INTRODUCTION

The reason gas companies odorize natural gas is simple: it is a legal requirement. In 1937, the high school in New London, Texas exploded, killing over 200 men, women, and mostly children. Natural gas emanating from a leak accumulated in the school’s basement and ignited when someone entering the area flipped on a light switch. No one knew about the leak because un-odorized natural gas has no odor. This disaster led federal and state regulators to enact new regulations that required suppliers to odorize natural gas.

Odorization remains one of the most important tasks performed by the gas company. Thus, it is critical that gas company management and employees have a clear understanding of the fundamentals of gas odorization. Knowledge of the basic characteristics of odorant compounds, the reasons for blending these compounds, and the potential problems that can arise is a vital component of an odorization program's success. The legal and human costs of natural gas accidents demand constant vigilance from everyone involved in an odorization program.

LEGAL REQUIREMENTS

The regulations requiring odorization of natural gas are enforced in the United States by the Department of Transportation's (DOT) Office of Pipeline Safety and are encoded within 49 CFR 192.625(a) and 192.625(f). The law clearly states natural gas must be odorized so that any leaks are readily detectable, by a person with a “normal” sense of smell, when the concentration of natural gas reaches 1/5th of the lower explosive limit. Setting the detection requirement of odorized gas at 1/5th (20%) of the LEL creates a safety factor that can buy time and save lives when a gas leak occurs. Leaking gas will be detected well before the mixture of gas and air is able to support ignition.

Numerous studies have been conducted throughout the years to find the best chemical compounds to use for odorization of natural gas. These studies have revealed that mercaptans, a class of organosulfur compounds, are the best chemicals to use for odorization of natural gas. Mercaptans have a repulsive smell that is detectable at extremely minute concentrations in the part per billion range. The vast majority of human beings can smell mercaptans at these extremely low levels, so these compounds are very effective at odorizing natural gas.

MERCAPTANS USED IN ODORIZATION

Not all members of the mercaptan chemical family are amenable for use in natural gas odorization. The low molecular weight mercaptans, such as ethyl mercaptan and methyl mercaptan, are much too reactive to use in natural gas systems. This means these compounds are easily converted to other less odorous forms via chemical reactions with other compounds found in natural gas systems. On the other hand, higher molecular weight mercaptans, such as nonyl mercaptan and dodecyl mercaptan, are not volatile enough to be effective. Thus, the mercaptans used in odorization are “middle of the road” in terms of molecular weight, volatility, and reactivity. Mercaptans typically used in the gas industry include:

1. tert-Butyl mercaptan
2. n-Propyl mercaptan
3. Isopropyl mercaptan
4. sec-Butyl mercaptan

tert-Butyl Mercaptan (TBM)

TBM is the most common odorant blendstock in North America. TBM has a strong, gassy odor at low concentrations, and is the most oxidation resistant of the mercaptans. However, its relatively high freezing point (34°F) means it must be blended with other organosulfur compounds with lower freezing points so it can be used in climates where the temperature regularly gets below freezing. TBM also features the best soil penetrability of all the mercaptans.

n-Propyl Mercaptan (NPM)

NPM is not a major blend component, although it is used in blends popular in the Northwestern region of the U.S. and Canada. Although NPM is the most easily oxidized of the mercaptans, its low freezing point makes it a very good blendstock to use with TBM. A strong odor and relatively high vapor pressure are two other good characteristics of NPM.
Isopropyl Mercaptan (IPM)

IPM is the second most popular blendstock in North America. IPM features a characteristic “gassy” odor, strong soil penetrability, and is second only to TBM in oxidation resistance. Its low freezing point (–203°F) and high vapor pressure are two good features of this mercaptan.

sec-Butyl Mercaptan (SBM)

SBM is the least used blendstock in North America. SBM is primarily used in Wick odorizers, where its low vapor pressure and high boiling point help prevent the possibility of over-odorizing with this equipment.

