

TECHNICAL BULLETIN

PREVENTION OF ODOR FADE IN CARBON STEEL PROPANE CYLINDERS AND TANKS

Introduction and scope

As with natural gas and other fuel gases sold on the retail market, an odorant is added to propane to effect a recognizable scent. If propane gas is allowed to leak undetected and accumulate until the flammable range of 2.15% to 9.6% in air is reached, a source of ignition can result in catastrophic consequences.

Although there are different formulations for odorants used in propane, ethyl mercaptan (EtSH) has been proven by scientific research to be the most effective and widely used odorant for propane in the United States. Ethyl mercaptan acts as a warning agent by providing an odor similar to rotten eggs that has been shown to be detectable by most people at a few parts per million (ppm) in air. For a proper perspective, the lower limit of propane gas flammability (2.15%) equates to 21 500 ppm in air. Any odorant that is used in propane shall provide a detectable odor when propane is at a concentration of at least one-fifth the lower limit of flammability in air or, in other words, at a level of 4300 ppm. Title 49 of the U.S. *Code of Federal Regulations* (49 CFR) Part 173.315(b)(1) Note 2 states that adding 1 lb (0.45 kg) of ethyl mercaptan to 10 000 gal (37 854 L) of liquid propane has been recognized to be an effective odorant that meets this requirement [1]. Some individuals are unable to detect the odor of ethyl mercaptan either temporarily or permanently, and it is possible that propane could be delivered with insufficient odorant or no odorant.

Under certain conditions ethyl mercaptan can react with materials that it contacts resulting in a diminished ability to act as a warning agent. This phenomenon is known as odor fade. It is the intent of this technical bulletin to provide information on odor fade to both tank and cylinder fabricators and to those who handle and fill liquefied petroleum gas (LPG) containers.

Depletion of ethyl mercaptan

The fabrication of carbon and low alloy steels at elevated temperatures results in an oxide or mill scale coating on the steel surface. This mill scale primarily consists of three sandwiched forms of iron oxide; ferrous oxide (FeO) on the inner or steel surface, ferroferric oxide (Fe₃O₄) in the middle layer, and ferric oxide or red rust (Fe₂O₃) on the outer layer. The percentage of each oxide layer present on the final sheet or fabricated plate is dependent on several factors. Most importantly, the amount of ambient oxygen that becomes available for exposure to the steel determines if the scale is more iron-rich (FeO) or more oxygen-rich (Fe₂O₃). Moreover, the outer layers of oxides are structurally weaker and therefore more likely to have been removed during the production process.

Further oxidation of FeO, Fe₃O₄, or the steel itself to Fe₂O₃ can occur during welding, pressure testing, or storage of the steel. Fe₂O₃ has the tendency to react chemically and oxidize ethyl mercaptan in the presence of air and moisture. FeO and Fe₃O₄ are not capable of oxidizing ethyl mercaptan directly since they must first oxidize to Fe₂O₃.

The U.S. Department of Transportation (DOT) and Transport Canada (TC) regulations limit the amount of propane that may be shipped in containers. The amount permitted to be shipped in ASME storage containers might be less than that permitted for DOT or TC specification containers. In accordance with 49 CFR 173.315(j), ASME containers with a propane capacity of 125 gal (473 L) or more “shall not be shipped when charged with liquefied petroleum gas to more than 5% of their water capacity” [1].¹ New containers that are put into service with only a 5% fill are most likely to experience a loss of odorant. The loss of odor appears to be more prominent in the vapor

¹ In Canada, a similar provision is contained in CSA B622, *Selection and Use of Highway Tanks, TC Portable Tanks, and Ton Containers for the Transportation of Dangerous Goods, Class 2*, which is referenced in the *Transportation of Dangerous Goods Regulations* [2, 3].

of the gas where the exposure of the ethyl mercaptan to rust on the container wall causes the odorant to react and be absorbed, adsorbed, or chemically reduced to a less odorous compound known as diethyl disulfide. A severe depletion of an effective scent can occur depending on the initial amount of odorized propane introduced into the container and the likelihood of the odorant interacting with the container walls.

During normal use, the interior surfaces of new cylinders and tanks that have been filled a few times usually become passivated as the interior surfaces become saturated with ethyl mercaptan. This saturation reduces the Fe_2O_3 content. Once passivated, the interior surfaces of the container contribute to virtually no further loss of odor unless the vessel is taken out of service and left open to the atmosphere.

Purging

New and used containers that have been left open to the atmosphere can contain air, water vapor, or free water. Following recommended container purging procedures to remove these undesirable elements is essential for proper operation of the fuel system. Correspondingly, air in the vessel can lead to increased container pressure, which can inhibit filling and lead to activation of the pressure relief valve. Air in the fuel delivery system can also extinguish a pilot flame or be a factor in other system malfunctions. Moisture can contribute to odor fade by promoting the rusting of a container's interior surface and can also disrupt gas service to a consumer's appliance by interfering with the operation of gas regulators. After removal of any free water in a container, measured injections of methanol are used to counter the effect of moisture residue.

Purging of containers is accomplished by positive pressurizations of vaporous propane or vacuum purging. Methanol may be added to aid in the removal of moisture from larger containers. Failure to properly purge containers can result in the creation of a number of operational problems including odor fade, but purging alone might not prevent odor fade.

Recommendations

During the manufacturing and storage of LPG containers, efforts should be made to minimize as much as practicable the formation of rust (Fe_2O_3).

The container valve shall remain closed when not in use to prevent entry of air or moisture into the container.

LPG containers that are taken out of service and allowed to remain open to the atmosphere should be subjected to the same procedures as new containers before being returned to service to minimize the potential for odor fade.

LPG containers shall be purged with LPG vapor or shall be evacuated to remove air and moisture.

Experience indicates that the potential for odor fade is minimized when new LPG containers are filled to the maximum allowable filling volume.

Check for the presence of odorant in the container.

Never bleed gas lines into an enclosed space.

If customers indicate that they are not able to detect the smell of odorant, they should be made aware of the availability of electronic gas detectors for use as a supplemental warning device.

Comments

Container manufacturers are attempting to address the odor fade problem by incorporating new processes into their fabrication systems. For example, before shipment some manufacturers draw a vacuum on new containers, which helps minimize oxidation of the inner walls of the container by removing any moisture-laden air that might exist inside the container.

Other approaches such as adding more odorant to containers than required (super stenching) have been used by propane marketers.