ODORANT LEAK MANAGEMENT

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ABSTRACT

All around the world, propane, butane and natural gas must be odorized. The odorization ensures a safe transport, distribution and use of this valuable energy to residential buildings. Regulations vary from one country or state to another. The natural gas can be odorized at different points of the gas grid: in some countries (France, Spain, South Korea…), odorization takes place at the entry points of the country's gas grid, either at the gas transmission pipes or at Liquefied Natural Gas (LNG) terminals just after vaporization. In other countries (USA, Canada, Mexico, Germany, Italy, Belgium, China…), natural gas is often odorized at "city gate" level, where gas is depressurized to allow distribution to residential points.
Odorants also may vary from one country to another, and within the same country as well. The International Organization for Safety (ISO) is listing in the ISO 13734[(1)] components commonly used: odorants are mainly composed of Sulfides (TetraHydroThiophene, MethylEthylSulfide, DiMethylSulfide) and Light Mercaptans (mainly TertiaryButylMercaptan, IsoPropylMercaptan). With the exception of TetraHydroThiophene which can be used as a standalone odorant, odorants are composed of blends of these thiochemical compounds. By definition, these odorant are flammable products and have a very low odor detection threshold: 0.3 part per billion in volume for TertiaryButylMercaptan[(2)]. Any small leak of odorant can trigger a misleading gas alert. A significant leak will do the same and may lead local authorities to evacuate large city areas to manage the public reaction and protect people against the potential fire and chemical risks.

From the production of odorant blends' components to the odorant storages at consumption points, there is a broad and complex supply chain to bring the right odorant at the right place and at the right time, safely and without odor incidents. The transport and delivery of gas odorants can be achieved in many different ways:

- Odorants can be transported in 6,000 gallon ISO tank Containers for sea transport.
- On land, odorants can be transported by railcars, containing about 20,000 gallons, or by tank trucks, with typical capacities ranging from 250 to 6,000 gallons. The odorant has to be unloaded safely and without odor release, usually using a close loop vapor recovery system, from the supplier container into the storage tank of a gas utility.
- In addition, odorants can be packaged in returnable cylinders, with typical sizes ranging from 5 to 250 gallons returnable cylinders up to 660 gallons for semi-bulk containers (SBCs). These cylinders are designed to be connected to the odorant injection system via dry-break couplings and can be used as the odorant storage tank at consumption point. Once empty they are replaced by a full one and the empty cylinder is to be returned to the odorant supplier to be refilled.
- Odorants can be packaged in one way drums from 1 gallon cans (pails) to 55 gallons drums, which have to be safely disposed of once emptied.

Odorant leaks can happen at any stage of this global supply chain. This paper will first report some past incidents, illustrating improper odorant handling or absence of spill emergency response protocol. Then odorant spill management basics will be presented.

Date:
23rd June 2006

Where in the supply chain?
During the transportation of odorant from the port to the local distributor's plant.

Location:
Sao Paolo, Brazil on the fast track Marginal Pinheiros, after the Garden City bridge

Source : Arkema

Incident description
Traffic accident, which lead to the toppling of several odorant returnable cylinders off a flatbed truck. These stainless steel SBC were 1,100 and 2,500 Liters capacity and were containing TertioButylMercaptan (TBM) and DiMethylSulfide (DMS). Ten heavy SBCs were standing on a flatbed truck and were transported from the Santo Port to a local plant, to be blended and sold as gas odorant. For reason still unknown, the truck slightly tilted to the right, and destabilized the load. This resulted in disruption of the securing straps causing the fall of the 10 SBCs. Despite the steel lids on top of these packaging, which was designed to protect the gas and liquid connections and valves, two of these pressured cylinders had broken valves. One of them was laying on the road, while the second was found in a wastewater ditch, difficult to access.

