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FUEL GAS COMPOSITION CONTAINING ODORANT

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FIGURE 1

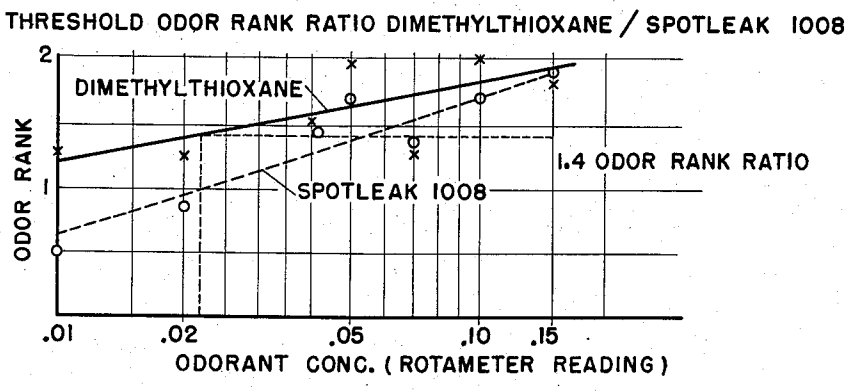
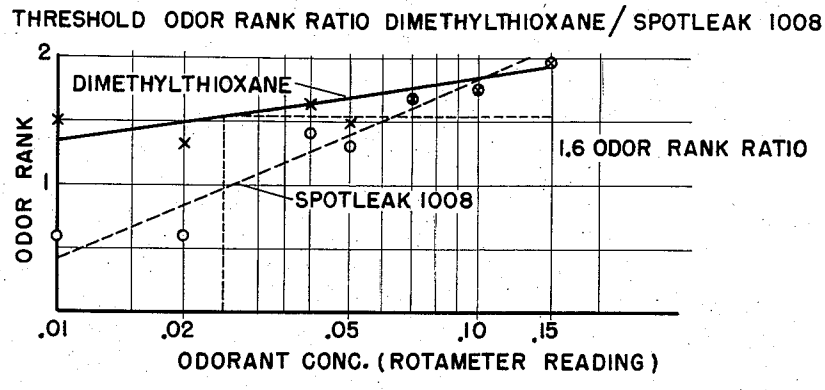


FIGURE 2



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FUEL GAS COMPOSITION CONTAINING ODORANT

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This invention is directed to odorized gas mixtures. More particularly, this invention is directed to commercial fuel gas compositions containing small amounts of dialkyl p-thioxanes as gas warning agents. The gas warning agents are added to gases having insufficient odors of their own, the purpose being to make the gases detectable in the atmosphere at lower than toxic or explosive concentrations.

The advantages and objects of the present invention will be seen from the following description taken in conjunction with the drawings in which Figures 1 and 2 are a graphical representation of the threshold odor rank ratio of dimethyl thioxane compared to a commercial fuel gas odorant Spotleak 1008 under two test conditions.

Gases which require odorization for their commercial use include natural gas, manufactured gas, mixtures of natural gas with manufactured gas, coke oven gas and liquefied petroleum gas. An odorant is not normally employed with manufactured gas since this gas has in most instances a characteristic odor. However, in some cases it is desirable to increase or modify the odor of manufactured gas for special purposes or when it is admixed with another gas of low odor content.

There are many chemicals possessing sharp, pungent or foul odors which one might expect would make excellent gas odorants. Usually, this is not the case. A gas odorant should have many special properties in addition to being merely odoriferous.

A good gas odorant should have a high threshold rank ratio, a high impact rating and a persistent warning character when diluted with air. Other related properties which a good gas odorant should have are low toxicity, a sufficiently high vapor pressure to permit easy volatilization into a gas stream and inertness to the surroundings. In regard to the latter the odorant must be substantially unreactive with the components of the gas with which it is carried under use conditions. Also, the water solubility should be quite low in order that the odorant is not washed out of the odorized gas by water in gas mains and gas holders.

We have now discovered that dialkyl p-thioxane when incorporated in commercial fuel gases provide compositions having valuable warning or alarm properties. Generally, the dialkyl substituents of p-thioxane useful in our invention are the methyl, ethyl, n-propyl and isopropyl substituents. The alkyl substituents may be identical as they are in dimethyl p-thioxane or they may be of mixed dialkyl groups such as methyl ethyl p-thioxane. Moreover, the term dialkyl thioxane is intended to refer to anyone or a mixture of the 2–5, 3–5 and 2–6 isomers of dialkyl p-thioxane. It is to be understood that the term dialkyl p-thioxane as used throughout this specification and the claims refers to alkyl substituted p-thioxanes as defined in this paragraph.

