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ODORIZATION OF COMBUSTIBLE HYDROCARBON GASES

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ABSTRACT OF THE DISCLOSURE

A warning agent for odorization of gaseous hydrocarbon fuels, based on mixtures of ethane dimercaptan with a monomercaptan or a sulfide.

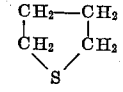
This application is a continuation-in-part of application S.N. 173,832, filed Feb. 16, 1962, now abandoned.

The present invention relates to mixtures of organic sulfur compounds suitable for the odorization of combustible hydrocarbon gases, such as natural gas, vapors and gases recoverable in the refining of petroleum, and other gases suitable as fuels for heating, illuminating and cooking purposes.

More particularly, the invention is directed to combustible gases suitable as fuels for heating, illuminating and cooking uses, and ordinarily having no marked inherent odor, which contain vaporized therein a small quantity of a mixture of organic sulfur compounds possessing a specific and persistent odor serving to warn of the escape of the combustible gas from containers, transmission lines or fixtures and, consequently, serving to warn of the danger of explosion and asphyxiation.

A number of organic sulfur compounds are known to be effective malodorants for combustible gases. These include monomercaptans, and acyclic and cyclic sulfides. Specific examples of these compounds, in which percentages are by weight, are the following:

(1) Thiophane,



herein referred to as "Odorant A".—Sometimes a small amount of some additive, such as to prevent freezing, is included. In some instances thiophane is admixed with a diluent, such as V.M. & P. naphtha,[1] in an amount, for example, of about 50%, and used diluted.

(2) Refinery by-product mercaptans, herein referred to as "Odorant B".—These are characterized by a boiling point range of about 100–215° F. and comprise C_2–C_4 mercaptans. Traces of C_5 mercaptans are sometimes present. Typically, this odorant contains 25% ethyl mercaptan, 35% isopropyl mercaptan, 15% n-propyl mercaptan, 20% sec.-butyl mercaptan, 3% isobutyl mercaptan, and 2% n-butyl mercaptan, although they can be present, respectively, within ranges of about 1 to 30; 15 to 50; 5 to 25; 10 to 30; 1 to 6; and 1 to 4.

(3) Mixed aliphatic sulfides of low molecular weight.—One alkyl group may be ethyl and the other group, ethyl, propyl, or butyl. These compounds often contain a small amount, e.g., about 5%, of refinery by-product mercaptans Odorant B, herein referred to as "Odorant C," although an amount as high as 10% by-product mercaptans can be present. A further specific example of mixed sulfides is a mixture of diethyl sulfide and ethyl propyl sulfide. See U.S. Patent No. 2,823,104.

[1] A mixture of aliphatic acyclic, straight- and branched-chain hydrocarbons with an ASTM distillation of 245° F. to 300° F.

(4) t-Butyl mercaptan.—Often contains refinery by-product mercaptans (Odorant B) in an amount of 15 to 50%, based on the two. A mixture of the two, herein referred to as "Odorant D," in which the refinery mercaptans are present in amount of about 20%, the mixture having a boiling point range of about 132–185° F. is given as a preferred example.

(5) A mixture of dimethyl sulfide and the refinery by-product mercaptans (Odorant B), in proportions, for example, of 90% dimethyl sulfide and 10% mercaptans, herein referred to as "Odorant E."—As little as 5% to as high as 60% mercaptans may be present.

It has now been found that the odor intensity of the above conventional malodorants can be increased by the incorporation in them of a small amount of ethane dimercaptan having the formula $HSCH_2CH_2SH$, ranging from about 1, preferably around 5%, to 20%, preferably about 15%, by weight, based on ethane dimercaptan and malodorant, referred to as "base odorant." For example, a mixture of 15% ethane dimercaptan and 85% thiophane used in a dosage of 0.3 pound per million cubic feet (m.c.f.) of hydrocarbon gas has the same odor intensity as thiophane alone used at a dosage level of 1 pound per million cubic feet of the same hydrocarbon gas, indicating a threefold improvement.