Consequences
1) About 420kg (935 lbs) of TBM and 800kg (1,765 lbs) of DMS spilled in the environment
2) A 8 kilometers section of a main highway in the heart of Sao Paolo was shut down from 4:30 am until 12:00pm.

Emergency response
Multiple organizations were involved in the response of this incident happening in a highly density area. First, the Traffic Engineering Company prohibited the access to this highway. Second, teams from the Fire Brigade and the Municipal Civil Defense isolated the area. Third, the Sao Paolo State Environment Agency (CETESB) coordinated an inspection of the semi-bulk containers. Due to the strong odor, the approach and entry in the area of accident were carried out using **self-contained breathing apparatus**. Once it was found that 2 containers were leaking, the CETESB clogged the leaks, using sealing wooden plugs and contained the leak, considerably minimizing the odor nuisance. As odorant are flammable products, the CETESB and the Fire Brigade monitored the flash indexes using explosimeters, and confirmed there was no risk of explosion. They finally destroyed the spilled odorant with sodium hypochlorite (bleach) to oxidize these sulfur compounds and eliminate the odor. A part of the product leaked in a waste water sewer ditch and an unquantified amount of products went to the river. No action was taken as it was assessed that the dilution and natural degradation in the environment would be enough to "treat" this pollution. Last, the Military Police Operations Center escorted the removal of damaged container, before reopening the highway.

Conclusion
The emergency response was quite well managed, with a great coordination of several different agencies and emergency response organizations. The most difficult part was the spill into the river, which could not be prevented. Dilution and natural degradation solved the potential odor issues.

FIGURE 1. June 2006 Odorant Incident

Date
19th May 2009

Where in the supply chain?
At a Gas firm odorant injection site during a scheduled maintenance

Location
Shah Alam City Gate, in Kuala Lumpur area, Malaysia.

S. Lavanya vomited after Tuesday's incident.

Source : New Straits Times

Incident description and OELs
A 80% TBM - 20% DMS blend leak at a City Gas station during a routine operations maintenance. Few information was reported on the incident causes: The local utility reported that a Mercaptan-based chemical, was released during a routine service check. It said that a "small quantity" escaped. The maximum temperature that week in that area was 96°F (~36°C)[3]. TBM boils at 147°F (~64°C) [4] but DMS is much lighter and boils at 99°F (~37°C)[4]. Under these conditions, the TBM-DMS blend natural gas odorant inside the storage tank might have gone above the max temperature reported that day, leading to vaporization of the blend. It resulted in a strong vapor phase composed mainly of DMS and also some TBM in the atmosphere, creating a strong odorization of the ambiant air, which can spread to a significant surrounding area. In this case, the exposure to the odorant was exceeding acceptable exposure limits.

An Occupational Exposure Limit (OEL) is an upper limit on the acceptable concentration of a hazardous substance in workplace air for a particular material or class of materials. It is typically set by competent national authorities and enforced by legislation to protect occupational safety and health. It is an important tool in risk assessment and in the management of activities involving handling of dangerous substances[5]. Different authorities have defined OELs for airborne workplace chemicals:

a) The Occupational Helath & Safety Administration (OSHA) of the US Department of Labor has defined Permissible Exposure Limits (PELs)
b) The National Institute for Occupational Safety & Health (NIOSH) of the US Department of Health and Human Services has defined Recommended Exposure Limits (REL)
c) The American Conference of Governmental Industrial Hygienists (ACGIH®) has defined the Threshold Limit Values® (TLV)

The OELs of ButylMercaptan and Dimethyl Sulfide, which are involved in the 2 incidents reported in this paper and also EthylMercaptan commonly used worldwide to odorize LPG are displayed in table 1.

