated.

The effective azeotrope-formers are not limited to hydrocarbons, but may include halogenated hydrocarbons, alcohols, ethers, esters, or other compatible organic compounds which are capable of forming minimium boiling azeotropes with ethyl mercaptan, dimethyl sulfide or both. However, the azeotroping agent should be substantially chemically inert with respect to the other ingredients in the system and relatively non-odorus. In particular, methyl formate is a preferred azeotrope-former for both ethyl mercaptan and dimethyl sulfide. Another preferred azeotroping agent for either or both of the sulfur odorant compounds named is isopentane. Yet still another preferred azeotrope-former is amylene, for example, a mixure of amylenes available as a side stream from certain petroleum refining operations. In general, it is unnecessary to have a high degree of purity for the azeotrope-former utilized. The commercial grades are of satisfactory purity and are usually preferred for reasons of economy.

The preferred odorant compositions are not the exact composition of the azeotrope itself but contain some azeotrope-former in excess of the amount required to form the azeotrope alone. The preferred azeotrope-formers are relatively non-odorous and chemically inert and by their presence in slight excess, such compounds become concentrated in the evaporation residues from an LPG vessel. Therefore, the residual liquid in this instance is *not* odorant-rich but becomes progressively richer in low-odor "azeotrope-former" as evaporation proceeds. This minimizes the aforementioned problems of pyrophoric mer-

captide/sulfide formation and progressive accumulation of obnoxious residual odorant.

A further advantage of the compositions of this invention is that the azeotropes, having lower boiling points than the individual odorant compounds themselves, will have an improved vapor-liquid distribution during the evaporation of the liquid from a full container of odorized LPG. The vapor concentration of odorant still increases from beginning to end of the evaporation but the over-all range of concentrations is less, there being more uniform odorization from the beginning to the end of a cylinder.

The following examples will serve to illustrate the present invention.

EXAMPLE I—Isopentane azeotropes

(a) A ternary azeotrope was prepared using isopentane (B.P. 27.9° C.) as the azeotroping agent. A level-boiling point azeotrope cut was fractionally distilled, and by chromatographic analysis the azeotrope was determined to have the following approximate composition:

	Percent by weight
Isopentane	73.5
Ethyl mercaptan	22.5
Dimethyl sulfide	4.0

The boiling point of the foregoing ternary azeotrope was 25.1° C.

(b) Binary azeotropes are known for both the isopentane-ethyl mercaptan system and the isopentane-dimethyl sulfide system as follows:

	Percent by weight
Isopentane	71–75
(1) Ethyl mercaptan	29
(2) Dimethyl sulfide	25
(azeotrope B.P. ° C.—25.7–26.6)	

It is to be observed that the approximate 10° C. reduction in boiling point from that of the odorant (ethyl mercaptan B.P.=35.0° C. and dimethyl sulfide=37.8° C.) produces a substantial advantage in terms of more uniform odorant concentration in the vapor evloved from the odorized propane-butane liquid. It is also apparent that the lower boiling point of the ternary system in Example I(a) renders the latter somewhat preferable over either of the binary examples I(b)(1) or I(b)(2). However, a slight excess of isopentane in any of the above examples is preferred for this invention in that the residual liquid would be richer in the low-odor azeotrope former. In the ternary composition of Example I(a) some excess dimethylsulfide is also advantageous since it would maintain gassy odor to the end of the vessel without an overpowering increased intensity or accumulation of pyrophoric residues. The intent is to have an excess of either dimethylsulfide or azeotropic agent but not excess ethyl mercaptan.

EXAMPLE II—Methyl formate azeotropes

(a) A ternary azeotrope using methyl formate (B.P. 31.7° C.) was isolated by fractional distillation of an ethyl mercaptan-dimethyl sulfide-methyl formate system Analysis for mercaptan sulfur and total sulfur produced the following calculated composition for the ternary azeotrope:

	Percent by weight
Methyl formate	64.4
Ethyl mercaptan	33.4
Dimethyl sulfide	3.2

The boiling point of the foregoing ternary azeotrope was 28.8° C.

