

ANEXO 1

Odor Fade - Possible Causes and Remedies
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Odor Fade - Possible Causes and Remedies



Introduction

Modern history conducts itself much differently than it did at the turn of the century. Public safety and care for the environment has gone from the bottom of the list of goals, right to the very top.

This has come about for a variety of reasons, including increased knowledge of the products, processes and services offered together with the hazards associated with them, greater awareness of the effects on the population and environment, and the introduction of legislation to ensure compliance with the standard practices necessary to ensure these goals are met.

For the gas industry, one essential way of providing this service to their customers, is by odorization of natural gas.

Odorization of natural gas has evolved from a fragmented, unregulated practice, into the current highly regulated and monitored practice we see today. The primary focus of odorization is safety, and this must be kept in mind as we develop, maintain and improve our odorization techniques and processes in a changing regulatory environment.

The main focus of this paper will be on "Odor Fade". A number of factors contribute to this phenomenon, and will be considered in some detail.

History

Odorization of gas was first proposed in Germany in the 1880's by Von Quaglios' use of ethyl mercaptan as a means of leak detecting the escape of blue water gas.

The manufactured gas used at the turn of the century contained by-products which to some extent, imparted a "gassy" odor to the gas. As high quality natural gas displaced lower quality manufactured gas, the by-products that caused the gassy odor in the lower quality gas were no longer present. Without these by-products, natural gas had little if any detectable smell to warn of leaks or accumulation. This undetectable gas caused the disaster at the New London Elementary school in 1937 that leveled the school, killing many children.

The gassy odor of manufactured gas was originally duplicated in natural gas by cheap refinery by-product streams. However, these by-product streams were unreliable

and varied in quality. The growth of the chemical industry during World War II resulted in the availability of high quality synthetic chemicals that proved well suited for natural gas odorization. These chemicals are the low molecular weight (C3-C4), branched chained alkyl mercaptans, alkyl sulfides and a cyclic sulfide. By 1960, virtually all natural gas odorization was done with blends of these synthetic chemicals.

Odor Fade

Odor Fade can be a major problem. Gas may be satisfactorily odorized at source, but if it no longer has the necessary odor impact and intensity by the time it reaches the customer, escaping gas can go undetected and result in a serious fire or explosion hazard.

To understand why it occurs and what can be done to overcome the problem, we have to consider the following:

1. Odorant blend types and the chemistry of the various components
2. Pipeline conditions
3. The quality of the gas to be odorized

Odorant Blends and Their Components

Odorant Characteristics

Odorant blends are extremely odorous, volatile, flammable liquids. Acceptable odorants must possess certain physical and chemical characteristics. These include "gassy odor", low odor threshold, high odor impact, resistance to pipeline oxidation and good soil penetrability. Vapor pressure of blend components used in vaporization type odorizers is also a very important consideration.

Odorant Components

The odorants used today are usually blends of two or more components which achieve the desirable characteristics.

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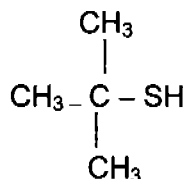


Therefore, it is important to understand the characteristics of the components. Basically there are three chemical groups from which odorants are blended:

1. Alkyl Mercaptans
2. Alkyl Sulfides
3. Cyclic Sulfide

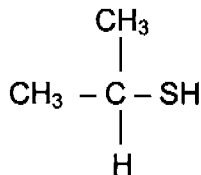
Mercaptan Components

Tertiary Butyl Mercaptan (TBM)



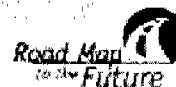
TBM is the leading single component used in natural gas odorants. Its low odor threshold, gassy odor, good soil penetration, and highest resistance to oxidation of the mercaptans, make TBM very desirable. However, the high freezing point of TBM (34°F) results in the need for blending with other components to prevent freezing. Otherwise, TBM would be an excellent "stand alone" odorant.

Isopropyl Mercaptan (IPM)

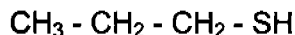


IPM has a strong, gassy odor and low freezing point (-202°F). Of the mercaptans it is the second most resistant to oxidation. IPM is commonly blended with TBM to depress the freezing point while enhancing the odor impact. IPM is also a stand alone odorant, but rarely, if ever, used as such.

