CHAPTER 25

HAZARDOUS MATERIALS: RECOGNITION AND IDENTIFICATION

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OUTLINE

- Objectives
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- Location and Occupancy
- Placards, Labels, and Markings
- Other Identification Systems
- Containers
- Senses
- Chemical and Physical Properties
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Photo courtesy of Baltimore County Fire Department

STREET STORY

While the news media tends to focus on the large and spectacular, the reality is that every day the fire service responds to literally hundreds of hazardous materials–related incidents. These incidents usually do not get much attention because they are small in scope and are handled with a minimal amount of fire department resources. Common examples include natural gas leaks and flammable and combustible liquid spills.

We have an old saying in the HAZMAT community that the initial ten minutes of an incident will dictate the tone for the first hour of an incident. Clearly, the actions—or inactions—of the first responders will set the tone for an incident. I think back to two incidents in my career that reinforce this point.

The first incident involved an engine company being sent to investigate a call regarding an unknown liquid spilled along a highway. Upon arrival, the engine company officer found a very viscous red liquid spilled along a long distance of a road, apparently from the rear of a tractor-trailer. Unsure of the identity and the potential hazard of the liquid, the officer requested a HAZMAT unit to respond to the scene and provide assistance. Using their monitoring and detection equipment, responders were eventually able to determine that the liquid posed no hazard to the community. In fact, the unknown liquid was eventually identified as strawberry syrup! Although the officer took some ribbing from his peers, he clearly made the proper decisions to ensure the safety of both his personnel and the community.

In the second incident, a police officer was called to provide assistance to a public works road crew that had discovered what appeared to be a 5-pound portable fire extinguisher wrapped in duct tape with a fuse on the top. Although he believed it to be a hoax, the officer still requested the response of the fire department bomb squad. After conducting a thorough risk assessment and requesting the additional assistance of a HAZMAT response team, the bomb squad was able to determine that the perceived hoax was, in fact, an actual explosive device. When the device was disrupted (i.e., blown up) by the bomb squad, it made a lasting impression on the police officer!

In both of these instances, recognition and identification by the first responders set the tone for the incident. If you do not know what to do, isolate the area, deny entry, and call for help.

—Street Story by Gregory G. Noll, Emergency Planning and Response Consultant, Hildebrand and Noll Associates, Lancaster, Pennsylvania

OBJECTIVES

After completing this chapter, the reader should be able to:

- Identify the nine hazard classes as defined by DOT.*
- Identify the hazards associated with each hazard class.
- Identify the standard occupancies where hazardous materials may be used or stored.
- Identify the standard container shapes and sizes and common products.
- Identify both facility- and transportation-related markings and warning signs.
- Identify the standard transportation types for highway and rail.
- Explain the use of the NFPA 704 system.
- Explain the use of transportation containers in identifying possible contents.
- Explain the location of emergency shutoffs on highway containers.
- Explain the importance of understanding chemical and physical properties of hazardous materials.

INTRODUCTION

This chapter is of primary importance to the emergency responder.

Safety It is through recognition and identification (R&I) that firefighters can impact their ability to stay alive.

The inability to recognize the potential for chemicals to be present and the inability to identify the chemical hazard can place firefighters in severe danger. Firefighting is inherently dangerous, but the response to a hazardous materials release creates an additional risk. Not only can there be immediate effects from some materials, but multiple exposures can have far-reaching effects. As depicted in the opening photo, firefighters are using proper PPE but taking a considerable risk to rescue a live victim. More information on this rescue and risk is provided in the case study in Chapter 28. Although fires have killed hundreds before, these types of fires are rare. Hazardous materials incidents have killed thousands and injured countless more. In 1984 a release of methyl isocyanate in Bhopal, India, killed more than 2,000 and injured thousands more. This incident was the basis for the Emergency Planning and Community Right to Know Act (EPCRA) because several facilities in the United States use this material.

Four basic clues to recognition and identification are (1) location and occupancy; (2) placards, labels, and markings; (3) container types; and (4) the senses. A mere suspicion in any of these areas should be enough to place a first responder on guard for the possibilities of a chemical release and its associated hazards, **Figure 25-1**.

LOCATION AND OCCUPANCY

Caution The size of the community does not impact the potential for hazardous materials; every community has hazardous materials.

