THE SMELL OF DANGER

by Bruce Goldfarb

When Oscar Stuckey's parents sold their home in Cordele, Ga., and moved to Florida, they had the electricity turned off. On the night of June 24, 1983, Stuckey entered the darkened house to retrieve an electrical extension cord his mother had left on the kitchen counter. Stuckey didn't even try the light switch. As he groped about the gloomy kitchen for the cord, he had no idea that he was surrounded by explosive propane gas that had somehow leaked into the room. To illuminate the room, Stuckey took out his cigarette lighter and struck it.

With a horrendous roar, an orange fireball filled the room and enveloped Stuckey's body. He turned and ran—more in shock than in pain.

Next door, neighbor Jimmy Rigsby was settling down to watch the 10 p.m. news when a loud "whoosh" made him look out the window. Stuckey was running from the house, flames licking at his clothes. Rigsby grabbed a blanket, ran outside, covered Stuckey, and wrestled him to the ground. Stuckey later testified that he never smelled the odor of gas.

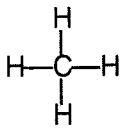
Stuckey suffered second- and third-degree burns on his face, neck, trunk, and arms. The house was only slightly damaged by the initial fire, but the next day smoldering embers reignited the fire, and the house burned to the ground. While Stuckey struggled to survive in the hospital, fire investigators sifted through the rubble to determine the cause of the accident. One investigator opened the valve on the propane storage tank and discovered that the gas had no odor. "Even with the gas hitting them full force in the face," says Stuckey's lawyer, Jim Hurt, "they couldn't smell a thing."

Propane, also known as LP (liquid petroleum) gas, is used in 4,200,000

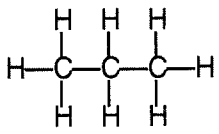
Natural gas and LP

Natural gas, the most widely used heating fuel in the United States, is obtained from geological deposits and is distributed to homes, offices, and factories by underground pipes. As distributed, it is typically a mixture of 92% methane (CH_4), 5% ethane (C_2H_6), and 3% other gases. Because natural gas has little or no odor, strong-smelling compounds such as tertiary butyl mercaptan and dimethyl sulfide are added to it. The odor rarely fades because natural gas is not stored for long periods but flows continuously through the distribution system.

In rural areas not served by gas pipelines, liquid petroleum (LP gas) is widely used as an agricultural and industrial fuel, as well as for home heating and cooking. LP is obtained from petroleum and contains 82% propane (C_3H_8) combined with a variety of other hydrocarbons. Propane's relatively high boiling point (-42 °C, compared with methane's -162 °C) permits it to be stored as a liquid at ordinary temperatures provided it is kept under pressure. LP is transported and stored as a liquid because the liquid occupies only 1/270 the volume of LP gas. When the pressurized tank is opened the LP vaporizes, yielding the gaseous fuel.



Methane, CH_4, is the primary compound in natural gas.



Propane, C_3H_8, is the primary compound in LP gas.

homes, or about one U.S. house in five. It is also widely used in agriculture, for everything from drying crops to warming greenhouses. Propane is a popular fuel for powering forklift trucks; heating recreational vehicles; and fueling barbecue grills, camping stoves, and soldering torches (see box, "Natural Gas and LP").

Gas odor

Propane has no color, taste, or smell. Therefore, to warn users of a propane leak and to prevent accidents, propane is *odorized* by mixing it with a strong-smelling substance. The chemical used to odorize propane is *ethyl mercaptan,* which is found in the aroma of skunks and rotting meat, and is listed in the *Guinness Book of World Records* as one of the smelliest substances known.

The National Fire Protection Association (NFPA) recommends that enough odorant be added to propane so that it can be detected when it has reached one-fifth the concentration needed for an explosion. This translates to 1 lb of ethyl mercaptan per 10,000 gal. of propane. As an extra precaution, many gas companies add an additional 50% of the odorant.

But critics say that this standard is inadequate because it regulates the amount of odorant that is *originally* added to the propane, not the amount that is present when it is used by the customer. Most important, the NFPA standard does not ensure that propane *remains* odorized while it sits in the customer's storage tank.