While the various alkyl substituents of p-thioxane of 1 to 3 carbon length are useful gas odorants for making the new compositions of our invention, we prefer to use the dimethyl p-thioxane because of its distinctive and intense odor.

Small quantities of dimethyl p-thioxane when incorporated into natural gas, mixtures of natural gas and manufactured gas, blast furnace gas and liquefied petroleum gas provide new compositions which are useful to gas producers and distributors.

The proportion of dimethyl p-thioxane required to impart a noticeable odor to a substantially odorless gas or gas-air mixture is extremely minute. As indicated in Tables 1 and 2 below, 0.037 pound per 100,000,000 cubic

Table 1

Sequence	Rotometer Reading	Lbs. odorant/10^8 CF gas-air mix	Percent odorized gas in air	A		B		C		D		E		Average Odor Rank	
				(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
2	.01	0.037	0.031	2,1	2,1	—,	2,	—,—	—,2	1,1	1,2	—,1	2,2	.66	1.55
4	.02	0.074	0.060	1—,1—	2—,1	—,	2,	—,1—	1,1	1,1	—,2	1,1	2,2	.612	1.39
5	.04	0.148	0.12	2,2	2,1	1,	2,	2,—	2,2	2,2	1,1	1,2	2,2	1.5	1.67
1	.05	0.190	0.16	2,2	2,—	1,	2,	—,2	1,2	2,2—	1,2	1,1	2,2	1.39	1.55
7	.07	0.259	0.22	2,2	1,2	2,	2,	2,2	2,2	2,1	1,2	2,1	2,2	1.78	1.78
3	.10	0.40	0.33	2,2	2,1—	2,	2,	2,2	2,2	2,2	2,2	1,2—	2,2	1.83	1.83
6	.15	0.60	0.50	2,2	2,2	2,	2,	2,2	2,2	2,2	2,2	2,2	2,2	2.00	2.00

Odor rank ratio (computed from Figure 1): 1.4.
(1) Refers to Spotleak 1008.
(2) Refers to dimethyl thioxane.
A, B, C, D, E refer to observers.

Table 2

Sequence	Rotometer Reading	Lbs. odorant/10^8 CF gas-air mix	Percent odorized gas in air	A		B		C		D		E		Average Odor Rank	
				(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
2	.01	0.037	0.031	—,1	1,1	—,1	1,2	—,—	1—,—	—,1	2,1	1,1	2,2	0.50	1.25
4	.02	0.074	0.060	1—,—	1—,—1	1,1	2,2	—,1	1—,—	1,2	1,2	1,1	2,2	0.85	1.25
5	.04	0.148	0.12	2,1	2,—	2,2	2,2	2,1	1,1	1,—	2,1	2—,2	2,2	1.45	1.50
1	.05	0.190	0.16	2,2	2,2	2,2	2,2	2,2	2,2	1,2	2,2	1,1	2,2	1.70	2.00
7	.07	0.259	0.22	2—,—	1,—	2,2	2,2	—,1	1,1	2,1	1,1	2,2	2,2	1.35	1.30
3	.10	0.40	0.33	2,2	2,2	2,2	2,2	1,2	2,2	2,1	2,2	1,2	2,2	1.70	2.00
6	.15	0.60	0.50	2,2	2,—	2,2	2,2	2,1	2,2	2,2	2,2	2,2	2,2	1.90	1.80

Odor rank ratio (computed from Figure 2): 1.6.
(1) Refers to Spotleak 1008.
(2) Refers to dimethyl thioxane.
A, B, C, D, E refer to observers.

feet of the gaseous mixture was at least perceptible to all but one observer and gave a definite or warning reaction in ten tests out of twenty.

In the commercial odorization of a fuel gas to safeguard against explosions it is important to maintain sufficient odorant in the gas to be definitely detectable in gas-air compositions which are below the lower explosive unit. In this connection it is generally considered satisfactory if a warning odor exists at a dilution of one volume of odorized gas with about 100 volumes of air.