Table 1. – Occupational Exposure Limits[6] in ppm and mg/ m^3

	Dimethyl Sulfide		Ethyl Mercaptan		n-Butyl Mercaptan	
	ppm	mg/m^3	Ppm	mg/m^3	Ppm	mg/m^3
OSHA PEL (ceiling)	10	25	10	25	10	35
NIOSH REL (ceiling - 15min)	N/A	N/A	0.5	1.3	0.5	1.8
ACGIH TLV® TWA	N/A	N/A	0.5	1.3	0.5	1.8

Ceiling: the OEL shall not be exceeded at any time during the working exposure
Ceiling - 15 minutes: the OEL shall not be exceeded over 15 minutes time-weight average (TWA) at any time during the work day. This REL is also called Short-Term Exposure Limit (STEL).
TWA: Time Weight Average exposure concentration for a conventional 8-hour work day.

When exceeding these OEL, workers are exposed to toxicologic risks detailed in the Safety Data Sheet of the concerned chemicals. In the case of this spill in Shah Alam City Gate (Malaysia), acute exposure to DimethylSulfide, which was the chemical the most present in the atmosphere, can cause irritation of eyes and skin; cough, sore throat; nausea; weakness.[4]

Consequences

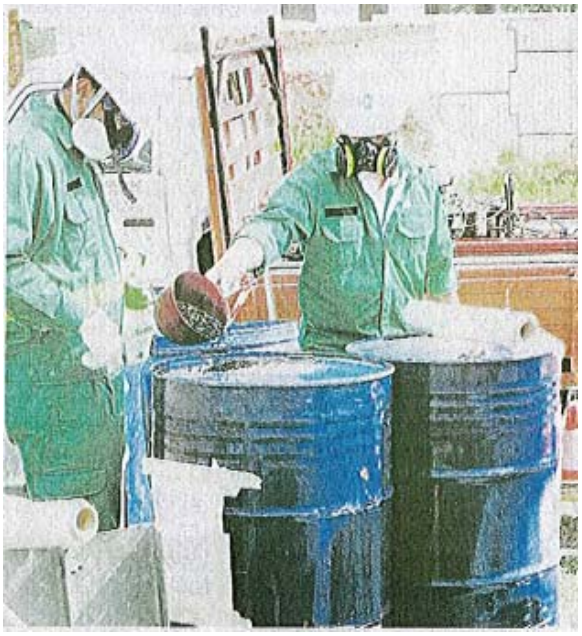
1) Neighbors immediately thought there was a gas leak. The local utility denied there was a gas leak.
2) 70 pupils at a nearby school, only 300 meters from the City gate station, fell ill and had difficulties breathing. They smelled something "pungent" in the air. Pupils complained of dizziness. 20 of them fainted after inhaling this pungent "gas". Those feeling unwell were taken to the hospital, while others went back home.
3) People were also very frightened as there were rumors of a "potential bomb" attack.
4) The following days, the local community was angry: some parents gathered at a local natural gas city gate station to protest against this leak resulting in their children being rushed to a hospital. Parent-teacher association filled a police report against the owner of the station as well as initiated legal proceedings.

Emergency response

The immediate response was obviously not properly managed. The gas utility had neutralizing agent, but did not know how to use it. Then, the gas utility took "measures to neutralize the smell of the chemical".

The Police, but also the Fire and Rescue Department cordoned off the road leading to the station during the cleaning-up of operations.

The Hazmat team sealed the leak 15 minutes after arrival and brought the situation under control. The operators, equipped with Personal Protective Equipment (PPE) used active carbon on top of some drums containing the odorant blend to absorb the remaining smell.



Conclusions

Medical check-ups and any related medical expenses were taken in charge by the Gas utility. In addition to this medical aid, they carried out community service projects at the school and provided corrective and preventive reports to reassure that this would not happen again.

FIGURE 2. May 2009 Odorant Incident

ODORANT SPILL RESPONSE

Any gas transmission or distribution company must have an emergency response plan in place to address an odorant spill incident. "Emergency" means there is no time to think about "What to do now?" which is why a plan must be put on paper first. Spelling out the right sequence of operations and then train all parties, on a regular basis, to this emergency response is fundamental.

