RAY ENERGY® CORP

Please read the attached "Technical Informational Bulletin" at your earliest opportunity.
Due to the importance of this information, please read the following sections thoroughly:



The Bulletin contains important safety information and discussion of practices for the retailer concerning LP-Gas odorization. Ray Energy Corp. recognizes that some of the practices described in the bulletin may not be standard operating procedures or mandated by applicable codes. Each retailer should determine what practices to undertake consistent with the applicable regulations for its locations and the standard industry customs and practices.


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# TECHNICAL INFORMATION BULLETIN



NOTE. This Technical Information Bulletin has been updated and revised. No change bars will be shown. Please read and inform all users of this product of the information contained herein.

SCOPE.

This Bulletin discusses the odorization of LP-Gas, odorant recognition, olfactory fatigue, adsorption, odorant fade, and industry practices to avoid odorant fade. This bulletin is primarily written to aid the odorant user and the LP-Gas: marketer, producer, and supplier.

REFERENCES:

NOTE: Refer to current editions of documents referenced below.

A. Other Standards, Codes or Regulations:

1. Federal, state and local laws, regulations and codes.
2. Department of Transportation Regulations.
3. NFPA 58 Liquefied Petroleum Gas Code.
4. NPGA "LP-Gas Safety Handbook" and bulletins
5. Title 49 CFR 173.315 Transportation, Compressed gases in cargo tanks and portable tanks. Department of Transportation.
6. Title 29 CFR 1910.110(b)(1) Basic Rules - Odorizing Gases.
7. GPA Standard 2194-94, Tentative Low-Pressure Field Method for Determining Ethyl Mercaptan Odorant in LP-Gas Using Length of Stain Tubes.
8. Canadian General Standards Board, CAN/CGSB-3.0 NO. 18.5-06-CAN/CGSB, Methods of Testing Petroleum and Associated Products Test for Ethyl Mercaptan Odourant in Propane, Field Method, 2006.
9. PERC CETP Textbook: http://www.propanesafety.com/textbook/.

B. Other Publications:

2. Johnson, Sung-I J., "Ethyl Mercaptan Odorant Stability in Stored Propane Gas", Presented at the Institute of Gas Technology Symposium on Odorization, May 1989.
3. Cain, William S. and Amos Turk, "Smell of Danger: An Analysis of LP-Gas Odorization", American Industrial Hygiene Association Journal, March 1985.
4. Amoore, J. E., "Properties of Olfactory System". Presented at the Institute of Gas Technology Symposium on Odorization, July 1976.
5. Whisman, M. L. et. al., "A New Look at Odorization Levels for Propane Gas", Bartlesville Energy Research Center Report BERC/RI-77/1, September 1977.

6. Matson, A. P. and R.E. Dufour, "Persistency of Odor of Accidentally Released Liquefied Petroleum Gas", Underwriters Laboratory Bulletin of Research Number 37 dated December 1946.

7. Proceedings, Symposium on LP Gas Odorization Technology, 4/18/89, Gas Processors Association.

8. Proceedings, Symposium on LP Gas Odorization Technology, 10/11/90, Gas Processors Association.

9. Material Safety Data Sheet for **Scentinel® A Gas Odorant**, MSDS# 100000013143.

10. Gas Engineer's Handbook, Fuel Gas Engineering Practices, Chapter 11, by J. S. Powell and F. E. Vandaveer, (The Industrial Press, 1965).

11. Proceedings, IGT Odorization Symposium, 1992.

12. Proceedings, IGT Odorization Symposium, 1994.

## I. GENERAL

A. LP-Gas in its processed state is virtually odorless; therefore, odorant is added to warn of the presence of LP-Gas. Detection of LP-Gas in the atmosphere is important because it is a flammable gas that can cause fires and/or explosions when improperly handled.

B. The driver of a propane tank truck should document any information regarding odorization of the propane from a terminal or loading facility on the bill of lading and retain a copy of the bill of lading in his files while leaving one with the loading facility. This is regardless of the method used to inject odorant in the LP-Gas during loading.

