AUTOMOTIVE GASEOUS ODORANT HISTORY AND SAFETY REVIEW

1.0 Background

The history of gas odorization had its beginnings in the 1880s, when ethyl mercaptan was added to natural gas, which was manufactured as "town gas" at that time. Town gas was odorized primarily because of its toxic carbon monoxide content. When natural gas was initially used as a fuel, its sulfur compounds—which are common components of pipeline natural gas—often resulted in a detectable odor. However, concentrations of natural sulfur vary from different gas sources. and some natural gas sources produce odorless gas. Because of this variability, efforts to find an effective odorant for natural gas began in the 1920s, and essentially there was no consideration for automotive applications.

The "gassy" odor of manufactured gas, and natural gas with naturally-occurring sulfur compounds, was originally duplicated by adding inexpensive refinery byproduct streams to otherwise odorless natural gas. These byproduct streams—produced by the gasoline sweetening process—contained a variety of sulfides, which resulted in a natural gas product with inconsistent odor characteristics. Natural gas producers resisted standardization of the odorization process for many years.

In 1937, a tragedy occurred at the New London High School in New London, Texas, that spurred a complete revamping of the practice of odorizing natural gas. New London High School used odorless natural gas, which was provided by a pipeline located in their oil- and gas-rich community, for heating and cooking. A leak occurred at the school that went undetected until the moment an electric sanding machine in the woodshop was unplugged causing a spark that ignited the accumulated gas. The explosion killed 239 people, mostly children. This accident is reported as the worst school disaster to date, and ranks with airline crashes as the most devastating in U.S. history.

Following the tragedy, Texas and other states adopted regulations that standardized natural gas odorization for pipeline gas for consumer use. Processes were developed to synthesize odorants from raw materials to produce "synthetic" odorants with more consistent characteristics, instead of employing "natural" odorants. Companies were formed to specialize in the production of natural gas odorants; for example, Natural Gas Odorizing, Inc. (NGO) was founded in 1942. A variety of synthetic odorants were used until the early 1950s, but by 1960, almost all natural gas was odorized by one or more odorant compounds of the following types:

Mercaptans
Alkyl sulfides
Cyclic sulfides

Today, all pipeline natural gas delivered to consumers in the United States must contain an odorant that alerts users to leaks. Liquefied petroleum gas (LPG), or propane sold in or dispensed into containers, is also odorized. Originally, however, the premise for odorization of these two gases did not take into account automotive applications or the expansion of available automotive gases such as hydrogen, nitrous oxide, and methane-hydrogen mixtures.

Virtually all compressed natural gas (CNG) used as an automotive fuel derives from pipeline gas and is therefore odorized. Odorants are not guaranteed to act effectively as a single warning agent by their smell and, thus, vapor leaks from gaseous powered vehicles or fueling stations may not be detected by an individual. For commercial applications, leak detection and proper education should be employed to ensure safe operation.

GAS ODORANT PROPERTIES AND CHARACTERISTICS

2.0 Common Gas Odorants and their Properties

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Table 1 depicts the most commonly used gas odorants, lists the acronyms used to designate each odorant, and comments on each odorant's application. Table 2 summarizes several key physical properties of these odorants, and lists each odorant's chemical-structural formula, molecular weight, sulfur weight percentage, freezing temperature, and boiling temperature.

The odorant chemicals, properties, and characteristics summarized here are based on information gleaned from more than 50 years of product development work by chemical and odorant injection equipment companies, and laboratory research for pipeline supplied natural gas or propane.

2.1 Odor Fade

Odor fade refers to a variety of circumstances rendering an initially odorized gas almost odorless and undetectable by smell when the time it reaches the end-user. Odor fade usually refers to factors affecting gas during pipeline transportation, processing, storage, and transportation situations. However, there are numerous cases wherein end users have filed lawsuits which include odorant fade as a key contributor to an accident.

Odor fade is usually caused by one of more of the following activities:

- Oxidation Contact with oxidizing agents (including rust) can convert the odorant to its corresponding disulfide, which has a weaker odor.
- Absorption Odorants can dissolve into liquids.
- Adsorption Odorants can attach to solid structures.
- Temperature Very low temperatures can reduce the amount of effective odorant in natural gas.