Qualification of the spill and odor event

Let's imagine that you are an Operation manager at a gas utility firm. A field operator of the gas utility is calling you to report an odor event. What are the questions would you ask over the phone to qualify the incident?

These questions could be, but are not limited to:

- Is it an odorant vapor release or an odorant liquid spill? Yes/No/Unknown
- Did the spill happen when you were on-site? Yes/No
- Does the spill occur in an open area? Yes/No/Unknown
- Is the location of the spill easy to access? Easy/Moderate/Difficult/Very difficult
- What is the estimated quantity of odorant spillage? Few drops, 1 gallon, several gallons…
- How strong is the odor? Acceptable, Unbearable

These questions can help a gas utility to build the tree of the incident qualification, in order to determine the adequate sequence of actions to put in front of different levels of incidents. You can also refer to the OSHA (Occupational Safety and Health Association) Hazardous Waste Operations and Emergency Response standard 29 CFR §1910.120. Training on spill response and on the development of a spill response is detailed in paragraph (q). The Chapter 5 (section 5.2.2) provides additional details on requirements for a Spill Prevention, Control and Countermeasure (SPCC) plan and emergency response.

The response plan should be customized to each site to take into account the design of the city gate, and should include proper valve labelling and schematics showing these valves. The plan should identify which valves are to be closed and in which sequence to safely shut down the system. [7]

An odorant leak can poison people, create a gas alert generating public panic and can even lead, in extreme cases, to an explosion. So you must first protect Life, then the Property and last the Environment. In the tree of actions, you will have to integrate spill response actions which are happening in two main steps: 1) Immediate actions and then 2) Spill management Immediate actions

Here is a simplified example of sequence to work on and repeat in training sessions:

1) As soon as an obnoxious odor is detected, it is essential to immediately leave to fresh air and get equipped with **a breathing apparatus**. You must check the validity of the filtering media and train employee working on a gas utility site on how putting this mask properly. You should have on site additional masks in case an odorant leak happens while contractors or visitors are presents.

2) **Notify** immediately the accidental release to the area safety manager and **coordinate** with the fire brigade and local authorities. Your response plan should clearly mention and keep up to date the names of the managers of these different entities. A priority order should be set-up.

3) **Evacuate** non-essential staff and those not equipped with individual protection apparatus. Define in the response plan who is supposed to lead and coordinate the emergency response plan and which personnel should be dismissed immediately.

4) Delimit a **safety zone**. The size will be determined according to the extent of the leakage. You must have on-site the necessary equipment to delimit this safety zone.

5) Read the **Safety Data Sheet (SDS)** of the concerned products. The SDS should be available at the city gate of the gas utility of the Liquefied Petroleum storing site. SDS content is regulated by each country. In Europe, the European Chemical Agency (ECHA) is providing a guidance[8]:

. Chapter 1 - Product and Company information lists emergency contacts for Transportation and Medical
. Chapter 2 - Hazards identification gives the main risks associated with this chemical together with Global Harmonized System (GHS) labelling, with associated statements. See Figure 1 below for t-Butyl Mercaptan:

GHS Labelling			
Statement	H225: High flammable liquid and vapor	H317: May cause allergic skin reaction	and H411: Toxic to aquatic life with long lasting effects

FIGURE 3. GHS Labelling for t-Butyl Mercaptan

. Chapter 3 - Composition / Information on ingredients
. Chapter 4 - First aid and measures
. Chapter 5 - Firefighting measures
. Chapter 6 - Accidental Release measures, in which you find a brief description of main spill response actions. See here-under extract of DMS SDS[4]

Personal precautions, Emergency procedures, Methods and materials for containment/clean-up:
Prevent further leakage or spillage if you can do so without risk. Evacuate area of all unnecessary personnel. Ventilate the area. Eliminate all ignition sources. Avoid generation of vapors. Contain and collect spillage with non-combustible absorbent material such as sodium bicarbonate, sodium carbonate, calcium carbonate, clean sand or non-acidic clay and then wet down (dampen) the mixture with water. Sweep or scoop up using non-sparking tools and place into suitable properly labeled containers for prompt disposal. The sweepings should be wetted down further with water. Avoid dispersal of spilled material and runoff and contact with soil, waterways, drains and sewers. Consult a regulatory specialist to determine appropriate state or local reporting requirements, for assistance in waste characterization and/or hazardous waste disposal and other requirements listed in pertinent environmental permits.