(b) The literature (Horsley supra) has listed two binary azeotropes involving methyl formate, as follows:

	Percent by weight
Methyl formate	30.0–62.0
(1) Ethyl mercaptan	70.0
(2) Dimethyl sulfide	38.0
(azeotrope B.P. ° C.—27.0–29.0)	

EXAMPLE III—n-pentane azeotropes

(a) A ternary azeotrope with a boiling point of 31.0° C. was isolated by fractional distillation of the system n-pentane, ethyl mercaptan and dimethyl sulfide. Analysis for mercaptan sulfur and total sulfur resulted in the following calculated composition for this azeotrope: n-pentane 50.4%, ethyl mercaptan 30.2%, dimethyl sulfide 19.4%.

(b) Binary azeotropes with n-pentane (B.P.=36.1° C.) are shown as follows:

	Percent by weight
n-pentane	49.0–55.0
Ethyl mercaptan	51.0
Dimethyl sulfide	45.0
(azeotrope B.P. ° C.—30.46–33.5)	

EXAMPLE IV—Isoamylenes azeotropes

Still another ternary azeotrope has been observed using "isoamylene" as the azeotrope-former. The "isoamylene" used was a mixture used commercially in the alkylation of phenol to form tertiary amylphenols and it contained about 96% of a mixture of 3-methyl butene-2 and 2-methyl butene-1. (3-methyl butene-1 does not form an azeotrope in mixtures with ethyl mercapan and dimethyl sulfide.) The isoamylene ternary has a boiling point of 34° C. and its composition has not been determined.

Any of the above binary and ternary azeotropes may be used as LPG odorants having improved vapor-liquid equilibrium characteristics. Improvement with respect to residual odor and chemical inertness of the residual liquid at the end of a cylinder is imparted by admixing additional small quantities of azeotrope-former and, optionally, dimethyl sulfide. The latter compound possesses the advantage of a different odor character (less obnoxious than ethyl mercaptan) and little or no reactivity with the ferrous metal surfaces of the container.

EXAMPLE V—Ternary azeotrope with excess isopentane and dimethyl sulfide

To compare the relative evaporation performance of one of the novel compositions of this invention against a standard system odorized with ethyl mercaptan, two separate systems of odorized propane were prepared. In one portion of the experiment, instrument grade propane was odorized on a laboratory scale with commercial grade ethyl mercaptan in a steel container fitted with a vapor discharge valve. In another portion of the experiment, instrument grade propane was odorized in a similar steel container with an "azeotropic" odorant utilizing one of the examples employing an azeotrope agent. The "azeotropic" odorant used in the test had a composition of 74.0% isopentane, 21.1% ethyl mercaptan and 4.9% dimethyl sulfide.

Each of the vessels of experimentally odorized liquid was successively connected through the valve to a pressure regulator feeding the vapor to a Barton #286 titrator. The model 286 Barton titrator is an electronic instrument which functions by the electrolytic titration of sulfur compounds with high sensitivity. The reaction in an electrolytic cell causes generation of free bromine from HBr, and the free bromine is stoichiometrically reacted with the sulfur compounds passing through the system. Electrolysis current is so controlled that it is directly proportional to the sulfur compounds present whereby electrolysis current is read out on a recording chart. A suitable conversion factor can then be applied to the chart reading and the quantity of sulfur compounds calculated directly. In the present experiment, the objective was to determine the concentration ratio of sulfur compound in

the vapor at the initial evaporation of a cylinder to the concentration thereof at the end of a cylinder. Therefore, it was of no interest to compute the actual concentrations of the compound itself and no conversion factor was applied. However, the ratio of scale reading was taken to indicate the concentration change that occurred for each odorant during the evaporation. The nature of the laboratory manipulation did not permit exact control of the initial odorant concentration in each of the experimental liquids so the starting concentrations were different in each case. Nevertheless, this does not affect the validity of the determination of the concentration ratio from the beginning to the end of the evaporation.