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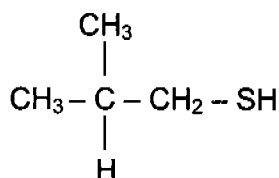


Normal Propyl Mercaptan (NPM)



NPM is not a major component in odorant blends, typically 3-6%. It is more easily oxidized than other mercaptans. However, NPM has a low freezing point (-171°F) and a strong odor. NPM was originally a co-product in the IPM manufacturing process. It is not a good stand alone odorant due to low oxidative stability.

Secondary Butyl Mercaptan (SBM)

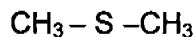


SBM, originally an impurity in TBM manufacture, is probably the least used component in odorant blends, typically 1-3% and at this low level generally makes no significant contribution to TBM blend performance. It is a branched chain mercaptan which resists oxidation. SBM has a strong odor, low freezing point, but high boiling point and low vapor pressure. The low vapor pressure offsets its odor impact.

Alkyl Sulfide Components

Alkyl sulfides are resistant to oxidation but they do not have the odor impact of the mercaptans. They are not considered "stand alone" odorants. Their primary function is to lower the freezing point of TBM.

Dimethyl Sulfide (DMS)

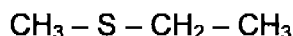


DMS has been widely used as a blend component, particularly with TBM. DMS will not oxidize in the pipeline and has good soil penetrability. DMS has a much higher vapor pressure than TBM, thus TBM/DMS blends are not suitable for vaporization type odorizers.

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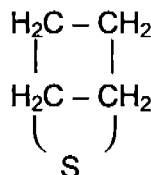
Methyl Ethyl Sulfide (MES)



MES is the latest addition to odorant blends with TBM. MES will not oxidize in pipelines. MES has a vapor pressure similar to TBM, therefore TBM/MES blends are suitable for injection or vaporization type odorizers.

Cyclic Sulfide

Tetrahydrothiophene (THT) or Thiophane



THT is the most resistant to pipeline oxidation. It has a gassy odor but low odor impact and poor soil penetrability. The low odor impact makes it difficult to over-odorize with THT. THT may be used in pure form or as part of a blend with TBM. THT is a "stand alone" odorant.

Blend Composition

The odorant blends in use today fall into one of three main categories, which are:

1. All mercaptan blends
2. Mercaptan/alkyl sulfide blends
3. Tetrahydrothiophene (THT) /mercaptan blends.

The following compositions (and minor variations thereon) are the most common blend types in use today. Also listed is the type of odorizing equipment which can be used.

Odor Fade - Possible Causes and Remedies



All Mercaptan Blends	
Component	Blend 1 (%)
TBM	79
IPM	15
NPM	6
Odorization Method - Vaporization or Liquid Injection	

Mercaptan/Sulfide Blends			
Component	Blend 1(%)	Blend 2(%)	Blend 3(%)
TBM	75	80	10
DMS	25	0	10
MES	0	20	0
IPM	0	0	70
NPM	0	0	10
Odorization Method	Liquid Injection	Vaporization or Liquid Injection	Liquid Injection

Tetrahydrothiophene (THT)/Mercaptan Blends		
Component	Blend 1(%)	Blend 2(%)
THT	100	50
TBM	0	50
Odorization Method	Vaporization or Liquid Injection	Liquid Injection

Odor Fade - Possible Causes and Remedies



Pipeline Conditions and Gas Quality

Odorization, especially by an injection system, is an accurate way of verifying that you have added the required ratio of odorant to gas. However, there are circumstances that

occur within distribution systems which can mask the odorant level in the gas stream or cause the odorant to 'fade'. There are basically three causes for this phenomenon and they are the following:

Oxidation - formation of di-sulfides in the presence of iron oxide (*rust*) and air (oxygen)

New pipe - Adsorption/absorption of odorant onto/into the surface of synthetic (plastic) pipe information of patina layer inside steel pipe

Gas Quality - Absorption, masking, or reaction of odorant components with impurities in the gas stream.

Some of the causes of odorant 'fade' are chemical reactions whereas the others are physical phenomena. Let us explore the possible causes of odor fade mentioned above.

Oxidation

The presence of rust and air within a pipeline will act as a catalyst on mercaptans causing them to oxidize into compounds that have virtually no detectable odor. Of the common mercaptan odorants, the following list represents how they will react in the presence of a rust/oxygen environment:

TBM	Most resistant to oxidation
IPM	↑↓
NPM	Least resistant to oxidation

All of the sulfide components (DMS, MES, & THT) used in odorant blends are resistant to oxidation.