. Chapter 7 - Handling and storage, in which you find basic recommendations for storing this class of chemicals, including a mention on non-compatible chemicals: Oxidizing agents must not be stored together with gas odorant. The reaction between these would lead to an exothermic reaction.
. Chapter 8 - Exposure controls / Personal protection, in which you can find OELs displayed here-above in this article.
. Chapter 9 - Physical and chemical properties
. Chapter 10 - Stability and reactivity
. Chapter 11 - Toxicological information
. Chapter 12 - Ecological information
. Chapter 13 - Disposal information
. Chapter 14 - Transport information
. Chapter 15 - Regulatory information
. Chapter 16 - Other information

6) In addition to the breathing apparatus, wear the appropriate **Personal Protective Equipment (PPE),** Figure 2 below, before going into the polluted site.

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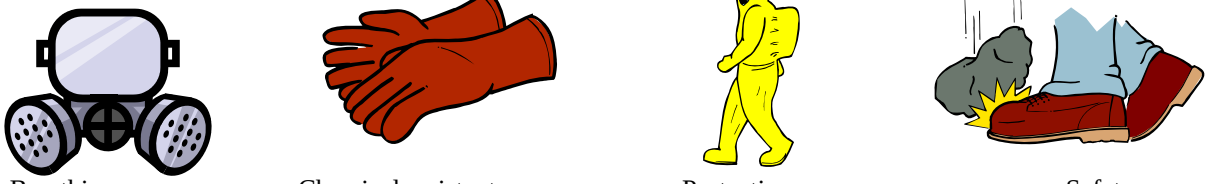

Breathing Apparatus | Chemical resistant gloves | Protective clothing | Safety boots

FIGURE 4. Typical Personal Protective Equipment

7) Insure all **draining systems are closed** in case of a liquid leak in a retaining area.

8) **Control the explosive nature of the contaminated atmosphere** before any intervention: use a gas odorant sensitive explosimeter. Within the odorant explosive limits, either ventilate the contaminated area, or vacuum the vapors where emitted, until being under the lower odorant explosive limit. In any case, prohibit sources of ignition and sparks. By definition, gas odorants are flammable products: Do not smoke, use no sparking tools, and avoid accumulation of static electricity by grounding the equipment.

Spill management

Main steps

Once immediate precautions to protect people from flammable, explosion and chemical risk are taken, then here are a few spill management basic steps:

1. **STOP** the leak: you have to spot the source of the leak and stop it
2. **CONTAIN** the spill: you can use dike pigs to prevent the liquid to spread further
3. **ABSORB** the spill: you can use absorbent powder or pads
4. **NEUTRALIZE** the odor: you can use a neutralizing or a masking agent to efficiently neutralize the odorant smell
5. **DISPOSE** of the material: you can use over-drum. Wastes are to be processed by a specialized company.