Figure 25-1 The four basic clues to recognition and identification are location and occupancy; placards, labels, and markings; container types; and senses.

**Reader's Note:* In the hazardous materials section, NFPA 1001 requires that the student receive hazardous materials training at either the Awareness level or the Operations level. The information in this text covers both levels and in some cases exceeds the Operations level. All of this information is important for firefighters' survival. See the discussion on NFPA standards and OSHA's HAZWOPER for more information on Awareness and Operations level training.

Figure 25-2 Agricultural supply stores have a large quantity of hazardous materials, including pesticides, herbicides, and fertilizers. In many cases they also have fuels, including propane.

Most communities have a gas station or a hardware store. The average home has a large amount of hazardous materials that can cause enormous problems during a response. In rural communities, farms present unique risks due to the storage of pesticides and fertilizers, **Figure 25-2**. All of these locations and occupancies provide the potential for the storage of hazardous materials. In general, the more industrialized a community is, the more hazardous materials the community will contain. Communities adjacent to industrialized areas or along major transportation corridors (interstate highways, rail, water) may also have the same hazards because these materials can travel through the community, **Figure 25-3**. Buildings that typically store hazardous materials include hardware stores, hospitals, auto part supply stores, dry cleaners, manufacturing facilities, print shops, doctors' offices, photo labs, agricultural supply stores, semiconductor manufacturing facilities, electronics manufacturing facilities, light to heavy industrial facilities, marine terminals, rail yards, airport terminals and fueling areas, pool chemical stores, paint stores, hotels, swimming pools, and food manufacturing facilities.

Figure 25-3 If a community has a road, the potential for a hazardous materials incident exists. One of the most common chemical releases is a gasoline spill.

PLACARDS, LABELS, AND MARKINGS

This section examines the first concrete evidence of the presence of hazardous materials. A number of systems are used to mark hazardous materials containers, buildings, and transportation vehicles. The systems result from laws, regulations, and standards, and in some cases from a combination of the three. As an example the **Building Officials Conference Association (BOCA)** code, which has been adopted as a regulation in local communities, requires the use of the NFPA 704 marking system, **Figure 25-4**, for certain occupancies.

Placards

The most commonly seen item for identifying the location of hazardous materials is the placard. The Department of Transportation (DOT) regulates the movement of hazardous materials ("dangerous goods" in Canada) by air, rail, water, roadway, and pipeline by means of 49 CFR 170-180. After meeting certain guidelines a shipper must placard a vehicle to warn of the storage of chemicals on the vehicle, an example of which is shown in **Figure 25-5**.

> **Note** The quantity of hazardous materials that must be carried in order to require placarding is 1,001 pounds, unless it is one of five classes of materials that require placarding at any amount.

Figure 25-5 The DOT requires some shippers of hazardous materials to provide placards to warn responders of chemicals that may be on the truck.

Table 25-1 and **Table 25-2** provide further explanations of the placarding system.

The DOT has established a system of nine hazard classes that uses more than twenty-seven placards to identify a shipment. The idea behind these hazard classes is to provide a general grouping to a shipment and to provide some basic information regarding the potential hazards. The placards, like the one shown in **Figure 25-6**, are 10¾ inches by 10¾ inches

Figure 25-4 The NFPA has developed a system for identifying potential chemical hazards in a building. The system is known as NFPA 704.

Materials That Require Placarding at Any Amount (DOT Table 1)

HAZARD CLASS OR DIVISION	PLACARD TYPE
1.1	Explosives 1.1
1.2	Explosives 1.2
1.3	Explosives 1.3
2.3	Poison gas
4.3	Dangerous when wet
5.2 (Organic peroxide, type B, liquid or solid, temperature controlled)	Organic peroxide
6.1 (Inhalation hazard Zone A or B)	Poison inhalation hazard
7 (radioactive label III only)	Radioactive

TABLE 25-1

Materials That Require Placarding at 1,001 Pounds (DOT Table 2)