The solution: *temporary increase in the odorant dosage rate*

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New Pipe

Plastic- The other potential cause for odor fade is a physical reaction caused in the presence of new plastic pipe. In this case, the odorant is being adsorbed and/or absorbed onto and into the plastic pipe. However, once equilibrium is achieved, the

amount of odorant going onto and into the surface of the pipe wall equals the amount coming back out. When this point is finally attained, odor detection with normal dosage levels should resume.

The solution: *temporary increase in the odorant dosage rate*

Steel- This same principle exists, to some extent, in the presence of new steel pipe although a chemical reaction, not physical. However, new steel pipe can be 'pickled' by introducing larger than normal quantities of odorant into the pipe at the start. Eventually an iron sulfide layer forms (*patina*) on the inside surface of the pipe and the conditions that would cause odor fade will diminish.

The solution: *temporary increase in the odorant dosage rate*

Gas Quality

The gas quality must also be considered when investigating causes of odor fade.

Is your gas supply

1. Dry - Not Naturally Odorized?
2. Wet - Not Naturally Odorized?
3. Dry - Naturally Odorized?
4. Wet - Naturally Odorized?
5. Peak Shaved Gas?

Odor Fade - Possible Causes and Remedies



1. Dry Gas - Not Naturally Odorized

Dry Gas, not naturally odorized is the easiest to odorize and does not cause odor fade. Any of the defined commonly used odorant blends will perform satisfactorily provided that continuous odorization is practiced. Low flow absorption may be an issue.

2. Wet Gas - Not Naturally Odorized

Condensed liquids in the pipeline absorb odorant components. Some odor masking may also occur due to the odor imparted by the impurities in the gas. Both give rise to "odor fade".

Odorants with the highest vapor pressure and lowest threshold values work best. Blends high in IPM (with its high vapor pressure) are considered best in this situation. TBM blends work well in overcoming masking but are not recommended where liquid levels are high.

Do not use THT or THT blends. Their low vapor pressure and low K_d values results in a higher degree of absorption in pools of condensate resulting in more rapid odor fade. Also, if drier gas is later introduced, condensates with a high level of dissolved odorant can rapidly evaporate, resulting in overodorization of the gas stream.

3. Dry Gas - Naturally Odorized

Dry, naturally odorized gas can cause odor fade because it contains among others, methyl and ethyl mercaptan, which can cause oxidation of TBM to disulfides, which have low vapor pressure and low odor impact. As the levels of natural mercaptans increase, it is best to use sulfide blends, which are oxidation resistant. THT blends are best. DMS is oxidatively stable but lacks odor impact, and is not considered a "stand alone" odorant.

4. Wet Gas - Naturally Odorized

It is almost impossible to satisfactorily odorize this type of gas. IPM based blends may work if liquids are the main problem. THT blends may work if natural mercaptans are the major contaminants. The best solution is not to purchase this quality of gas.

Odor Fade - Possible Causes and Remedies



5. Peak Shaving

This practice which involves addition of propane diluted with air to natural gas results in a similar situation to that of naturally odorized gas in which the ethyl mercaptan used to odorize the propane promotes oxidation of mercaptan based odorants resulting in "odor fade". Also the addition of oxygen and moisture increases the possibility of mercaptan oxidation. So even if unodorized propane is purchased conditions for oxidation, albeit reduced, still exist. THT blends are considered best if conditions are severe.

NOTE:

Sulfides Oxidative Resistance - As previously mentioned, alkyl sulfides (DMS, MES) and the cyclic sulfide (THT) are resistant to oxidation. However, THT is the only sulfide which will act as an effective stand-alone gas odorant. Both DMS and MES do not possess the required "gassy" odor and are therefore ineffective as stand-alone gas odorants. Additionally, both DMS and MES are typically used in minor concentrations (-20%-30%) further reducing the chances of odor detection should 100% of the mercaptan in the blend be oxidized.

Conclusion

Hopefully, the information in this paper will increase your knowledge of odorant behavior. As you can see, there are many factors that can contribute to odor fade, and very often, it is a combination of contributing factors that causes the problem.

Always remember that "safety of the public" is our prime concern. Proper odorization allows your customers to safely use natural gas by providing an adequate warning level allowing them to recognize a leak, should one exist, prior to the gas reaching an explosive level.