The causes and effects of odorant fade have been studied extensively. There is substantial literature on this subject and training courses to educate pipeline related employees regarding odorant fade. There appears to be little information related to automotive applications and odorant fade.

2.2 Individual Odor Perceptibility

Relying on an individual's odor perceptibility and sense of smell has numerous challenges in light of automotive applications. The perception is that, if a person can smell odorized natural gas within a home, heater closet, or basement, it follows that one can smell gas in and around a vehicle or refueling station. Unfortunately, the following are examples of why using an odorant as a single safety device for commercial, transit, school bus and refueling station applications does not meet today's real world demands:

- State of mind e.g., attentiveness: distractions can provide lessened awareness.
- Permanently impaired sense of smell some individuals have a reduced sensitivity to certain odors, and there are those who have no sense of smell at all.
- Temporarily impaired sense of smell e.g., due to colds, allergies, smoking.
- Olfactory fatigue caused by exposure to other strong odors.
- Olfactory adaptation over time, an individual can become accustomed to odors, including odorized gas.
- Other odors present may mask natural gas odorants.

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The normal human sense of smell detects and recognizes parts per billion amounts of mercaptans and organic sulfides commonly used to odorize gas. Characteristics of the ability to detect smells have been widely studied and documented. However, the precise functions of the human olfactory system remain somewhat obscure, especially in regard to accurately determining odorant level. Sensitivity to an odor varies among individuals, and can also vary with the same individual, depending on the circumstances. Quantification of odor perception has, therefore, proved difficult. Early measures of odor included the 1931 Bureau of Mines odor scale used by Fieldner, which involves five levels:

0 - No odor	1 - Very faint odor
2 - Faint	3 - Moderate
4 - Strong	5 - Very strong

As previously discussed, factors that reduce human odor sensitivity include head colds, medicine used, smokers, sinus problems, advanced age, the presence of several odors simultaneously, and length of exposure. In addition, there exist a small percentage of individuals who are unable to detect specific odors or whose olfactory systems do not function at all. Studies of odorants have shown a distinction between "detection" threshold and "recognition" threshold. Furthermore, sensitivity or insensitivity to specific odorants varies from one individual to another. Sensitivity to an odor varies and depends upon a multiplicity of daily circumstances.

Another mediating factor regarding employing an odorant as a single warning device in everyday vehicle gas applications is that, in many parts of the United States today, no type of gaseous fuels (propane or natural gas) are used to cook or heat homes. Many parts of the United States have become an almost exclusive electric society and use of natural gas or propane for heating and cooking is almost nonexistent. In-school training for odorant warning signs has vanished, and lack of its use would prompt one to expect that many within our society may not recognize the smell of an odorant as a danger signal.

2.3 Gas Odorants as Leak Warning Agents

Using odorants to warn of gas leaks has led to numerous legal challenges. Most of these challenges have been based on effectiveness issues such as odor masking, fade, and perceptibility due to sense of smell variations. However, the greatest challenges may be forthcoming with the increased use of vehicle gaseous fuels. There appears to be no documentation that validates use of an odorant as a single safety item for gaseous automotive applications for any of the present day or near future automotive gaseous fuels.

3.0 Natural Gas Automotive Applications

Federal regulation 192.625 addresses pipeline gas, and is not application-specific outside of the delivery of pipeline natural gas to locations throughout the United States. However, the National Fire Protection Association (NFPA) developed a document specific for compressed (CNG) and liquefied natural gas (LNG) automotive applications. NFPA 52-2006 provides automotive and refueling stations guidelines, in part or in full, for CNG, LNG, LNG-CNG, Hydrogen, and Hydrogen/methane mixtures. It should be noted that the CNG and hydrogen/methane portions of the document require an odorant, while other gas applications make no mention of odorizing gas.

The NFPA 52-2006 CNG portion of the document relates to an odorant specification as follows: "Natural gas introduced into any system covered by this standard shall have a distinctive odor potent enough for its presence to be detected down to a concentration in air of not over one-fifth of the lower limit of flammability." This is taken directly out of the old Federal regulation 192.625 which does not have automotive validation. The inclusion of odorant references in the NFPA document assumes that the pipeline odorant specification will

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be an effective carryover for the safe warning application of natural gas as an automotive fuel. It does not refer to a specific specification for this application, nor does it reference levels or types of odorants, and offers no reference validation that an odorant at this level will serve as an effective safety function for the automotive end user.