OTHER COMPOUNDS USED IN ODORIZATION

Thiophane

Thiophane, also known as tetrahydrothiophene (THT), is the only cyclic organosulfur compound used in odorization. THT is one of the most prevalent blendstocks in Europe and the Western United States, and is the only organosulfur compound used in its pure form to odorize natural gas. THT is sometimes blended with TBM, if it's blended at all. Compared to the mercaptans used in odorization, THT is the most oxidation resistant, but has a low odor impact and poor soil penetrability.

Sulfides

The other components used in odorant blends are a class of organosulfur compounds called sulfides. Sulfides are blended with mercaptans for various reasons, such as lowering the freezing point of a blend or imparting stronger anti-oxidation characteristics to the blend. Sulfides have much higher odor thresholds than mercaptans, so their odor impact is not nearly as strong. However, sulfides are extremely resistant to oxidation and are not very likely to oxidize under pipeline conditions. Two examples of sulfide compounds typically used in odorant blends are dimethyl sulfide and methyl ethyl sulfide.

WHY BLEND?

All organosulfur compounds used in the odorization of natural gas are blended to make odorants. As mentioned previously, thiophane is the only organosulfur compound that can be used in its pure form to odorize natural gas. All others must be used as part of a blend.

The reason for blending is simple: no single organosulfur compound is 100% effective as an odorant in natural gas. While all organosulfur compounds used in odorization have good characteristics, they also have shortcomings that preclude their use in their pure form as gas odorants. For example, TBM must be blended with other compounds to lower the overall freezing point of the blend to an acceptable level.
Factors Affecting Odorant Quantity

There are times when odorants are “scrubbed” out of the natural gas. In this case, unlike masking, the odorant is actually taken out of the gas stream, via a chemical or physical pathway.

The most obvious cause of a lack of odorant in the gas stream is odorizer malfunction. After all, odorizers are mechanical devices that can occasionally fail to work properly. Eliminating the chances for odorizer malfunction requires frequent inspections and maintenance of equipment to insure it functions properly at all times.

Adsorption of odorant occurs whenever the odorant molecules in the gas stream attach themselves to a surface. When this happens, the odorant is no longer homogeneously mixed with the gas stream and is essentially taken out of commission. Adsorption effects are commonly observed on newly deployed pipe. This is why it is recommended that new pipe be “pickled” with gas containing a higher concentration of odorant than normally applied. Once the pickling process is complete, odorization levels can be returned to normal.

Absorption of odorant, on the other hand, occurs whenever odorant molecules go into solution with gas liquids found in the pipeline. Even though absorption into liquids does occur, it is not considered an important factor.

Chemical reactions can also lead to odorant performance problems. In this case, the odorant is actually depleted and cannot be recovered, because a chemical change is involved that transforms the molecules comprising the odorant blend into a less odorous chemical form. The most common pathway for chemical change is oxidation. When a mercaptan is oxidized, it is converted to a less odorous compound, namely a disulfide. The following simplified reaction shows this effect:

\[ 2 \text{R-S-H} + \text{Oxidizer} \rightarrow \text{R-S-S-R} \]

The odor threshold for a disulfide is much higher than that of a mercaptan, so odorant performance, defined by odor impact and intensity, is adversely affected when the mercaptan components of a blend are chemically converted into disulfide.

Air in the pipeline can be a troublesome issue that chemically affects the odorant. The presence of air in the pipe will reoxidize pipes and form an oxide of iron which oxidizes the mercaptan into a disulfide:

\[ \frac{1}{2} \text{O}_2 + 2\text{Fe}_3\text{O}_4 \rightarrow 3\text{Fe}_2\text{O}_3 \]
\[ 3\text{Fe}_2\text{O}_3 + 2\text{RSH} \rightarrow \text{RSSR} + 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} \]

“Naturally odorized” gas typically contains mercaptans and/or sulfides, and the presence of these compounds can present special problems. Synergistic effects have been documented in the literature, whereby the presence of reactive, lower molecular weight mercaptans and sulfides can increase the reaction rate for mercaptan oxidation. In other words, when you have a relatively reactive and a relatively unreactive mercaptan present in the gas, the rate of conversion to the corresponding disulfide for the entire mercaptan blend becomes that of the more reactive mercaptan.