CLASS OR DIVISION	PLACARD TYPE
1.4	Explosives 1.4
1.5	Explosives 1.5
1.6	Explosives 1.6
2.1	Flammable gas
2.2	Nonflammable gas
3	Flammable
COMBUSTIBLE LIQUID	**COMBUSTIBLE**
4.1	Flammable solid
4.2	Spontaneously combustible
5.1	Oxidizer
5.2 (Other than organic peroxide, type B, liquid or organic peroxide solid, temperature controlled)	Organic peroxide
6.1 (Other than inhalation)	Poison
6.1 (PG III)	Keep away from food
6.2	None
8	Corrosive
9	Class 9
ORM-D	None

TABLE 25-2

Figure 25-6 "Corrosive" placard. Not to scale.

and are to be placed on four sides of the vehicle. Labels are $3\frac{9}{10}$ inches by $3\frac{9}{10}$ inches and are affixed near the shipping name on the container. Labels, for the most part, are smaller versions of placards and are designed to provide warnings about the package contents. There are labels for some materials that do not have or require placards.

The system is designed so that materials designated by the DOT as potentially harmful to the environment, humans, and animals are easily identified. Such a material has to present an unreasonable risk to the safety, health, or property upon contact. The DOT has two placarding tables, which are called Table 1 and Table 2. The materials that are on Table 1 (as shown in **Table 25-1**) are those that are most hazardous and require the use of a placard no matter what the quantity being shipped. The materials in DOT Table 2 (as shown in **Table 25-2**) are those that require placarding at 1,001 pounds. The criteria establishing this 1,001-pound rule are not clearly defined, but responders should be aware that a spill of 999 pounds of a material can be as hazardous as 1,001 pounds. The shipper uses the hazardous materials tables (49 CFR 172.504) to determine which labels and placards are required. The tables may also list a packing group for the material, which indicates the danger associated with the material being transported.

- *Packaging Group I:* Greatest danger
- *Packaging Group II:* Medium danger
- *Packaging Group III:* Minor danger

Packaging groups are only assigned to classes 1, 3 through 6, 8, and 9 as shown in **Table 25-3** through **Table 25-6**. These are determined based on flash points, boiling points, and toxicity.

Note Placards are useful because they take advantage of four ways to communicate the hazard class they represent.

Packing Groups

FLAMMABILITY—CLASS 3 PACKING GROUP (PG)	FLASH POINT (°F)	BOILING POINT (°F)
I		≤ 95
II	< 73	> 95
III	≥ 73 and ≤ 141	> 35

TABLE 25-3

Division 2.3, Poisonous Gas

HAZARD ZONE	INHALATION TOXICITY—LETHAL CONCENTRATION (LC_{50})*
Hazard Zone A	LC_{50} less than or equal to 200 ppm
Hazard Zone B	LC_{50} greater than 200 ppm and less than or equal to 1,000 ppm
Hazard Zone C	LC_{50} greater than 1,000 ppm and less than or equal to 3,000 ppm
Hazard Zone D	LC_{50} greater than 3,000 ppm and less than or equal to 5,000 ppm

*LC_{50} is the lethal concentration to 50 percent of an exposed population (gases).

TABLE 25-4

Division 6.1, Packing Materials That Are Toxic by a Route Other Than Inhalation

PACKING GROUP	ORAL TOXICITY—LETHAL DOSE (LD_{50})* (MG/KG)	DERMAL TOXICITY—LETHAL DOSE (LD_{50}) (MG/KG)	INHALATION BY DUSTS AND MISTS LC_{50} (MG/L)
I	≤ 5	≤ 40	≤ 0.5
II	$<5, \leq 50$	$>40, \geq 200$	$>0.5, \leq 2$
III	Solids: $>50, \leq 200$ Liquids: $>50, \leq 500$	$>200, \leq 1{,}000$	$>2, \leq 10$

*(LD_{50}) Lethal dose to 50 percent of the exposed population (solids and liquids).

TABLE 25-5

Division 6.1, Toxic Materials Poisonous by Inhalation

PACKING GROUP	VAPOR CONCENTRATION AND TOXICITY
I (Hazard Zone A)	$V \geq 500\ LC_{50}$ and LC_{50} 200 mL/m^3

TABLE 25-6

They have distinct colors, they have a picture at the top of the triangle depicting a representation of the hazard, they state the hazard class in the middle of the placard, and they display the hazard class and division number in the bottom triangle.