The problem is that although the propane held in a storage tank is stable, the ethyl mercaptan may undergo a chemical reaction that converts it to a far less smelly substance.

Odor fade

Under certain conditions ethyl mercaptan can undergo a chemical *oxidation* reaction in which two molecules of ethyl mercaptan join to form one molecule of diethyl disulfide. The new compound has an unpleasant, but far weaker odor. Many experts believe that if the storage tank is properly maintained, the oxidation reaction does not occur. However, if the inside of the steel tank is rusty, iron oxides in the rust can promote the reaction.

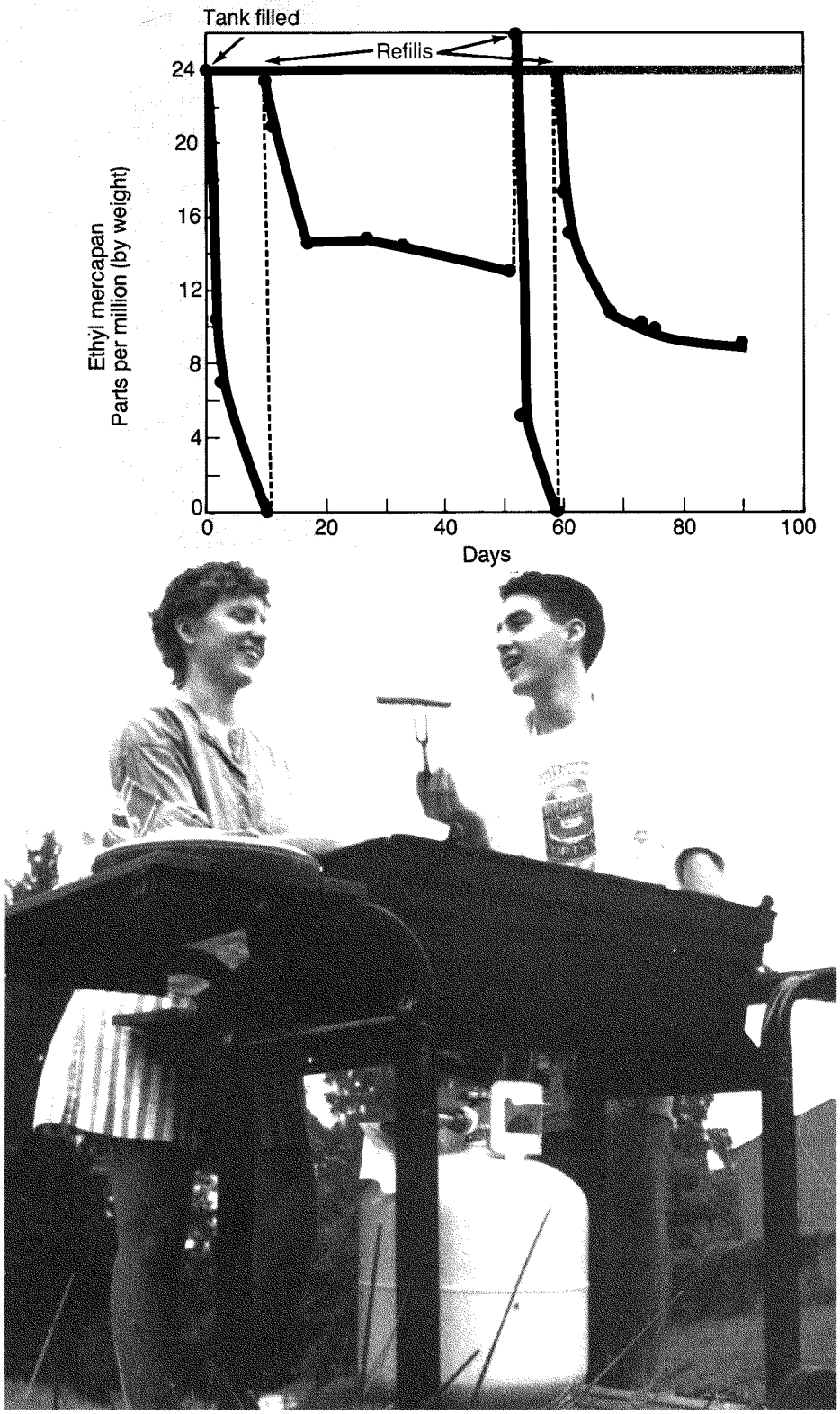
$$3\,Fe_2O_3 + 2\,\underset{\text{ethyl mercaptan}}{CH_3CH_2SH} \longrightarrow$$