In separate experiments each system was allowed to evaporate at room temperature over a period of several hours while the odorant concentration in the vapor was measured by the Barton titrator. The results obtained are as follows:

TABLE I

Relative evaporation behavior of odorants from propane (EtSH vs. isopentane azeotrope)

	Net scale div. (Barton)	
	EtSH	Isopentane azeotrope
Wt. percent propane evaporated:		
2.5	23	5-6
5.0	30	8
95.5	510	116
Concentration factor:		
95/5% evap.	17.0 (510/30)	14.5 (116/8)
95/2.5% evap.	22.2 (510/23)	19.3 (116/6)

The different "concentration factors" indicate clearly that there is less overall concentration change in the case of the isopentane azetrope. Hence, distribution of odorant will be more uniform in the latter case.

In order to further test the commercial efficacy of the ternary isopentane-ethyl mercaptan-dimethyl sulfide azeotrope using excess isopentane and excess dimethyl sulfide and correspondingly a reduction in ethyl mercaptan concentration, a "blend" of the foregoing Example V composition was utilized as follows:

	Percent
Isopentane	74.0
Ethyl mercaptan	21.1
Dimethyl sulfide	4.9

Two individual stainless steel cylinders were loaded with propane and odorized with the foregoing blend such that the concentration of the blend in propane was 95 p.p.m. in each cylinder. In each cylinder, the active odorant (ethyl mercaptan and dimethyl sulfide combined) was accordingly 24.7 p.p.m. Still a third cylinder was charged with propane odorized with just ethyl mercaptan at a concentration level of 29 p.p.m.

The three cylinders were presented to each of 22 observers in separate "blind-fold" type tests for odor observation, wherein each observer was asked to identify one cylinder with an odor different from the other two. After odor observations were made on the initial vapor from the loaded cylinders, the cylinder contents were allowed to evaporate at a moderate rate until less than 10% remained from the original charge. Each cylinder was then recharged with a mixture approximately its initial composition, odor observations were repeated and the contents again allowed to evaporate until less than a 10% residue remained. Odor observations were conducted on this residue. The process was then repeated for another loading and evaporation cycle. The total number of observers in any given test varied from 17 to 22. Odor observations are tabulated in Table II.

TABLE II

Filling cycle	EtSH cylinder	Blend— Cylinder 1	Blend— Cylinder 2	No selection	Total observers
I. Initial vapor:					
1 Total times selected	12	4	3	3	22
1 Stronger	7	0	0		
1 Weaker	1	3	1		
1 Unclassified	4	1	2		
2 Total times selected	13	3	4	2	22
2 Stronger	8	1	2		
2 Weaker	2	1	2		
2 Unclassified	3	1	0		
3 Total times selected	7	5	4	1	17
3 Stronger	4	1	3		
3 Weaker	2	4	1		
3 Unclassified	1	0	0		
II. Residue (>10% evap.):					
2 Total times selected	15	4	1	0	20
2 Stronger	14	1	0		
2 Weaker	0	2	0		
2 Unclassified	1	1	1		
3 Total times selected	15	2	3	0	20
3 Stronger	14	0	2		
3 Weaker	1	2	1		
3 Unclassified	0	0	0		

As is typical in this type of test, the observers were not unanimous but a significant majority (14–15 out of 20) selected the ethyl mercaptan as being stronger in the residue after 90% or more evaporation. This effect did not occur in the initial vapor. Thus a composition in accord with the concept of this invention results in a reduction of obnoxious odor in evaporation residues by comparison with the use of ethyl mercaptan alone.

Two more filling and evaporation cycles were carried out with each of the three cylinders.