The implications of the reactions shown above are that the mercaptan, the active element in an odorant blend which imparts the high impact, low threshold smell, is chemically converted to a less odorous compound, namely a disulfide. Supplemental odorization is required whenever odorant performance deteriorates due to chemical conversion.

THE IMPORTANCE OF DOCUMENTATION

Documentation is critical to the success of an odorization program. Keeping thorough documentation does not only shield the gas utility from potential liabilities, it is also a powerful tool that can be used to proactively improve performance. There is no way to gauge the effectiveness of an odorization program without data. And, the only way to collect this data is to keep records.

Some of the records to keep include:

- Maintenance records of odorization equipment
- Measurement records of odorant usage and storage
- Equipment inspection records
- Injection rates records
- Odorometer test results
- Quantitative results from ancillary measurements, such as gas chromatographic analysis
- Odorant supplier Certificates of Analysis
- Technician calls

A WORD ON ODORANT TRANSPORTATION

A question often facing utilities centers on DOT (Department of Transportation) requirements that govern the transportation of hazardous materials. The DOT is the principal regulatory agency that governs the transport of hazardous materials on America’s public highways. Failure to adhere to DOT regulations when transporting hazardous materials can result in significant fines.

First, some definitions: a container with a maximum liquid capacity greater than 119 gallons is considered a “bulk” container. On the other hand, a container with a maximum liquid capacity of less than 119 gallons is considered a “non-bulk” container. It is important to keep these volumetric limits in mind when transporting odorants on public highways, as they directly impact regulatory labeling and placarding requirements.

49 CFR Subpart E (Labeling) requires that non-bulk packages offered for transportation shall be labeled per
the requirements specified in the DOT Hazardous Materials Table and in Subpart E of the DOT regulations. Many popular odorant blends are assigned the UN number UN3336 in the DOT's Hazardous Materials Table and a Hazard class of 3 (Flammable liquid). Thus, a non-bulk container's label name must say FLAMMABLE LIQUID and the label design must follow the specifications set forth in 49 CFR 172.7419.

49 CFR Subpart F specifies the requirements for placarding of containers carrying hazardous materials offered for transportation. According to the regulations, any bulk container must be placarded per the requirements in 49 CFR 172.504 and 49 CFR 172.505. The regulations contain some exemptions to this rule; containers meeting the exemption requirements can placard just 2 opposite sides of the packaging or container or use labels instead. A container meets the placarding exemptions if it is:

- A portable tank with a capacity of less than 1,000 gallons
- A DOT 106/110 Multiunit tank car tank
- Bulk packaging other than portable tank, cargo tank, or tank car with a volumetric capacity of <640 cubic feet
- An intermediate bulk container

These exemptions are defined under 49 CFR 172.514(c).

Thus, a vehicle carrying a bulk vessel containing an odorant blend assigned a Hazard class of 3 must be placarded with the name FLAMMABLE. Moreover, this placard must be designed per the specifications prescribed under 49 CFR 172.542. Placards are not required on a vehicle carrying non-bulk containers with an aggregate gross weight of less than 1001 pounds of hazardous materials covered by Table 2 in 172.504 (e). Essentially, this means that if the aggregate weight of non-bulk packages being carried on a vehicle exceeds 1001 pounds, the vehicle must be placarded.

The price for non-compliance with DOT regulations can be severe, so care must be taken to abide by all labeling and placarding requirements at all times.

CONCLUSION

As the New London explosion tragically demonstrated, the consequences of handling and using un-odorized gas are severe. It is the duty of the gas utility to insure that gas supplies are properly odorized at all times. Understanding the odorization process and maintaining records to are key elements of a successful odorization program.

Sixto Ortiz, Jr.