$$2\,Fe_3O_4 + \underset{\text{diethyl disulfide}}{CH_3CH_2SSCH_2CH_3} + H_2O$$

Timothy Dunn, a chemical engineer in Atlanta, Ga., has been asked by insurance companies and lawyers to investigate more than 250 propane fires. In about 10% of the cases in which propane had been stored in steel tanks, Dunn says, chemical analysis revealed that the ethyl mercaptan odorant was no longer present "in any significant amount." Generally the culprit tanks are either brand new or they are old tanks that have not been in continuous use. It is believed that after exposure to mercaptan for some months or years, a steel tank will become seasoned and will no longer promote the oxidation of the odorant. But, if an unused tank is left open, air and moisture will form a new layer of rust. If the tank is later put back into use, oxidation of the odorant begins anew. Dunn has conducted experiments showing "considerable depletion of odorant in as little as three weeks."

The odor fade phenomenon was confirmed by a 1987 study conducted by Arthur D. Little Inc. for the U.S. Consumer Product Safety Commission (CPSC). Under carefully controlled conditions, significant odor fade was observed within 5-7 days after a propane tank was filled. "Everybody admits that odor fade exists, but the question is how much it occurs and how significant it is," says Ron Medford of the CPSC. "Those are questions nobody has been able to answer."

Until recently, experts believed that



LYNN K. SIBLEY

The graph above shows the propane odorant levels in a "barbeque-size" steel tank. The odorant concentration was measured over a period of 90 days as the cylinder was filled and emptied four times. After two of the refills, the odorant was gone within 10 days; after the other two refills, it dropped to half the recommended concentration (colored line). In similar tests a Teflon-lined steel tank and an aluminum tank showed no odorant fade. The study was conducted at the Esso Research Center, Sarnia, Canada, from 1985 to 1986.

rust compounds were necessary for the oxidation of mercaptan odorants. However, the CPSC study found that mercaptan depletion can occur in clean stainless steel tanks. Thus there may be more than one chemical reaction that causes odor fade. Nonetheless, the iron in the container apparently plays some role because aluminum tanks and Teflon-lined tanks show little or no odor fade. The research also showed that porous masonry can absorb ethyl mercaptan from propane vapor (see box, "Adsorption and Absorption").

Additional research performed in Canada focused on odor fade in portable tanks. Chemist Ian Campbell, who supervised the research for Esso Petroleum Canada, found that although ethyl mercaptan will fade in all types of steel tanks, aluminum tanks appear to resist odor fade. Esso researchers also tested the popular 1-lb propane cylinders that are used on camping stoves and hand-held soldering torches. The fuel in nine cylinders was tested approximately six months after the cylinders had been filled; in six cylinders, no measurable ethyl mercaptan was left in the gas. This could be a problem because these disposable cylinders can easily sit on a hardware store shelf for six months. "Any fading that occurs does occur very quickly," Campbell says. At this time no one understands why the odor fades in some tanks but not in other apparently identical tanks. Clearly, more research is needed.

Boiling points

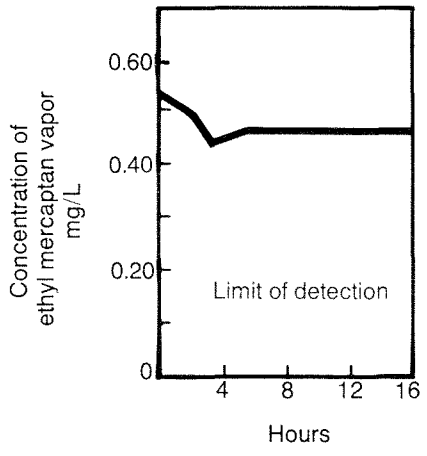
Another factor that can affect the concentration of odorant is the difference in boiling points (and vapor pressures) of ethyl mercaptan and propane. Ethyl mercaptan, which has a boiling point of 35 °C (95 °F), is much less volatile than propane, which boils at -42 °C (-44 °F). When a tank has just been filled, the propane vaporizes more readily than ethyl mercaptan, and the first gas drawn off the tank will have the least odorant. The concentration of odorant in the vapor phase increases as the propane is used up. "You can have more than a 30-fold difference in mercaptan concentration when the propane tank is filled compared to when the tank is near empty," says fire investigator Dunn.