The following table summarizes the concentration of added odorant and the percentage of evaporation residue left after each of the five loading and evaporation cycles:

Cycle	R.p.m. added * EtSH cylinder	Blend— Cyl. 1	Blend— Cyl. 2	Percent odorant in evaporation residue EtSH cylinder	Blend— Cyl. 1	Blend— Cyl. 2
1	29	95	95	7.5	3.2	4.2
2	27	95	95	6.5	4.1	4.3
3	26	95	95	1.8	2.6	2.8
4	28	99	99	4.3	1.8	3.7
5	27	94	94	3.2	1.2	2.2

* EtSH added to "EtSH Cylinder"; Blend added to "Blend Cylinders 1 & 2."

The residues after the fifth cycle were analyzed with the following results:

	Analysis EtSH, p.p.m.	DMS, p.p.m.
EtSH cylinder	113	0
Blend cylinder 1	26	29
Blend cylinder 2	60	75

It is clear from this analysis that (1) when ethyl mercaptan is used as the sole odorant, it accumulates to a much larger degree in the evaporation residues than when it is used as a component of a blend meeting the specifications of this invention, and (2) when the odorant blend is used, the residues are selectively enriched with respect to DMS and leaner with respect to ethyl mercaptan. The ratio DMS/EtSH has increased from 0.23 in the original odorant blend to an average of 1.2 in the residue after five loading and evaporation cycles.

The difference in the results for blend cylinder 1 and blend cylinder 2 are accounted for by the differing percentage residues in the five consecutive evaporation cycles.

Other tests were conducted to demonstrate the effect of the above blend on the composition of the vapor in an early stage of evaporation from odorized propane. Propane odorized with this blend was analyzed for initial liquid composition, and was then allowed to evaporate slowly. The vapor was analyzed when 1% of the liquid had evaporated. Control experiments were performed in a similar way on propane odorized with ethyl mercaptan alone, and on propane odorized with dimethyl sulfide alone. To provide a uniform basis for comparison, the vapor compositions after 1% evaporation was expressed as percentages of the concentration of odorant in the initial liquid.

	Vapor concentration at 1% evaporation (percent of initial liquid concentration)	
	DMS	EtSH
DMS control	10.8	
EtSH control		10.4
Blend	19.1	16.5

Thus the use of an odorant blend representing the practice of the present invention resulted in a relative enrichment, in an early stage of evaporation, of 77% in the case of dimethyl sulfide; and 58.5% in the case of ethyl mercaptan, i.e.

Percent enrichment DMS via blend=(19.1−10.8)/10.8 =77%

Percent enrichment EtSH via blend=(16.5−10.4)/10.4 =58.5%

Although this invention has been described in considerable detail, such description is intended as being illustrative rather than limiting, since the invention may be variously embodied, and the scope of the invention is to be determined as claimed.

What is claimed is:

1. In combination with liquefiied petroleum gas, an odorant composition consisting essentially of (A) at least one organic sulfur compound selected from the group consisting of ethyl mercaptan and dimethyl sulfide, and (B) a relatively non-odorous azeotropic agent, said azeotropic agent being an organic compound which is miscible with and forms a minimum boiling point azeotrope with (A).

2. The odorant composition of Claim 1 wherein the azeotropic agent is present in excess of the amount required to form an azeotrope with (A).

3. The azeotrope of Claim 1 wherein the system is ternary.

4. The odorant composition of Claim 3 wherein dimethyl sulfide is present in excess over the amount required to form an azeotrope with ethyl mercaptan and (B).

5. The azeotrope of Claim 1 wherein the azeotropic agent is selected from the group consisting of methyl formate, n-pentane, isopentane, and amylene.

6. The azeotrope of Claim 5 wherein the amylene comprises a mixture of 3-methyl butene-2 and 2-methyl butene-1.

7. An azeotropic ternary composition comprising ethyl mercaptan, dimethyl sulfide and an organic azeotrope-forming compound selected from the class consisting of methyl formate, n-pentane, isopentane and amylene.

8. The composition of Claim 7 wherein the dimethyl sulfide is present in excess of azeotropic proportions.

9. The composition of Claim 7 wherein the organic azeotrope-forming compound is present in excess of azeotropic proportions.

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