C. Ethyl mercaptan is the predominant odorant of choice (95%) in the propane industry. Ethyl mercaptan is used to odorize LP-Gas because of its overall effectiveness as a warning agent. A level of 1.0 pound of ethyl mercaptan per 10,000 gallons of liquid LP-Gas has been shown to produce an effectively odorized gas; however, the normal industry practice is to add 1.5 pounds, and as much as 2.5 pounds can be used. The odorant level of 1.0 pound of ethyl mercaptan per 10,000 gallons of propane is specified in NFPA 58 Liquefied Petroleum Gas Code, and is specified as such in most, if not all states. WARNING: All marketers should be aware of the circumstances that may reduce the effectiveness of ethyl mercaptan as an odorant and so inform their customers. These factors are discussed in detail in Sections III through VII of this bulletin.

D. The presence of an odorant should be verified by a sniff-test each time it changes custody in the distribution network, and a permanent written record should be made of the verification. To test for odorant, open a vapor valve on the supply tank enough to obtain a small quantity of gas leaving the tank (10-20 mL per minute) and note the odor or lack of odor in the atmosphere. Do not place your head or any part of the body directly over the valve outlet. The valve should remain open for only a few seconds. Prolonged breathing of the gas may cause illness and ultimately deprive a person of required oxygen. If there is a question regarding the amount of odorant present in the propane, a stain tube test should be conducted.

E. The bill of lading for tank cars or transports should certify that the gas has been odorized, the type of odorant, and the amount used. The receiving plant should review the bill of lading (to confirm the certification), perform its own sniff test, and make a record of the sniff test.

F. If there is any doubt about adequate odorization, then proper testing should be conducted and additional odorant shall be added as required or product replaced with properly odorized propane.

G. If an LP-Gas incident involving personal injury, death, or property damage should occur, contact the LP-Gas supplier immediately, and follow the procedures.

H. Anytime there is a question about the presence of gas or if a customer reports a gas leak, immediate evacuation should be recommended. The presence of a leak or the presence of gas should be determined using a leak detection procedure. The building should not be reoccupied without determining that it is safe to reenter. This should be determined by the use of a combustible gas indicator or other suitable technique, performed by trained personnel.

## II. REGULATIONS

A. Most state regulatory agencies require LP-Gas odorization in accordance with NFPA Standard 58 paragraph 1-4.1, which states:

"All LP-Gases shall be odorized prior to delivery to a bulk plant by the addition of a warning agent of such character that they are detectable, by a distinct odor, down to a concentration in air of not over one-fifth the lower limit of flammability."

"Exception: Odorization, however, is not required if harmful in the use or further processing of the LP-Gas, or if such odorization will serve no useful purpose as a warning agent in such further use or processing."

A bulk plant is defined in NFPA standard 58, paragraph 1-7 as "A facility, the primary purpose of which is the distribution of gas, and which receives LP-Gas by tank car, tank truck, or piping, distributing this gas to the end user by portable container (package) delivery, by tank truck, or through gas piping. Such plants have bulk storage [2,000 gal (7.6 $m^3$) water capacity or more] and usually have container filling and truck loading facilities on the premises. Normally no persons other than the plant management or plant employees have access to these facilities. A facility that transfers LP-Gas from tank cars on a private track directly into cargo tanks is also in this category."

B. The Department of Transportation Code of Federal Regulations, contains similar requirements for LP-Gas in cargo and portable tank containers.

## III. ODORANT RECOGNITION

A. Anyone using LP-Gas should be alerted to check by sniff test to determine if their LP-Gas has a distinctive odor, and to report to their LP-Gas dealer any suspicion that the odor may be weak. This check should be conducted immediately following delivery of the LP-Gas and on a monthly basis.

B. Scratch-N-sniff leaflets should be obtained and used by all marketers as an aid in educating people about the type of odor in odorized LP-Gas. This odor is a mixture of ethyl mercaptan and tertiary butyl mercaptan, which is very similar to the odor found in LP-Gas. The scratch-N-sniff leaflet also can be used to identify individuals with an impaired sense of smell. It is recommended that all LP-Gas marketers use such training aids to educate their customers (and the customer's family) to some of the hazards associated with propane use, and to improve their ability to identify odors. Scratch-N-sniff leaflets are available from the Propane Education and Research Council (866) 905-1075, www.propanemarc.com and from your propane supplier.