Masking or neutralizing agents

First we distinguish the term “masking” from “neutralizing”. Masking is about superposing another strong odor on the gas smell. Some would say a masking agent “disguises” the smell. These masking agents contain Volatile Organic Compounds (VOCs), which can create allergic or asthmatic reactions. The odor masking term is also used for natural gas “when the gas does not smell gas”, despite having the usual odorant quantity (ref.). If the gas is not clean, some impurities can mask the gas smell. Neutralizing is about “capturing” the odorant molecule, “encapsulating” the chemicals. Whereas masking agent can be solvent or water-based, neutralizing agent are water based. The role of these agents is to control the odor event. Then, before disposing the waste or contaminated equipment, you have to chemically destroy the sulfide or mercaptan. Microorganism or bacteria can be used. But most often, a strong oxidizing agent like Bleach or Hydrogen Peroxide is used for that operation before disposal. Before selecting a masking or a neutralizing agent, please consider the following criteria in Table 1:

Solvent	Organic solvent / Water / Emulsion
Alcohol type (used as an antifreeze agent)	Flammable alcohol / Non-flammable alcohol
GHS labelling and toxicological information a) d-Limonene, is a terpene commonly used in masking agents b) water-based surfactants *Always refer to the SDS to know the chemical and toxicological risks before using.*	Two examples of labelling: a) GHS label of d-limonene  b) Most of water-based agents contain low concentration of chemicals. They may be labelled: 
Method of application	Pouring / Spraying

TABLE 1. Neutralizing Criteria

Having the product, ready to use, at the right location is essential in a spill response program. It is as important to know how to use it. A water-based neutralizing agent without spraying system, even a basic one, is useless.

Carbon filters

Activated carbon is part of the tools which are used to capture and filter ~~the~~ odors. For airborne odors, meaning diluted in the ambient air, this can be an efficient way to prevent a gas smell dispersion. For instance, when a gas utility maintains an injection system and has to open it after purging, the vacuum system coupled with a carbon filter can be useful to keep the environment without gas smell. Carbon filter can also be used to clean the ambient air of gas odorant filling station in closed building.

However, to treat a direct vent saturated with odorant, activated carbon filter are not recommended without specific cautions. The removal of VOCs can create hot spots and sometimes carbon bed fires. The adsorption of a chemical is an exothermic reaction (meaning the reaction creates heat). Moreover, if oxygen is present, oxidation of the adsorbed mercaptan can happen on the surface of the carbon grain. This oxidation reaction is also exothermic. These 2 reactions combined can lead to hot spots and ultimately fires if enough oxygen is brought to the activated carbon.

A major accident at the Powell Duffryn Terminals Inc in Savannah, Georgia was investigated and reported by the EPA in 1998[9]. On April 10th, 1995 explosion and fire occurred at that facility. Duffryn Terminals Inc was storing crude sulfate terpene (CST), a flammable liquid. These terpenes are very odorant and these closed CST tanks directed vapor to a vapor control (VC) system. This vapor control system was composed of a two fifty gallon drums of activated carbon. The installation was supposed to be equipped with a flame arrester. It was present on site but not installed.

FIGURE 5. April 1995 Odorant Incident

The VC system design permitted the backflow of outside air through the activated carbon drums. The EPA reported that "organic sulfur compounds in CST can produce heat when they are adsorbed by the activated carbon. Enough heat may be produced in the drums to raise the temperature above the auto ignition temperature of CST.(…) If outside air is permitted to be drawn through the drum containing the activated carbon (…) air can provide oxygen needed for combustion."

CONCLUSION

Following the accident in Sao Paolo, transport of gas odorant are no longer permitted to go through the city. An alternative route is now used to by-pass it. The number of SBCs on a truck has been limited not to exceed 7 metric tons. These SBCs are either transported in closed ISO-container or truck on which an anti-slide mat is placed between the SBC base and the trailer floor. The blocking and bracing on top and bottom of these SBCs have been improved with up to 6 straps per SBC. The transport company is trained so that straps are properly used and kept in good conditions. In Malaysia, the gas utility is now better prepared on spill management. A local gas odorant distributor has developed a Gas Odorant Leak Management System (GOLMS) which provides a quick intervention unit and all necessary equipment described in this paper. Emergency responses can either be outsourced or managed internally by gas utility firms. Such spills do happen randomly, which makes it challenging to have employees ready to implement an emergency plan. Training is essential to make the emergency response plan operational, effective and safe.

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