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Natural Gas Odor Fade

Introduction

A recent incident shows the importance of using gas detection equipment to test for the presence of natural gas verses relying on smelling the odor of the gas. A worker was tasked with determining if natural gas was flowing to a recently installed large, enclosed air handling unit (AHU). After opening the valves and pressurizing the line to the AHU, the worker relied on the lack of any odor to determine that natural gas was not flowing to the equipment. Subsequently, the worker walked to the door of the AHU and lit a cigarette (against company policy). The resulting explosion and fire caused second and third degree burns on the worker's torso and over \$120,000 in equipment replacement costs – not including labor.

Background

Natural gas (methane) is odorless. As a safety precaution against undetected leaks, the Department of Transportation (DOT) requires an odorant be added (49CFR192.625 – Pipeline Safety Regulations). The odorant must provide a warning that prompts the public to take action when detected. Specifically, 192.625 requires "A combustible gas in a distribution line must contain a natural odorant or be odorized so that at a concentration in the air of one-fifth of the lower explosive limit (LEL), the gas is readily detectable by a person with a normal sense of smell." One-fifth the LEL is twice the level OSHA allows for entry into confined spaces. Therefore, a confined space with a gas level of one-tenth the LEL would fall under OSHA's permit-required confined space regulations, but the gas smell may not be noticeable – even though the odorization complies with DOT.

Except in limited situations, DOT does not specify where the odorant will be added, as long as it is added prior to the final point of use. Usually, the odorant is added in the gas transmission lines or the gas distribution lines. However, the odorant may be added by a separate system just prior to the distribution line entering a property.

The odorant most often used is tertiary butyl mercaptan (TBM). It has a low odor threshold and "gassy" odor but a relatively high freezing point of 34F. Typically it is blended with isopropyl mercaptan (IPM) to depress the freezing point. IPM has similar characteristics to TBM but has a freezing point of minus 202F.

Odor Fade – Natural Gas

Odorization is a critical part of gas use safety. However it is not 100% foolproof. The odor of the mercaptans can fade for several different reasons:

- Oxidation – rust and oxygen inside the pipe may react with the mercaptans and convert them to disulfides with a much weaker odor.
- New pipe
 - Plastic pipe will absorb/adsorb the mercaptan until equilibrium is reached. Until that equilibrium occurs, the odorant concentration in the pipe can be significantly less.
 - Steel pipe – The steel in new pipes can react with the mercaptans. Again, the concentration of mercaptan will be reduced until the pipe is conditioned or "pickled." A layer of iron sulfide forms (patina) that stops the reaction.

The usual solution for these situations is to temporarily increase the odorant addition rate until the reactions have played out.

Other factors that may affect the mercaptan concentration include: extremely cold weather and condensed liquids in the pipe. The mercaptan may be absorbed by the condensed liquids. The solution to this problem is to keep moist air and other liquids out of the pipe and drain any condensation that does occur.

If a leak occurs underground, the soil may absorb the odorant, while the natural gas, for the most part, passes through. The leaked gas may then have minimal, if any odor.

Alternatively, the individual worker may not be able to detect the odorant – even when it is present in adequate concentrations. Reasons include:

- Worker lacks a sense of smell
- Worker has an impaired sense of smell due to colds, allergies, smoking
- Other odors present may mask the gas odorant smell (e.g. musty basements, other chemical odors)
- Worker experiences olfactory fatigue
- Worker is mentally distracted and simply does not notice the odor

Odor fade – Propane

Similarly, propane is odorized and fading can occur here too. Propane tanks used on construction sites (e.g., temporary heating) are usually odorized with ethyl mercaptan. The same chemical reactions and physical sensing limitations for natural gas and pipe lines noted above apply to propane and tanks. One study by the Arthur D. Little, Co., for the Consumer Product Safety Commission (CPSC), found that odor can significantly fade within 5-7 days of the tank being filled. Brand new tanks (not yet conditioned or “seasoned”) and old rusty ones appear to be the most likely to have low mercaptan concentrations. Empty tanks that are left open to the air can rust on the inside. Subsequent refilling can create a situation where the mercaptan is quickly reacted out of the propane. Therefore, it is important to never let a tank run “dry” and always keep the valve tightly closed when not in use.

Conclusion

Odorization of natural gas and propane is an important factor in the safe use of these materials. However, the lack of odor should not be used as the sole means of determining if these gases are present in the air. High quality, properly calibrated gas monitoring equipment used by trained workers should be used whenever there is a potential for gas leaks or a flammable atmosphere.

Workers and supervisors should also be regularly reminded that all sources of ignition must be eliminated when a flammable gas may be present.

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