Simply increasing the amount of ethyl mercaptan added to a batch of

Adsorption and absorption

Adsorption and absorption—different phenomena with similar names—both reduce the concentration of odorants in gas. *Ad*sorption is the attachment of a molecule to the surface of a solid. Charcoal is an excellent deodorizer because vapor molecules readily adsorb on its surface, and clay soils can adsorb some gas odorants. The iron oxide in pipes *may* adsorb gas odorants (more research is needed).

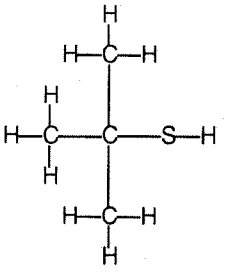
*Ab*sorption is the taking up of a substance into the porous interior of a solid—like a sponge absorbing water. Absorption does not occur in pipelines or storage tanks because no porous materials are present. However, gas odorants are readily absorbed by concrete and concrete blocks, the materials of basement walls. In a recent laboratory test of absorption conducted for the U.S. Consumer Product Safety Commission, a mixture of air, propane, and ethyl mercaptan was placed in a plastic test chamber. The graph below shows the normal concentration of ethyl mercaptan in the chamber (black line), and the concentration when a concrete block was placed in the chamber (colored line). After six hours none of the odorizing ethyl mercaptan could be detected. This suggests that if gas with the proper amount of odorant leaks into a basement, it may become deodorized in a few hours.



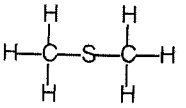
Odoriferous compounds

Mercaptans (also known as thiols) are organic compounds with a -SH group. They have a characteristic garliclike odor that most people perceive as "gassy." Mercaptans can be detected at very low concentrations. Sulfides have a weaker, rotten-egg-like odor. Each of these odorant compounds (and others not listed) has specific advantages and disadvantages. The *perfect* odorant has not been discovered.

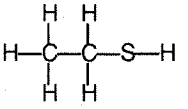
- **Tertiary butyl mercaptan** is the most commonly used natural gas odorant. It penetrates soil well and resists chemical oxidation, but because it has a high freezing point, it is less effective at low temperatures. Its skunklike odor is detectable when one liter of its vapor is mixed with one billion liters of air (0.001 part per million volume).



- **Dimethyl sulfide** is not as smelly as tertiary butyl mercaptan, but is more resistant to fading by chemical oxidation. These two odorants are often used in combination in natural gas.



- **Ethyl mercaptan** has a penetrating skunklike odor of about the same strength as tertiary butyl mercaptan. It is widely used in LP because it vaporizes adequately at winter temperatures.



propane is not a practical solution. Over-odorization leads to an excessive number of false leak reports, and still does nothing for the many persons unable to smell ethyl mercaptan.

Odor blindness

The sense of smell varies widely. The most frequent cause of reduced sensitivity is the common cold, but conditions such as Alzheimer's disease and multiple sclerosis can interfere with the sense of smell. Approximately 1% of Americans cannot smell at all, and millions more have *specific anosmia*, a sort of odor blindness. They are physically unable to smell certain odors, a trait that usually runs in families.

In 1986, *National Geographic* magazine and the Monell Chemical Senses Center in Philadelphia, Pa., joined forces to conduct the world's largest smell survey. The magazine included six scratch-and-sniff odor strips in its September issue, and Monell researchers Charles Wysocki and Avery Gilbert analyzed the questionnaires returned by 1.5 million readers. They found that odor blindness to gas odorants is not unusual and that it rises in direct proportion to age. More than half of the respondents over 60 did not recognize the odor of gas. "We were surprised to see the rather dramatic fall off in how the elderly are treating that warning stimulus," Wysocki says. "It's the older people who are at most risk to begin with. They're the ones having most of the accidents with gas."