C. Anyone handling or using LP-Gas should be aware that some personal conditions may affect their ability to detect odor at any particular time. For example: sinus congestion, allergies, head colds, smoking, or recent use of alcohol or drugs all decrease the ability to smell. Some medications may also diminish the sense of smell. Some people

may not be able to smell propane odorants at all due to a nasal blindness condition called anosmia. People with olfactory deficiencies should be aware that propane gas detectors are commercially available. Certain environmental conditions may exist that diminish odor detection. For example:

1. The odorized gas may be masked or covered up by other odors. These odors can include cooking odors, certain foods eaten and musky or damp smells that may be found in basements.

2. High concentrations of odor can shock, or diminish the sense of smell.

D. Even though the stench of an odorant will rapidly spread throughout a room, a person should be made aware that the strongest odor may be near the floor where LP-Gas may tend to concentrate. This is particularly important when gas is released in basements or other confined areas where there is little air movement. Consumers should be warned of possible floor-to-ceiling concentration gradients, which mean that the strongest odor may not be at nose level. For this reason, it is recommended that, at regular intervals, consumers sniff close to the floor in any room that contains propane appliances or piping.

E. Gas detectors are considered to be an additional method for detecting propane leaks. The installation of gas detectors should be considered in areas of the home as suggested by the gas detector manufacturer.

F. The presence of a strong propane odor at a time when the tank is approaching empty should not be considered to be normal. When a tank is low, there may be a momentary whiff of gassy smell when burners are ignited. If the smell of propane continues, there may be a serious propane leak. Propane is more heavily odorized as the liquid level in a vapor service tank goes down and the odor of small leaks should be readily apparent. A differential pressure test ("woosh" test), or other suitable test to check the pressure integrity of the system, and a visual external system inspection should be conducted if a customer indicates that they are out of gas because "it smells like we are out of gas". If leaks are detected using this method, they should be repaired before the customer resumes service.

## IV. ODORANT DETECTION

A. There are various methods that can be used to measure the odorant concentration in LP-Gas. These tests should only be performed by qualified individuals using proper test methods.

B. The primary method, and the simplest, is a sniff test. Periodic "sniff tests" of vapor from tanks prior to refilling may help identity a potential problem. If there is any doubt about adequate odorization, quantitative tests methods, such as those discussed below, should be used.

C. Another common method used to determine the odorant concentration in LP-Gas is a stain tube test. This test measures the concentration of odorant by pulling a measured amount of gas through a stain tube and indicates the concentration directly on the tube.

D. The concentration of odorant in LP-Gas is also commonly measured using gas chromatography. This method separates out the various components of LP-Gas and identifies each of them individually. In the case of odorant measurements, the detector is usually one that selectively identifies sulfur compounds, i.e., mercaptans, sulfides, and disulfides.

## V. OLFACTORY (ODOR) FATIGUE

A. A person continuously smelling the same odor may become accustomed to this odor within a few minutes. The odor will seemingly diminish in intensity until it may not be detected unless the person goes outside and allows his sense of smell to readjust. A person should not ignore the odor of propane in situations where it is not normally found.

This includes situations where the odor intensity seems to decrease with time. A trained LP-marketer should be called to determine if there is a leak present at the facility.

B. The rate of propane gas leakage can also affect a person's ability to detect odor. Odor fatigue may occur before the odorant reaches a detectable level. The lower the odor concentration, the faster the adaptation to that odor will occur.

## VI. ODOR FADE (DEPLETION)

A. The amount of ethyl mercaptan odorant in LP-Gas can decrease (causing an "odor fade") because of the following:

1. Odorant can adsorb (stick) to the metal surfaces of containers and piping. This is pronounced in cases where the container or piping is new. It can also be pronounced in containers or piping that have been exposed to air while out of service.

2. The presence of ordinary rust (iron or ferric oxide) inside a container, or in piping, or the subsequent formation of rust as a result of the presence of oxygen (air) and moisture. The presence of rust causes mercaptans to oxidize into other sulfur compounds with a different odor character and lower intensity. This diminishes the amount of mercaptan stench in the LP-Gas within the container. Residual oxygen from air in the container may increase the rate of oxidation, or at least cause new rust to form. The more interior rust that is present, the greater the risk of odor fade.

3. Selective adsorption (filtering) of odorant molecules by soils in the care of underground piping and container leaks.

4. Odorant can adsorb onto household surfaces. These include masonry, wood, rock, concrete block, draperies, furniture, and carpets. This type of adsorption can remove some odorant from LP-Gas. In most cases, a continuous leak of odorized propane will still be detectable by odor.