A fuel gas, such as natural gas, when mixed with as little as 0.04 pound of dimethyl p-thioxane per million cubic feet has a distinctive odor which is strongly apparent to people of good olfactory perception even when the gas is diluted to 1% in air and is noticeable to most people at this safe dilution. Thus, a fuel gas so odorized is far less hazardous for distribution and use than the unodorized gas.

In general, however, it is desirable from the standpoint of safety from explosions to use higher concentrations of dimethyl p-thioxane and a concentration of at least 0.2 pound per million cubic feet of fuel gas is preferred. All gas volumes mentioned herein are at standard temperature and pressure unless otherwise specified.

The dimethyl p-thioxane is compatible with other gas odorants normally encountered, and it is entirely feasible to use it in conjunction with one or more other odorants. Such odorant mixtures may be blended prior to introduction into the fuel gas, or may be introduced separately into the gas whereby vapor phase mixing takes place due to the turbulence and convection currents of the gas stream. Thus, dimethyl p-thioxane may be introduced into preodorized gas from a transmission line in order to suitably adjust the odor level and quality for local distribution. In such event and in other situations involving supplementary odorization, the concentration of dimethyl p-thioxane required in the gas will naturally be less than when it constitutes the sole odorant.

Dimethyl p-thioxane may be used if desired at unusually high concentrations in fuel gas, for example, at 5 pounds per million cubic feet, without causing difficulties of physical or chemical nature, such as corrosion or condensation. For ordinary purposes of leak detection and warning of explosion hazard in fuel gas transmission and distribution systems, however, it is almost never necessary to exceed two pounds per million cubic feet and rarely more than one pound.

Dimethyl p-thioxane is stable toward reaction with oxygen and other components of commercial fuel gas systems under pipeline conditions. It is furthermore very insoluble in water and is not scrubbed out of the gas by liquid water with which it comes in contact in pipelines and gas holders. Thus, it is resistant to "fading," a serious defect of many existing gas odorants under certain conditions of gas composition and flow. It is therefore possible by use of dimethyl p-thioxane to maintain a desired, constant level of odorization throughout the entire system being odorized. This is of great practical value since underodorization of portions of the system due to fading creates a hazardous condition there; and attempts to correct this by introducing excess odorant at the odorizer often result in increased nuisance complaints, due to the detection of trivial concentrations of gas from non-hazardous sources, which complaints require investigation at considerable cost.

The use of dimethyl p-thioxane to provide warning of gas leaks and the potential development of explosive gas-air mixtures has been discussed above. Dimethyl p-thioxane is also useful in toxic fuel gases wherein its concentration may be maintained at a sufficient level to provide warning of the presence of a detrimental concentration of toxicant in the atmosphere. For example, dimethyl p-thioxane may be incorporated into a coke oven gas containing carbon monoxide. The concentration in the toxic gas of dimethyl p-thioxane required for adequate warning will of course depend upon the degree of toxicity of the gas which in turn depends upon the kind and amount of toxicant present. Blast furnace gas as ordinarily produced in steel mills may contain about 30% carbon monoxide, and about 2 pounds of dimethyl p-thioxane per million cubic feet of such gas will suffice for adequate warning. However, much higher concentrations of dimethyl p-thioxane may be incorporated into a toxic fuel gas, such as five pounds or more per million cubic feet without detriment to the usefulness of the gas or harm to the equipment. The use of such high proportions of our odorant may be desirable in particular circumstances.

When dimethyl p-thixane is added to gaseous fuels in an amount of at least 0.2 pound per million cubic feet, the odorized gas when mixed with approximately 100 volumes of air is of high impact odor value. That is, it is immediately perceptible to the normal observer and is of an odor character which arrests the observer's attention. Moreover, the odor at this concentration has sufficient impact to warn the observer. The stimulation of the olfactory nerve center persists for a considerable period of time.

Dimethyl p-thioxane is readily volatilized into commercial fuel gas streams by the standard methods for adding gas odorants. One method consists of pumping or otherwise injecting the liquid at controlled rate into the main gas stream whereby contact with gas stream causes it to vaporize and mix uniformly with the gas stream. A second method known as by-pass odorization involves passing a predetermined minor fraction of the gas stream to be odorized over a pool of liquid odorant or alternatively, over a wick maintained wet with liquid odorant. The highly odorized by-pass stream is then recombined with the main gas stream. These are conventional expedients in the art and any type of odorizing equipment can be used. In the case of liquified petroleum gas (LPG) the odorant in liquid form is normally dissolved in the liquid hydrocarbon.