Research performed by odor chemist Amos Turk and psychologist William Cain of the John B. Pierce Foundation Laboratory confirms that propane leaks are especially risky for the elderly. Turk and Cain found that the average 70-year-old's threshold

for detecting ethyl mercaptan is 10 times higher than that of the average 18-year old.

Legal explosion

U.S. fire companies report an annual average of 2590 LP gas explosions that cause 330 injuries and 18 deaths. No one knows how many of these incidents may have involved odor fade, but victims who said they didn't smell the gas have filed lawsuits against companies that produce and distribute the fuel.

Hal Faulconer, vice president of technical services for the National Propane Gas Association, insists that propane has an "excellent safety record" and is perfectly safe if properly used. He describes fading as a rare phenomenon that occurs only "under a special set of circumstances." Faulconer says, "Any time there is any incident with propane gas, the very first allegation made is [the victim] didn't smell it. There might be some cases when that is true. But I know that in a majority of the cases the allegation is untrue." Although the evidence is often destroyed, a claim that the gas had no odor "wears well with juries," he says.

Kansas City attorney James Wirkin says that the propane industry has known about the phenomenon of odor fade for more than 40 years, but has not adequately informed the public. The sellers of propane "aren't doing anywhere near the job they ought to in terms of education," he says.

Fortunately, that is changing. The suppliers of propane and natural gas have distributed millions of scratch-and-sniff cards to their customers to make them aware of the smell of odorized gas. And, through safety pamphlets, the National Propane Gas Association is now warning customers about the possibility of odor fade.

But the reeducation of millions of customers will take time. Just as it took years to get propane users to be careful when they *smell* gas, it will take years to get them to be equally careful when they *don't* smell gas.

To use LP gas safely...

• **Know your nose.** Learn what the gas odor smells like. Get a scratch-and-sniff card from your local gas company or from the National Liquid Propane-Gas Association, 1301 West 22nd St., Oak Brook, Ill. 60521. Check members of your family for impaired sense of smell. Remember that a cold, cigarettes, alcohol, and age can reduce the sense of smell. To be safe, assume that elderly people cannot smell gas.

• **Read the instructions** that come with all your gas-fueled products, and follow them. Learn where the master shutoff valve is and how to operate it.

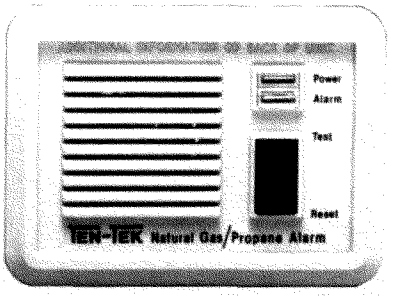
• **If you smell gas,** turn off gas appliances, open the windows, and ventilate the area thoroughly; then check for inoperative pilot lights and oven burners. **Do not strike a match, use an open flame, or turn electrical switches on or off.** If you can't locate the leak, leave the house, shut off the propane at the supply tank (if you know how to do this), then call the gas company or fire department from a neighbor's house.

• **If you relight a pilot light** after running out of LP and having the tank refilled, proceed **very** carefully because many accidents occur during pilot relight. Sniff near the floor; propane can collect there because it is denser than air. Better yet, have the service representative from the gas company relight the pilot lights.

• **Don't store tanks indoors** or in a vehicle where vapor can accumulate. (Don't keep that gas barbecue grill in the basement.) You can check outdoor equipment for leaks by brushing a soap solution on the valve, tubes, and connections and watching for bubbles. Leave indoor leaks to the experts.

• **Refill portable tanks** before they are completely empty whenever possible. If a tank is emptied completely, ask your supplier to purge the tank before refilling it.

• **Buy a gas alarm.** Similar to smoke alarms, gas alarms sound off when propane or natural gas is present.



This $70 alarm sounds off if natural gas or propane gas reaches 1/4 the concentration required for explosion. At this time, Ten-Tek Electronics of Willowbrook, Illinois, is the only maker of home gas alarms.

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