5. Absorption of the odorant into hydrocarbon liquids.

B. If "odor fade" is occurring, then the container (or piping) should be passivated, or treated to render the interior surface inactive (e.g., a surface that does not diminish the odorant through oxidation or adsorption). The procedures below can be used to minimize "odor fade" in containers and piping.

1. After manufacture and/or hydrostatic testing, immediately drain all moisture from the container, and dehydrate the container using an acceptable method.

2. All new or unused containers that will be shipped or placed in storage, should be free of moisture and have all valves closed. Treat new cylinders as per manufacturer's recommendations.

3. Before placing a container in service, any air in the container should be purged. You can refer to the NPGA "LP-Gas Safety Handbook" and NPGA bulletins for additional guidance as to proper procedures and NFPA 58, Section 4-3.2. The interior of the container must be protected from air, moisture, and the possibility of resulting rust.

4. Repeated fillings of LP-Gas containers with odorized LP-Gas has been shown to reduce odor fade. As containers in regular use are refilled, the amount of odor-reducing rust that may be present in the container is diminished. Additional rust will not form if care is taken to prevent air (oxygen) and moisture from entering the container. When a container becomes empty, it should be sealed as soon as possible to minimize air and moisture from entering. Fresh (new) carbon steel surfaces tend to selectively adsorb mercaptan odorants out of LP-Gas. These surfaces soon become saturated with odorant and, consequently, containers in continuous service usually cease to experience odor fade after a few filling cycles.

5. Treatment of a container with super-odorized propane, or other chemical agent, can also result in passivation. When using the super-odorization method, the container is filled with propane containing odorant above the normal dosage (usually 1.5 to 3 times the normal dose). The container is then allowed to set for 24 hours, after which time the odorant level can be checked to determine whether supplemental odorant should be added, or whether the container should be emptied in a safe manner and refilled with odorized propane.

C. Canadian General Standards Board-3.0 NO. 18.5-06-CAN/CGSB: To determine if a procedure has adequately passivated a container, the odorant concentration should be measured over time using stain tubes, or other industry acceptable procedures. Failure of the odorant concentration to decrease serves as proof that the container has been adequately passivated. As a general guideline, the odorant concentration should be measured over a period of time commensurate with observed odorant decrease.

D. Small LP-Gas cylinders have a larger ratio of interior surface to loading capacity. This gives greater opportunity for odor fade from adsorption by the metal surface, and from oxidation of the odorant by rust. It is best to put such cylinders into continuous use so they can be refilled frequently with odorized propane. Because such cylinders are under the control of the general public, and often not in the hands of people knowledgeable about propane, they are often not properly handled or maintained. Marketers should be alert to these problems and adequately warn and instruct their customers.

   The marketer should conduct sniff tests prior to filling small LP-Gas cylinders to determine if the cylinder is a container that is experiencing odor fade. If odor fade is noted, an exchange of this small cylinder for a passivated cylinder should be strongly considered. If the cylinder is not exchanged, then the cylinder should be passivated following one of the procedures above.

E. All LP-Gas users, marketers and handlers should be familiar with the odor of propane. As they use or handle propane, they should conduct frequent sniff tests. If there is ever any suspicion as to the adequate presence of the expected odor, they should immediately report the situation to a responsible individual, or to a factory or office supervisor, tell others around them of the danger, and shut off the propane supply if possible. The LP-Gas dealer should be called to check the odorant level. If the marketer determines that a leak is present, the fire department should be notified.

   If there is a suspected leak, evacuation and notification of the local fire department and LP-Gas dealer should be done immediately from a place of safety.

F. A bulk tank or bob-tail or other propane distribution container may appear to be underodorized if it is allowed to remain unused and unmoved (static) for an extended period of time prior to sniff-testing or stain tube testing. If this is found to be the case, withdrawal of some liquid from the system, or in some way agitating the system, should restore odorant levels in the gas phase to normal levels. This is considered to be a normal circumstance. If the odorant is not found at normal levels after these actions, the LP-Gas may not be adequately odorized, and actions should be taken to correct the situation.

This phenomenon should NOT be observed in customer tanks. If it is, immediate action should be taken to adequately odorize the customer tank.