The method of mixing the conventional or base odorant and the odor-boosting ethane dimercaptan is not critical. Since these materials are low-boiling liquids, one or the other can be added to the other in the indicated proportions, i.e., in a manner applicable to the mixing of any compatible liquids.

To show the odor-boosting effectiveness of the odorant mixture of the present invention, determinations were made according to the so-called "Walk-in Room Test," the test utilized in the following tabulated examples.

According to this test, odor intensity is determined by a panel of at least five persons, preferably ten or more, according to the scale hereinbelow set forth.

A room with a volume of approximately 1500 cubic feet is used. The room has facilities for ventilation between tests and is free from any significant air movement during the tests. No odor other than that of the warning agent being tested is present during the test.

A 3.2 ml. of ethanol solution of the odorant is then vaporized into the room, the vaporization taking not more than 5 minutes to occur. The odorant concentration in the 3.2 ml. solution is such as to give a concentration equivalent to that obtained from odorized gas (methane) diluted to 1% gas in air. Thus, at a concentration corresponding to one pound odorant per 1,000,000 cubic feet gas and one volume percent gas concentration in the room, the ethanol solution will contain 2.13 g. odorant per liter of solution.

The person vaporizing the odorant does not participate in rating the samples to be tested, and at least 15 minutes is allowed between each test to allow the olfactory nerve to recover. After vaporization into the room, a five-membered or larger odor panel rates odor intensity of the compositions according to the following scale:

Odor intensity:	Rating
No odor	0
Barely noticeable	1
Easily noticeable	2
Strong	3

The odor intensity is judged immediately after entering the room. Any unusual character of the odor is noted and recorded. The average ratings are then calculated, rounded off to the nearest one/tenth. Finally, the results are interpreted using the above scale.

Tabulated below are given averaged panel results determined as described above. The odor intensities of the

various odorants alone and of odorant compositions containing the indicated proportions of ethane dimercaptan are given. The odor intensity determinations were made using the indicated amounts of ethane dimercaptan and base odorant, the letters corresponding to those already given in identifying the base odorant.

TABLE I.—EFFECT OF ETHANE DIMERCAPTAN ON ODOR INTENSITY OF NATURAL GAS ODORANTS

Example No.	Odorant composition			Average Rating
	Base Odorant		Ethane Dimercaptan (gm./liter)	
	Type	Gms./liter		
1	A	2.13	0	1.9
1a	A	2.02	0.11	2.5
1b	A	1.81	0.32	2.7
2	B	2.13	0	2.3
2a	B	2.02	0.11	2.7
2b	B	1.81	0.32	2.8
3	C	2.13	0	1.8
3a	C	2.02	0.11	2.1
3b	C	1.81	0.32	2.3
4	D	2.13	0	2.2
4a	D	2.02	0.11	2.4
4b	D	1.81	0.32	2.6
5	E	2.13	0	1.9
5a	E	2.02	0.11	2.2
5b	E	1.81	0.32	2.7

On the basis of the work of Katz et al.,[2] ethane dimercaptan at a concentration equivalent to one pound in one million cubic feet of gas (methane) diluted to one percent in air gives a rating on the same basis as Table I, of 1.1; and a rating of 0, at concentrations of 0.11 and 0.32. However, the odor-boosting effect of ethane dimercaptan is clearly evident. To illustrate: when a small amount (about 5%) of ethane dimercaptan is added to thiophane (Example 1*a*), odor intensity is markedly increased. Increasing the amount of ethane dimercaptan to about 15%, further enhances odor intensity (Example 1*b*); yet these amounts of ethane dimercaptan used alone are reportedly ineffective. Similar results as shown in the table are obtained with the other base odorants.

The tabulated experiments below further show the effectiveness of the malodorant compositions of the present invention as compared with base odorant without the odorant booster.

