

## UNITED STATES PATENT OFFICE

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## GAS ODORIZING

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This invention relates to improvements in the distribution of combustible or fuel gas, such as natural gas, manufactured gas, or their mixtures.

More particularly my invention relates to improvements in the odorization of odor deficient gases of the foregoing class by the addition of malodorants generally added to raise the odor intensity of the gas to aid in the detection of leaks, and wherein the malodorants employed are composed essentially of alkyl mercaptans.

It has, however, been found that when pure alkyl mercaptans are employed that their characteristic odor tends to fade and disappear due to progressive oxidation of the mercaptan content of the odorant when the gas is transported for appreciable distances in ferrous mains such as iron pipes or cast iron conduits which contain rust and moisture, or when the gas contains small amounts of oxygen or both oxygen and moisture in addition to rust in the transporting mains. This progressive diminution of odor produces dangerous situations in that gas that is satisfactorily odorized with high mercaptan content odorants at the point of odorant introduction becomes almost odorless at the extreme ends of the distribution system. Such conditions constitute a potential hazard in the distribution of combustible gas as both the public and distribution personnel have learned to depend upon the odor of the gas for detection and consequently explosions or asphyxiation can occur in a gas system that has been conscientiously endeavoring to provide every safety factor against them.

It is therefore the object of my invention to provide a method for the successful and dependable employment of alkyl mercaptan odorants for the odorizing of combustible gas in distribution systems therefor in a manner whereby the efficiency of the odorant will be maintained from the point of introduction to the extreme ends of the distribution system, and the mercaptans permitted to flow unhindered throughout the system with the gas and odorize the gas until it is burned or otherwise utilized. Also, by proceeding in accordance with the method of my invention, the efficacy of the introduced alkyl mercaptan odorant may be maintained in substantially uniform degree over several hundred miles of distribution mains without necessity for unequal or too high odorization at the point of introduction or distribution points adjacent thereto, or requirement for re-introduction at successive points in the system, all with an attendant economy in materials, and labor, more satisfactory and uni-

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form results, and the attendant enhanced factor of safety.

In general I accomplish the objects of my invention by preventing the oxidation of the mercaptans in the gas distribution system, or rather by inhibiting the polymerization of the mercaptans, since it appears that their polymers, rather than their monomers are subject to oxidation under the conditions prevailing, as will be later more fully described. The antioxidants, or rather polymerization inhibitors which I employ by vaporization in admixture with the mercaptan odorants, or by direct vaporization into the gas mains are the mono or polyhydric derivatives of benzene or its homologs, and particularly the mono and polyhydric phenols, having a boiling point not greater than about 210° C., atmospheric pressure, such as cresol, ortho tertiary butyl phenol, 2-4 di-tertiary butyl phenol and the like.

Typical systems wherein the practice of my invention is adapted may be illustrated by the average city distribution system utilizing either a mixture of natural gas and manufactured gas or straight natural gas, or by the high pressure transmission of natural gas derived from distillate producing wells that operate under a partial vacuum. In the latter instance although the gas is substantially dry, any leakage on the suction side of the first compressor station results in air leaking into the gas with the oxygen content sometimes rising to as much as 2%.

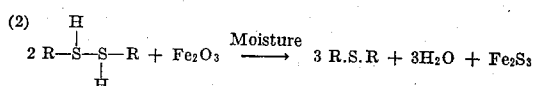
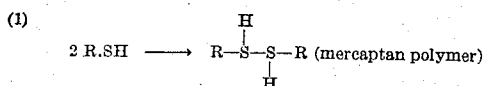
Experience has proven that when pure or substantially pure alkyl mercaptans are utilized under such circumstances, the odor cannot penetrate or be relied upon to completely penetrate to the extreme ends of the distribution system, and in a system containing rust and moisture but substantially free of oxygen, this situation prevails until the iron oxide in the system has been saturated with mercaptan, but which may require several years for the condition of equilibrium to be reached with attendant intervening hazard. Thus in a gas distribution line containing iron oxide ( $\text{Fe}_2\text{O}_3$ ), moisture and vaporized alkyl mercaptan, the iron oxide, in the presence of the moisture, reacts with the mercaptan to form water, iron sulfide and relatively odorless alkyl sulfides. If no oxygen is admitted, the system after a long time will become "saturated" and the odor will progress to the end of the line. However, pockets or odorless areas remain in the distribution system for as much as seven or eight years after odorization has begun, because of the

slow flow of gas in these particular areas and thereby constitute potential hazards.

In the event that the system contains in addition an appreciable amount of oxygen, the oxygen reacts with the iron sulfide formed as above, to form sulfur and iron oxide, the regenerated iron oxide being then again free to react with the mercaptan. In the event that the system contains iron oxide but where the gas is a substantially dry, but oxygen containing natural gas, the iron oxide acts as a catalyst for the reaction of the mercaptan with oxygen to form free sulfur, water and alkyl sulfides. In the system containing both moisture and oxygen in addition to the iron oxide, it appears that both reactions take place, that is, direct reaction of the mercaptan with the iron oxide and reaction of the mercaptan with oxygen under the influence of the iron oxide.

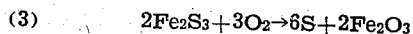
The following reactions appear to be typical and further illustrative of the conversion of the malodorous mercaptans to relatively odorless compounds. They further illustrate that the destructive action results from reaction with the polymers, rather than the mercaptan monomers, that is, it is first necessary for two molecules of mercaptan to come together in order to split off two molecules of hydrogen and one of sulfur to produce the reaction products. That such is the mechanics of the reaction has been demonstrated by for example the polymerization of amyl mercaptan in the liquid phase to a relatively non-volatile liquid. When this polymerized material was distilled at atmospheric pressure, regular amyl mercaptan was recovered. In employment of the mercaptans as odorants, the normally liquid material is vaporized into the gas line in a similar manner, but from the resulting reactions in the gas distribution system it is apparent that it polymerizes therein.