Another characteristic of dimethyl p-thioxane useful in gas odorant application is its low order of toxicity. Moreover, the combustion products of dimethyl p-thioxane and a gaseous fuel are non-toxic and non-irritating at the concentrations normally encountered in fuel odorization.

Probably, the most important requirement of a gas odorant is that it be perceptible in gas-air mixtures at extremely low concentrations; that is, that the odorant have an extremely low threshold concentration. The threshold concentration is that concentration of the odorant in a gas which is barely perceptible to a human observer. Since human observers are widely different in their perception of odors, and moreover, since the same individual will vary from day to day, the practical method in measuring threshold concentrations requires a statistical analysis of many human observations.

Odorants of relatively high threshold concentration suffer the disadvantage of high cost per unit volume of gas odorized and excessive bulk of odorant material to be handled, and in the case of sulfur containing odorants, excessive contribution of sulfur to the gas itself. A high sulfur concentration leads to corrosion of equipment and sulfur dioxide odor upon combustion.

Many techniques of presenting the odor to test subjects and of averaging the results of individual observations have been used, but we have found that none of the usual techniques have given sufficiently consistent and reproducible results to indicate anything more than a major distinction among odorants.

After extensive research into the determination of odor threshold values, we have developed a method which, upon laboratory scale, gives greater precision and reproducibility than methods used heretofore. By our method a threshold odor rank ratio may be determined with respect to any other odorant of roughly similar

odor intensity. Our experimental procedure is described below.

An odorized gas-air mixture of known and controlled odorant concentration is prepared in an apparatus which permits adjustment, both of the odorant concentration in the gas and of the concentration of odorized gas in air. The odorous mixture thus prepared is presented to an observer through a funnel-shaped opening. The observer sniffs the mixture and, upon request, may also sniff unodorized air for reference purposes. The observer then reports his olfactory reaction by one of three designations:

(—) No perceptible difference from purified air;
(1) Barely perceptible difference from purified air; and
(2) Definite perception e. g. sufficient to permit characterization of odor type.

Similarly, tests are run at other selected concentrations, suitably spaced, over the entire gamut of concentrations under consideration. The lowest concentration submitted to the panel is always zero, the highest is normally the concentration at which substantially all observers report a definite odor perception (value of 2 as defined above). For improved precision a duplicate set of observations are made after the first set has been completed. Following the collection of the above data, the arithmetical average values of the observations for each concentration are calculated.

In computing the arithmetical averages the "No perceptible difference" observation is given a numerical value of zero while the 1 and 2 observations are given the value of 1 and 2 respectively. These average odor ranks for dimethyl p-thioxane and for Spotleak 1008, a high intensity commercial odorant, are presented in the last two columns of Tables 1 and 2 above representing two different series of tests spaced several weeks apart. In the tables "Sequence" represents the order in which the concentrations are presented to the observers. The capital letters represent the different observers.

These average odor rank values are then plotted against the log of the concentrations to which they pertain, and the best fitting straight line is drawn through the points. Any convenient units of concentration may be used in making this plot, providing only that the same units are used for each of the two odorants being compared. In Figures 1 and 2 the concentrations plotted are the rotometer readings which in this case are directly proportional to the concentration of the odorant in the gas-air mixture as presented to the observers.

The resulting curve is used to compute the threshold odor rank ratio relative to a selected control or comparison odorant. This is accomplished by repeating the entire procedure as given above except that a control odorant is substituted for the test odorant. By this procedure the straight line showing the odor rank versus log of the concentrations for the said control odorant is determined. The threshold odor rank ratio of the test odorant, in this instance, dimethyl p-thioxane, in comparison with the control odorant, in this instance, Spotleak 1008, is determined readily from the respective odor rank curves discussed above. For this purpose these curves are plotted on the same graph as in Figures 1 and 2, and the desired ratio is the numerical value of the average odor rank of dimethyl p-thioxane at the concentration for which Spotleak 1008 has an average odor rank of 1. Thus, in Figure 1 said ratio is about 1.4, in Figure 2 about 1.6.

The threshold odor rank ratio thus compares the odor intensity of the test odorant as compared to a comparative odorant at the concentration when the comparative odorant is barely distinguishable from purified air. As seen in Figures 1 and 2 the odor of dimethyl p-thioxane was found to be 40 and 60% more intense

than those of Spotleak 1008 at the threshold concentration for Spotleak 1008.