As an example the placard shown in **Figure 25-6** is black and white, which represents the corrosive class. The top of the placard has a picture of a hand and a steel bar being eaten away by the corrosive material being poured on it, the middle of the placard states corrosive, and at the bottom the class number 8 shows.

The DOT also requires the addition of a four-digit number, known as the United Nations/North America (UN/NA) identification number, either on a placard or on an adjacent orange strip. This identifies a bulk shipment of over 119 gallons and provides an identity to the material. A tank truck carrying gasoline, which would be considered a bulk shipment, would display a flammable placard[1] with the number 1203 either in the middle of the placard or on an orange strip adjacent to the placard as shown in **Figure 25-7**. This provides an additional bit of information to the responder, because without the UN/NA number, the only information provided would be that a flammable liquid was on board.

The nine hazard classes and subdivisions[2] are discussed next.

Class 1, Explosives (Figure 25-8)

- *Division 1.1.* Mass explosion hazard, such as black powder, dynamite, ammonium perchlorate, detonators for blasting, and RDX explosives.
- *Division 1.2.* Projectile hazard, such as aerial flares, detonating cord, detonators for ammunition, and power device cartridges.
- *Division 1.3.* Fire hazard or minor blast hazard. Examples include liquid-fuel rocket motors and propellant explosives.
- *Division 1.4.* Minor explosion hazard, which includes line throwing rockets, practice ammunition, detonation cord, and signal cartridges.
- *Division 1.5.* Very insensitive explosives, which do have mass explosion potential but during nor-

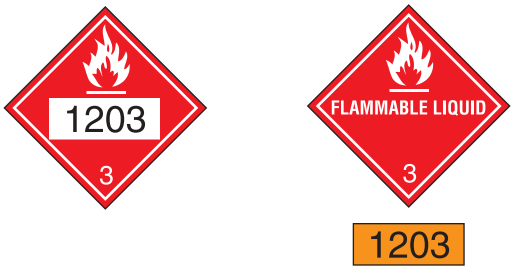


Figure 25-7 There are three ways to signify the four-digit ID number for bulk shipments. The most common is for the four-digit DOT identification number to be placed in the middle of the placard.

mal shipping would not present a risk. Ammonium nitrate and fuel oil (ANFO) mixtures are an example of this division.

- *Division 1.6.* Also very insensitive explosives that do not have mass explosion potential. Materials that present an unlikely chance of ignition are part of this grouping.

Safety Incidents involving explosives can be very dangerous, especially when involved in fire.

Making a tactical decision to attack a fire involving explosives can endanger the responders, especially if the fire has reached the cargo area of the vehicle. The recommendations in the **Emergency Response Guidebook (ERG)** should be followed, paying particular attention to the isolation and evacuation distances. When explosives are involved in traffic accidents not involving fire, the actual threat is minimized depending on the circumstances. As long as the explosives were transported legally and as they were intended to be transported, the responders should face little danger. Some cities require an escort and that the explosives be transported at nonpeak hours. Spilled explosive materials may present a health hazard if inhaled or absorbed through the skin.

Figure 25-8 "Explosive" placards and labels.

ANFO Explosion On November 29, 1988, an engine company from the Kansas City, Missouri, Fire Department was dispatched to a reported pickup truck fire. While en route to the incident the engine company was told to use caution because explosives were reportedly involved. When they arrived they found that they had two separate fires, one in the pickup truck and the other in a trailer. The first engine began to extinguish the fire in the pickup truck and requested a second engine for assistance as well as the district battalion chief. They attempted to contact the second engine to warn them of the explosives on fire on top of the hill. The second engine arrived and began to attack the fire on top of the hill. They requested the assistance of the first engine and also requested a squad for water. From the radio communications with the battalion chief the crews thought that the explosives had already detonated.

The battalion chief was a quarter of a mile away where he had stopped to talk with the security guards when the explosives detonated. The explosion moved the chief's car 50 feet and blew in the windshield. The blast was heard for 60 miles and damaged homes within 15 miles. The chief requested additional assistance and staged the responding companies. There was a report that there were more explosives on the hill that had not yet detonated. Luckily the chief did not let any other responders into the scene because shortly after pulling back, a second explosion went off, reportedly larger than the first one.