Thus in a system containing alkyl mercaptan, rust and moisture, the following reactions appear to occur.



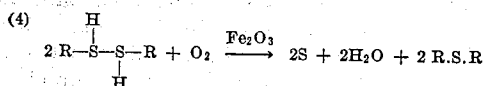
when all of the ferric oxide has been reacted with, further action stops and if no oxygen is admitted to react with the ferric sulfide then the line is said to be "saturated" and the odor will not be adversely affected in the "saturated" part of the distribution system.

Should the system, however, contain oxygen, the oxygen reacts with the ferric sulfide to regenerate ferric oxide as follows:



whereupon the cycle repeats itself, the ferric oxide reacting with mercaptan polymer as in (2) above.

In addition to the foregoing when the system contains both oxygen and moisture, the ferric oxide appears to react with mercaptan under the influence of the ferric oxide as a catalyst as follows:



In a system containing rust, oxygen and substantially dry gas, such as the natural gas high pressure transmission system previously described, the reaction is essentially the latter (4).

In accordance with my present invention I have found that oxidative destruction of these odorants can be prevented by inhibiting the polymerization of the mercaptans vaporized into the gas line by incorporation with the mercaptan approximately  $\frac{1}{2}$  of 1% by weight thereof of a suitable polymerization inhibitor. These inhibitors are of the class generally useful as vapor phase gum formation inhibitors in gas distribution systems and, as previously described comprise the mono and poly hydric derivatives of benzene and its homologs, particularly the mono and polyhydric phenols, such as cresol, the alkylated phenols, etc., which boil preferably below  $210^\circ \text{C}$ . By the employment of the inhibitor, normal use may be made of small proportions of the conventional alkyl mercaptan odorants such as ethyl, propyl, butyl and amyl mercaptans or mixtures thereof.

Thus I have found that the use of cresol and its homologs as an inhibitor will cause the odor produced by the mercaptan to be detected in two days in a city gas distribution of the class previously described, where previously odorant in the form of pure mercaptan had been added to the gas for over a year without penetration to the ends of the system.

I have also found that a mercaptan based malodorous with a suitable inhibitor added to it will enable the odor of the mercaptan to be detected at the extreme end of a 400 mile long high pressure gas distribution main containing up to 2% of oxygen in the gas with only  $\frac{3}{4}$  pound of mercaptan odorant per million cubic feet of gas. Without the use of the inhibitor, even as much as thirty pounds of pure mercaptan failed to give a sufficiently strong odor at the end of the line, even though the gas immediately downstream from the point of odorant introduction was too highly odorized.

These inhibitors may be vaporized into the gas stream near the introduction point of the mercaptan odorant, or added to the odorant and jointly vaporized therewith into the gas stream. A suitable composition has been found to be a petroleum distillate fraction containing in admixture both ethyl, propyl and butyl mercaptans together with ortho, meta and para cresols.

I claim as my invention:

1. A method for preventing odor fading due to oxidation of mercaptan bearing odorant in a combustible gas-free from gum forming constituents which comprises incorporating and vaporizing with said odorant a small proportion of a compound selected from the class consisting of mono and poly hydric derivatives of benzene and its homologs boiling below about  $210^\circ \text{C}$ .

2. A method for preventing odor fading due to oxidation of alkyl mercaptan odorant contained in a combustible gas stream free from gum forming constituents which comprises vaporizing into the gas stream, adjacent the point of introduction of the mercaptan odorant, a compound selected from the class consisting of the mono and poly hydric phenols boiling below about  $210^\circ \text{C}$ .

3. A method for preventing odor fading of alkyl mercaptan odorant contained in a combustible natural gas stream by oxidation due to the presence of iron oxide and moisture which comprises incorporating therewith in vaporous form a small proportion of a compound selected

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from the class consisting of the mono and polyhydric phenols boiling below about 210° C.

4. A method for preventing odor fading of alkyl mercaptan odorant contained in a combustible natural gas stream by oxidation due to the presence of iron oxide and oxygen which comprises incorporating therewith in vaporous form a small proportion of a compound selected from the class consisting of the mono and polyhydric phenols boiling below about 210° C.

5. A method for preventing odor fading of alkyl mercaptan odorant contained in a combustible natural gas stream by oxidation due to the presence of iron oxide, oxygen and moisture which comprises incorporating therewith in vaporous form a small proportion of a compound selected from the class consisting of the mono and polyhydric phenols boiling below about 210° C.

6. A method for preventing odor fading due to polymerization and subsequent oxidation of alkyl mercaptan odorant vapors introduced into a combustible gas stream free from gum forming constituents contained in a ferrous conduit which comprises incorporating therewith in vaporous form a relatively small amount of a compound selected from the class consisting of the mono

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and poly hydric phenols to inhibit polymerization of said odorant, said compound being normally liquid and having a boiling point below about 210° C.

7. A method of odorizing an odor deficient combustible gas stream free from gum forming constituents and for preventing odor fading thereof due to oxidizing agents present in the gas distribution conduits which comprises introducing into the gas stream in vaporized form alkyl mercaptan odorant and a small proportion of a compound selected from the class consisting of the mono and poly hydric phenols boiling below about 210° C.

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