All observations of the test odorant and the control odorant in one series are made on the same day in order that various extraneous factors such as humidity of the reference air are minimized.

Another comparison using the procedure described above was made with four observers making duplicate observations at each of seven concentrations employed. Dimethyl p-thioxane was compared with tetrahydrothiophene and Spotleak 1008—both of them being high intensity commercial gas odorants. The average odor ranks of this test series are presented in Table 3.

Table 3

Concentration (arbitrary units)	Average Odor Rank		
	THTP (tetrahydrothiophene)	Spotleak 1008	Dimethyl p-thioxane
.01	0.9	1.1	1.9
.02	1.1	0.75	1.9
.04	1.9	1.6	2.0
.05	1.4	1.75	1.9
.07	1.7	1.75	2.0
.10	2.0	1.9	2.0
.15	2.0	2.0	2.0

Again, the superiority of dimethyl p-thioxane over the two reference odorants was outstanding at the lower concentrations. The concentration and odor rank figures are the same as described in Tables 1 and 2.

Dimethyl p-thioxane may be prepared by the method of Harman and Vaughn described in U. S. 2,562,145, granted July 24, 1951, or it may be prepared by the reaction of dichloroisopropyl ether with alcoholic sodium sulfide as described in J. A. C. S., vol. 57, p. 1696. The pure compound has a sulfur content of 24.28% and boils at 162° C.

Commercial dimethyl p-thioxane contains minor amounts of impurities such as unreacted dichloroisopropyl ether and a seven membered saturated heterocyclic compound containing one oxygen, four carbon and two sulfur atoms, the latter being at the 4,5 ring positions. Since this latter compound possesses useful gas odorant characteristics, its presence in dimethyl p-thioxane is not at all detrimental. The sulfur content of commercial dimethyl p-thioxane ranges from 25 to 33% while the chlorine content will range from 0 to 3%.

While the above discussion and examples have been specific to dimethyl p-thioxane, it is to be understood that the discussion and examples are equally applicable to the dialkyl-p-thioxanes in which the alkyl substituents are of 1 to 3 carbon content.

Examples of other dialkyl-p-thioxanes useful in practicing our invention were presented earlier in this specification.

We claim:

1. The composition comprising a member of the group consisting of natural gas, mixtures of natural gas and manufactured gas, coke oven gas and liquefied petroleum gas and at least 0.04 pounds dialkyl p-thioxane per million cubic feet of the said gas, the alkyl substituents of the said dialkyl p-thioxane being limited from 1 to 3 carbon atoms.

2. The composition of claim 1 in which the alkyl substituents are identical.

3. The composition of claim 2 in which the alkyl substituents are methyl.

4. The composition comprising natural gas and at least 0.04 pounds of dialkyl p-thioxane per million cubic feet of natural gas in which the alkyl substituents are limited from 1 to 3 carbon atoms.

5. The composition of claim 4 in which the dialkyl p-thioxane is present at a concentration of from 0.04

pound to 5.0 pounds per million cubic feet of the said natural gas.

6. The composition of claim 5 in which the alkyl substituents are methyl.

7. The composition of claim 5 in which the alkyl substituents are methyl.

8. The process of odorizing a member of the group consisting of natural gas, mixtures of natural and manufactured gas, coke oven gas and liquefied petroleum gas comprising introducing an odor perceptible quantity of dialkyl p-thioxane into the said gas, the alkyl substituents of the said dialkyl p-thioxane being limited from 1 to 3 carbon atoms.

9. The process of odorizing natural gas comprising introducing an odor perceptible amount of dialkyl p-thioxane into the said gas, the alkyl substituents of the dialkyl p-thioxane being limited from 1 to 3 carbon atoms.

10. The process of claim 9 in which the concentration of the dialkyl p-thioxane is at least 0.04 pound per million cubic feet of natural gas.

11. The process of claim 8 in which the dialkyl p-thioxane is dimethyl p-thioxane.

12. The process of claim 9 in which the dialkyl p-thioxane is dimethyl p-thioxane.

13. The composition of claim 1 in which the dialkyl p-thioxane is present in the range of from 0.04 to 5.0 pounds per million cubic feet of the said gas.

14. The process of claim 8 in which the quantity of dialkyl p-thioxane introduced into the said gas ranges from 0.04 to 5.0 pounds per million cubic feet of gas.

15. The process of claim 14 in which the dialkyl p-thioxane is dimethyl p-thioxane.

No references cited.