Note that 52-2006 also provides the following: "Natural gas or blends not meeting this definition shall have site and onboard methane detection systems installed and certified by a qualified engineer wit expertise in methane detection or fire protection." Therefore, safety considerations for gas releases are highly dependent upon two items: proper odorants and the sense of smell of the individuals working in natural gas facilities, or drivers of natural gas burning vehicles. Assuming that a vehicle driver possesses the finite ability to smell odorant at safe levels prior to the gas reaching dangerous levels is a serious risk. Running out of a building is much easier than jumping out of a vehicle if you smell gas. In addition, transit, school buses, vehicles for hire, and special needs buses require time to evacuate passengers. Close attention

should be paid to employee sensory abilities and dependence on odorants in automotive applications if they are a single warning agent for gas leaks.

Gaseous automotive applications that depend solely on the use of an odorant to warn of gas leaks, along with the unknown sensory abilities of individual drivers' daily health are highly questionable from a safety perspective. Basic odorant literature indicates that odorants are only intended to provide a warning, within the boundaries of known limitations. We have been unable to find medical or safety references to applications beyond pipeline injection specifications of odorants and none that reference automotive applications.

4.0 Federal Regulations

Current federal and state regulations, interpretations, and a practice pertaining to the odorization of natural gas are used in pipeline operations. “Pipeline operations,” in this context, includes natural gas gathering (at production sites), transportation (interstate and intrastate pipelines), and distribution, including “natural gas utility” operations.

The most important regulation affecting the odorization of natural gas used in pipeline operations is the Code of Federal Regulations (CFR) Title 49, Part 192.625, “Transportation of Natural or Other Gas by Pipeline: Minimum Federal Safety Standards Odorization of Gas.” Note that CFR 192.625 is written in terms of the odorization effect rather than the required odorant chemistry and concentration. Specifically, Subpart (a) states, “A combustible gas in a distribution line must contain a natural odorant or is odorized so that at a concentration in air of one-fifth of the lower explosive limit, the gas is readily detectable by a person with a normal sense of smell.”

5.0 Example: Natural Gas Odorization Corporation (NGO) Literature Information

There is strong confidence in the use of odorants for pipelines. This is supported by data provided from odorant manufacturers However, odorant manufacturers do point out that there are variables in their use, and odorants should not be the only means of alerting the presence of natural gas leaks. Specifically, the following information supplied by Natural Gas Odorization Corporation (NGO), excerpted directly from their literature, supplies us with insights into the natural gas applications which can be related to gaseous odorant uses as follows:

- Natural gas odorants are highly odorous sulfur-containing hydrocarbons that are added to the natural gas stream to provide a warning of a gas leak.

- **No one odorant or no one rate of odorization will be 100% effective in warning of the presence of natural gas**. Basic knowledge of the properties and characteristics of

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natural gas and odorants used for natural gas can be extremely helpful for those involved in the gas odorization process.

- Loss or diminished odor intensity can be caused by chemical reactions including oxidation, adsorption and/or absorption, and masking by other components in pipes and distribution systems carrying odorized natural gas.
- Chemical Oxidation: Contact with rust or other oxidation agents can, under certain conditions, cause the odorant to convert to its corresponding disulfide that has a weaker odor than the original odorant.
- Adsorption: The odorant can adhere to the surfaces of solid structures or liquids with which it is in contact, thus reducing the amount of odorant remaining in the gas stream.
- Absorption: The odorant can dissolve into liquids with which it is in contact, thus reducing the amount of odorant remaining in the gas stream.
- **Extremely cold weather can affect the amount of odorant in natural gas and, thus, may reduce odorant effectiveness.**
- **The physical condition and state of mind of an individual, as well as the surroundings and the individual's attentiveness can affect the ability to detect odors including, but not limited to, natural gas odorants (i.e., natural gas odorants and/or an individual sulfur compound).**
- **Absence of an odor must not be taken to mean the absence of natural gas. Nor should a judgment of the concentration of natural gas be made by the intensity of the odor.**
- **There is no odorant that will be effective in all situations.**
- Examples: lost or diminished odor intensity caused by chemical reactions, adsorption and/or absorption, and masking by other components can occur in pipes carrying odorized natural gas.
- In addition, an individual's physical condition, surroundings, concentration, and state of mind can each affect the ability to detect odors including, but not limited to, natural gas odorants.
- **Some people have an impaired sense of smell that results in reduced sensitivity to all odors or, alternatively, results in no sense of smell for only certain odors (i.e., natural gas odorants and other sulfur compounds).**
- **Some people have no sense of smell and can detect no odors.**
- **Common colds, allergies, and smoking can also decrease an individual's ability to smell.**
- Other odors in the area, such as those present in a musty basement, may mask or cover the natural gas odor.
- In some cases, the natural gas odor is not detected simply because people are concentrating on something else and their minds are distracted from detecting the odor.
- Since loss of the distinctive odor of odorized natural gas can occur under certain conditions, periodic testing is advisable to determine that the rate of odorization is adequate to comply with all regulatory requirements and safety considerations.