## VII. SUPPLEMENTARY ODORIZATION BY PROPANE MARKETERS

A. When propane that is odorized with ethyl mercaptan is moved from pipeline terminals to marketing bulk storage area in dedicated tank trucks, or from plants to bulk station in dedicated rail tank cars, odor fade is generally not a problem (except with regard to new equipment, or equipment that has been out of service for an extended period): There also is little likelihood that any measurable odor fade of ethyl mercaptan occurs in the large storage tanks at the marketers' bulk storage facilities, or when the propane is moved in dedicated bob-tail trucks.

The greatest potential problem exists in the tanks and piping of the retail customers. If there is any indication of odor fade from a sniff test or if the tank has been empty and out of service for any period of time, marketers should perform a stain tube test periodically to determine (and record) the odorant level in the customers' tanks (See also Part B, below). If a lower than anticipated level of ethyl mercaptan (i.e., less than 1.5 lb/10,000 gal.) is discovered, additional odorant or more odorized propane should be added, and the tank should be checked again in a few days to see if the odor level has stabilized, at or above this level. **It is strongly suggested that the tank not be used by the consumer if a lower than anticipated level of ethyl mercaptan is discovered.**

B. If a marketer notes that a tank has been out of use, the odorant level should be tested, and the marketer should talk with the customer and suggest that the tank be shut off and sealed (with a warning tag). Special care should be taken at those times to see that all gas lines that are not in use are properly capped. When the customer is ready to put the tank back into regular use, the marketer can again test the odorant level in the tank, and determine whether it is safe to relight the appliances that have been out of service.

C. In order to minimize the potential that (notwithstanding the proper purging and handling of a customer's tank and lines) a propane leak will not be detected due to total oxidation of the normal dose of ethyl mercaptan, supplementary odorization with ethyl mercaptan can be considered. Over the years some propane gas companies have "super-odorized" their propane with up to two point five (2.5) pounds of ethyl mercaptan per 10,000 gallons of propane. If more than that amount is used, the consumers will begin to smell a gas odor on a more or less constant basis at or near the burners of the appliances, and a false sense of security may result.

VIII. WARNING: THERE IS NO SINGLE ODORANT OR ODORANT BLEND KNOWN THAT GIVES AN EFFECTIVE WARNING OF THE PRESENCE OF A PROPANE GAS LEAK IN EVERY POSSIBLE CIRCUMSTANCE TO EVERY SINGLE INDIVIDUAL WHO MIGHT BE PUT IN DANGER BY A LEAK. WHENEVER PROPANE IS USED, THE ABSENCE OF A STRONG AND DISAGREEABLE ODOR, OR ANY ODOR, SHOULD NOT BE TAKEN TO MEAN THERE IS NO DANGER. COMMON SENSE ON THE PART OF LP-GAS USERS, COUPLED EDUCATION OF THE USERS BY THEIR RETAIL MARKETERS, IS NEEDED TO DECREASE THE RISK OF DEATH OR A VERY SERIOUS INJURY CAUSED BY A PROPANE FLASH-FIRE OR EXPLOSION. PROPANE IS FLAMMABLE, AND MUST BE USED WITH APPROPRIATE CAUTION.

IF A LEAK IS EVEN SLIGHTLY SUSPECTED, ACT QUICKLY TO EVACUATE ALL PERSONS IN THE AREA. CALL FOR A TRAINED PROFESSIONAL LP-GAS MARKETER TO ASSIST IN EVALUATING THE SITUATION AND NOTIFY THE LOCAL FIRE DEPARTMENT.

IF THERE IS EVER ANY SUSPICION AS TO THE ADEQUATE PRESENCE OF THE EXPECTED ODOR, THE USER SHOULD REPORT THE SITUATION TO A RESPONSIBLE INDIVIDUAL OR TO A FACTORY OR OFFICE SUPERVISOR, TELL OTHERS AROUND THE AREA OF THE DANGER, AND SHUT OFF THE PROPANE SUPPLY, IF POSSIBLE. THE LP-GAS DEALER SHOULD BE CALLED TO CHECK THE ODORANT LEVEL. IF THE MARKETER DETERMINES THAT A LEAK IS PRESENT, THE FIRE DEPARTMENT SHOULD BE NOTIFIED.

IT IS RECOMMENDED THAT THE MARKETER SHOULD ALSO LIGHT OR RELIGHT PROPANE GAS APPLIANCES, UNLESS INSTRUCTED NOT TO DO SO BY THE RETAIL CUSTOMER.