TABLE II.—QUANTITY OF MIXED ODORANT REQUIRED TO GIVE THE SAME ODOR INTENSITY AS ONE POUND OF BASE ODORANT IN ONE MILLION CUBIC FEET OF NATURAL GAS

Base odorant	Pounds of mixed odorant per million cubic feet of gas	
	95% base odorant, 5% ethane dimercaptan	85% base odorant, 15% ethane dimercaptan
A	0.4	0.3
B	0.7	0.4
C	0.6	0.4
D	0.7	0.4
E	0.5	0.2

The data in the table indicate that compositions prepared in accordance with the invention are equally effective, although used in smaller quantities, as untreated base odorant used in larger quantities. For example Odorant E (dimethyl sulfide-mercaptans) when containing 5% and 15% ethane dimercaptan is just as effective in quantities of 0.5 pound and 0.2 pound, respectively, as 1 pound of untreated Odorant E.

The malodorant mixture herein described is eminently suitable for use in combustible gases, such as natural gas used in the home or in industry for cooking or illumination. It possesses a distinctive odor, thereby providing a timely warning of escaping gas, even though present in small concentration. Although effective, the malodorant of the present invention is not so offensive that users of the combustible gas object to its presence. Further, it is odorless when burned. The malodorant mixture herein described in the amounts used does not cause any objectionable skin irritation, lachrymation, or other harmful physiological effects. Finally, with the present malodorant composition, a gradual cumulation of odor intensity does not cause olfactory fatigue to the extent some other odorants do.

[2] Bureau of Mines Technical Paper 480, "Intensities of Odors and Irritating effects of Warning Agents for Inflammable and Poisonous Gases" (1930).

I claim:

1. A warning agent suitable for the odorization of gaseous hydrocarbon fuels, said agent consisting essentially of a mixture of ethane dimercaptan and a gas odorant selected from the group consisting of monomercaptans, acyclic and cyclic sulfides, said ethane dimercaptan being present in said mixture in an amount, by weight, based on said mixture, ranging from about 1–20%.

2. A warning agent as defined in claim 1, wherein the gas odorant is thiophane.

3. A warning agent as defined in claim 1, wherein the gas odorant is a mixture of C_2–C_4 aliphatic monomercaptans having a boiling range of about 100–215° F.

4. A warning agent as defined in claim 1, wherein the gas odorant is a mixture of low molecular weight sulfides.

5. A warning agent as defined in claim 1, wherein the gas odorant is dimethyl sulfide.

6. A warning agent as defined in claim 5, wherein there is present in addition a minor amount of C_2–C_4 monomercaptans having a boiling range of about 100–215° F.

7. Process for the odorization of a hydrocarbon fuel gas which comprises incorporating in said gas from about 0.3 to 1 pound per one million cubic feet of said gas of a warning mixture consisting essentially of ethane dimercaptan and a gas odorant selected from the group consisting of monomercaptans, acyclic and cyclic sulfides, said ethane dimercaptan being present in said warning mixture in an amount, by weight, based on it and gas odorant, ranging from about 1–20%.

8. Process according to claim 7, wherein the ethane dimercaptan is present in amount of 5–15%.

9. Process according to claim 8, wherein the gas odorant is thiophane.

10. Process according to claim 8, wherein the gas odorant is a mixture of C_2–C_4 aliphatic monomercaptans having a boiling range of about 100–215° F.

11. Process according to claim 8, wherein the gas odorant is a mixture of low molecular weight sulfides and a minor amount of C_2–C_4 monomercaptans having a boiling range of about 100–215° F.

12. Process according to claim 8, wherein the gas odorant is a mixture comprising dimethyl sulfide and a minor amount of C_2–C_4 monomercaptans having a boiling point range of about 100–215° F.

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Katz et al.: Bureau of Mines Technical Paper 480, Intensities of Odors and Irritating Effects of Warning Agents for Inflammable and Poisonous Gases, pages 7–9, 12–27, 33, 34 (1930).

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