PRINCIPLES OF ODORIZATION

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INTRODUCTION

The detection of natural gas leakage has long been a concern to the natural gas industry, but never more so than today. Increased public awareness of safety and huge increases in the cost of product liability litigation has resulted in a greater focus on gas odorization.

While it must be recognized that no odorant will be 100% effective in warning of the presence of natural gas, basic knowledge about the properties and characteristics of odorants used for natural gas and an understanding about some of the potential problems in the odorization of such gas can be extremely helpful for those involved in the gas odorization process.

ODORANT COMPONENTS

Since natural gas odorants are virtually all blends of two or more components, we must first gain some knowledge of the components used. These components are divided into three general groups:

Mercaptans
Alkyl Sulfides
Cyclic Sulfides

Mercaptans

- Tertiary Butyl Mercaptan (TBM)
  Leading component used in natural gas odorants
  Most resistance to oxidation of the mercaptans
  Best in soil penetrability of the mercaptans
  Low odor threshold
  "Gassy" odor
  High freeze point (34°F)
  Usual concentration - 75-80% of the total blend

- Isopropyl Mercaptan (IPM)
  Second in usage of the mercaptans
  Not as resistant to oxidation as TBM, but stable enough to be used as the primary component
  Second in soil penetrability of the mercaptans
  Low odor threshold
  "Gassy" odor
  Usual concentration - 10-80% of the total blend

- Normal Propyl Mercaptan (NPM)
  Not a major component
  Least resistant to oxidation of the mercaptans
  Last in soil penetrability of the mercaptans
  Low odor threshold
  Strong "gassy" odor contributes to the overall blend impact
  Usual concentration 3-10% of the total blend

- Secondary Butyl Mercaptan (SBM)
  Least used component
  Similar to IPM in resistance to oxidation
  Third in soil penetrability of the mercaptans
  Low odor threshold
  "Gassy" odor
  Difficult to mask
  Usual concentration 2-6% of total blend
  Used as a single component odorant in wick odorizers

Alkyl Sulfides

- Dimethyl Sulfide (DMS)
  Will not oxidize in the pipeline
  Best in soil penetrability of all of the odorant components
  High odor threshold
  Does not have "gassy" odor
  Usual concentration 20-25% of the total blend
  Blends usually restricted to liquid injection type equipment

- Methyl Ethyl Sulfide (MES)
  Will not oxidize in the pipeline
  Soil penetrability similar to TBM
  High odor threshold
  "Gassy" odor
  Usual concentration 20-50% of the total blend
  Can be used in both liquid injection and vaporization type equipment

Cyclic Sulfides

- Tetrahydrothiophene (THT)
  Used both as a blend component and as a single component odorant
  Most resistant to pipeline oxidation of all odorants when used as a single component odorant
  Soil penetrability similar to NPM
  Usual concentration 30-50% of total blend
  When blended restricted to liquid injection type equipment
  Difficult to mask

ODORANT BLENDS

As previously stated, most natural gas odorants are blends. While there are approximately twenty different blends available, only the most commonly used ones will be discussed. These blends fall into two general groups;

All Mercaptan
Mercaptan/Sulfide

All Mercaptan Blends	
1	2
75-80% TBM	70-80% IPM
15-23% IPM	8-10% TBM
2-10% NPM & SBM	8-10% NPM

Mercaptan/Sulfide Blends		
1	2	3
75-80% TBM	50-80% TBM	50-70% THT
20-25% DMS	20-50% MES	30-50% TBM

ODORANT SELECTION AND RATE OF ODORIZATION

Considering all the factors bearing on the efficiency of odorization, there is no one odorant or one concentration rate which can be recommended for all gas systems, or for the same system all of the time.

Some of the potential problems that may influence both the type of odorant and/or the rate of odorization are:

Soil Penetration
Masking/Scrubbing/Odorant Contamination
Pipeline Adsorption
Chemical Reaction

SOIL PENETRATION:

This has been known and discussed more widely than any other potential problem concerning the odorization of natural gas. It is associated with the passage of escaped natural gas through soil. Depending upon the facts and circumstances surrounding the escape of natural gas (i.e. rate of leak, amount of soil through which the gas must pass, etc.), certain types of soil — clay being the worst — can remove some or all of any odorant from the natural gas for a period of time. As noted above, TBM is considered the best of the mercaptans in soil penetration. IPM is considered the second best mercaptan for soil penetration; NPM is third; and SBM is considered last of the mercaptans in penetrating the soil. DMS, an alkyl sulfide is considered the best of all odorants in soil penetrability. MES, another alkyl sulfide, is believed to have soil penetration approximately the same as TBM. THT, a cyclic sulfide, has the same soil penetration as NPM.

MASKING/SCRUBBING/CONTAMINATION:

These potential problems are associated with "wet" natural gas or gas containing high amounts of C4+Hydrocarbons. These Hydrocarbons can "mask" or cover up the odorant in the gas stream. They also tend to gather in low areas of the pipeline and "scrub out" or remove the odorant as the gas flows through the liquid. Another problem is hydrocarbon contamination of the odorant in by-pass vaporization type odorizers. The obvious solution is to remove the liquids at the processing plant, however this is not always possible. Therefore either higher rates of an all mercaptan blend containing TBM as the major component or addition of difficult to mask odorants such as Secondary Butyl Mercaptan or Tetrahydrothiophene should be attempted.

PIPEWALL ADSORPTION:

Adsorption of the odorant on interior pipewalls during periods of low gas flow, on dead ends, and in new piping is another potential problem in odorization. The only solution that I am aware of is the local addition of more odorant during these conditions. This problem has nothing to do with the type of odorant used.

CHEMICAL REACTION:

There are two potential reactions involving natural gas odorants.

1. Oxidation Reaction
2. Reaction with low molecular weight mercaptans

OXIDATION:

Oxidation of the mercaptans in natural gas odorant is usually associated with new piping systems where an active type of rust is available. In this reaction, the mercaptan is converted to a disulfide which has much less odor. The solution is the addition of high amounts of the odorant until the pipelines reaches a passive state.

REACTION WITH LOW MOLECULAR WEIGHT MERCAPTANS:

This refers to the reaction of the odorant mercaptans with either Methyl Mercaptan or Ethyl Mercaptan in the gas stream. Either or both of these mercaptans occur naturally in some gas production areas and are sometimes left in the gas. When they are present, a reaction can occur that will remove the odorant by converting it into a disulfide. Possible solutions to this problem are odorant addition at the last possible point in the system to shorten the contact time or the use of Tetrahydrothiophene which will not react with the mercaptans. Another source of Ethyl Mercaptan is in propane peak shaving since Ethyl Mercaptan is the odorant used in propane. One possible solution would be to buy unodorized propane and add the same odorant that you use in the natural gas as it is unloading into the storage tank, or buy propane odorized with Tetrahydrothiophene.

RECORDS

All phases of the odorization program should be well documented with permanent records. When location and proper equipment availability allow, continuous recording should be considered. These records may include, but not be limited to the following:

Odorization Policy

A comprehensive statement of the odorization program and procedures should be on file.

Odorization Equipment

All maintenance records

Filling and gauging reports

Odorant usage reports

Test Results

Odor intensity test results (odorometer, room test, etc.)

Certificate of Analysis from odorant supplier

Leak Reports — frequency and pattern of all leak reports