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- **It should be established that all persons expected to be in contact with odorized natural gas, including customers' age, are adequately warned in advance about the properties, characteristics, propensities, and limitations of odorants when used as warning agents.**
- **Olfactory fatigue caused by exposure to other odorous products may reduce an individual's ability to detect natural gas odorant.**
- **Olfactory adaptation to the odorant can occur if an individual does not quickly and immediately respond to the presence of the natural gas odorant.**
- **Sleeping persons may not be awakened by, and therefore may not detect, the odor of escaped odorized natural gas.**
- **Since loss of the distinctive odor of odorized natural gas can occur under some conditions, periodic testing by all persons handling natural gas, before sale to the ultimate consumer, is advisable to determine that the rate of odorization is adequate to comply with all regulatory requirements and safety considerations.**

NGO does not have access to your customers. NGO provides this warning to educate you and strongly suggests that you educate your customers. You should confirm that all persons having contact with the product, including your customers, are adequately warned about the properties, characteristics, propensities, and limitations of natural gas and natural gas odorants when used as a warning agent in natural gas. For instance, persons having contact with natural gas should know that natural gas vapor is lighter than air.

Table 1. Commonly Used Gas Odorants

ODORANT	OTHER DESIGNATIONS	REMARKS

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Tertiary butyl mercaptan	**TBM**	**The** most commonly used odorant in natural gas blends. Oxidation resistant. Good soil penetration. High freezing temperature (34° F). Commonly used natural gas odorant.
Isopropyl mercaptan	**IPM**	**Medium** oxidation resistance. Frequently blended with TBM to lower freezing point.
Normal propyl mercaptan	**NPM**	**Occasionally** used in natural gas odorant blends. Relatively low oxidation resistance.
Secondary butyl mercaptan	**SBM**	**Used** in natural gas odorous blends. Medium oxidation resistance.
Ethyl mercaptan	**EM**	**LPG** odorant.
Dimethyl sulfide	**DMS**	**Used in LPG** and natural gas odorant blends. Highly oxidation resistant. Best soil penetration characteristics of all odorants. Slightly different smell. Toxic.
Methyl ethyl sulfide	**MES**	**Most recently in**troduced odorant used in blends for natural gas. Highly oxidation resistant. Good soil penetration.
Tetrahydrothiophene	**THT, thiophane**	**A cyclic sulfide**. Commonly used in LPG and natural gas odorant blends. Highly oxidation resistant.

Table 2 Key Physical Properties

ODORANT	STRUCTURAL FORMULA	MOLECULAR WEIGHT	SULFUR WEIGHT %	FREEZING (°F)	BOILING (°F)
Tertiary butyl mercaptan	$C(CH_3)_3SH$	90.19	35.5	34	148
Isopropyl mercaptan	$(CH_3)_2$-CHSH	76.16	42.0	-203	127
Normal propyl mercaptan	CH_3-CH_2-CH_2SH	76.16	42.0	-172	154
Secondary butyl mercaptan	CH_3-CH_2-CHSH-CH_3	90.19	35.5	-220	185
Ethyl mercaptan	CH_3-CH_2SH	62.13	51.6	-234	95
Dimethyl sulfide	$(CH_3)_2S$	62.13	51.6	-145	99
Methyl ethyl sulfide	CH_3-S-CH_2-CH_3	76.16	42.0	-159	152
Tetrahydorthiophene	-CH_2-CH_2-CH_2-CH_2-S-	88.17	36.4	-141	250

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