The next morning a team of investigators went to the site to begin the investigation. They discovered that six firefighters were killed in the blast and the explosion was very devastating. Only one engine was recognizable; the other was reduced to the frame rail. The first blast was from 17,000 pounds of an ammonium nitrate, fuel oil, and aluminum mixture. It also had 3,500 pounds of ANFO. The second explosion involved 30,000 pounds of the mixture. The use of ANFO is common throughout the United States for blasting purposes. Ammonium nitrate is commonly used as a fertilizer in the agricultural business and is used on residential lawns. The Oklahoma City Alfred P. Murrah Federal Building explosive was devised of ammonium nitrate and nitromethane, very similar to ANFO. The World Trade Center bombing in 1993 used an explosive made up primarily of urea nitrate and three cylinders of hydrogen. Both explosives are comparable to each other, and when they are used improperly the results can be devastating.

Class 2, Gases (Figure 25-9)

- *Division 2.1.* Flammable gases that are ignitable at 14.7 psi in a mixture of 13 percent or less in air, or have a flammable range with air of at least 12 percent regardless of the lower explosive limit (LEL). Propane and isobutylene are examples of this division.
- *Division 2.2.* Nonflammable, nonpoisonous, compressed gas, including liquefied gas, pressurized **cryogenic gas**, and compressed gas in solution. Carbon dioxide, liquid argon, and nitrogen are examples.
- *Division 2.3.* Poisonous gases that are known to be toxic to humans and would pose a threat during transportation. Chlorine and liquid cyanogen are common examples of this division. Gases assigned to this division are also assigned a letter code identifying the material's toxicity levels. These levels are discussed further in the section on toxicology. The hazard zones associated with this division are:

  Hazard Zone A: LC_{50} less than or equal to 200 ppm
  Hazard Zone B: LC_{50} greater than 200 ppm and less than or equal to 1,000 ppm
  Hazard Zone C: LC_{50} greater than 1,000 ppm and less than or equal to 3,000 ppm
  Hazard Zone D: LC_{50} greater than 3,000 ppm and less than or equal to 5,000 ppm

The hazard zones are a quick way to determine how toxic a material is. Hazard Zone A materials are more toxic than Hazard Zone B materials, and so forth. The shipping papers will identify these by the addition of Poison Inhalation Hazard (PIH) Zone A, B, C, or D.

Class 3, Flammable Liquids (Figure 25-10)

- Flammable liquids have a flash point of less than 141°F. Gasoline, acetone, and methyl alcohol are examples.
- Combustible liquids are those with flash points above 100°F and below 200°F. The DOT allows liquids with a flash point of 100°F to be shipped as a combustible liquid. Examples include diesel fuel, kerosene, and various oils.

> **Caution** The difference between a flammable liquid and a combustible liquid is based on the material's flash point. The flash point is the temperature of the liquid at which there could be a flash fire if an ignition source is present. The fire service usually refers to a flammable liquid as one that has a flash point of 100°F or lower. The DOT classifies any liquid with a flash point of 141°F or lower as being a flammable liquid. Any liquid with a flash point greater than 141°F is considered combustible by the DOT. It can be confusing when using the terms *flammable* and *combustible* to describe a liquid material. Most references, with the exception of the DOT, use 100°F as the criteria for flammable and combustible.

Figure 25-9 "Gas" placards and labels.

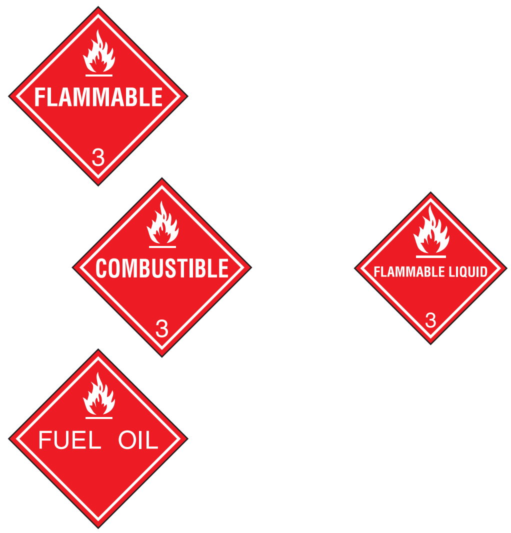


Figure 25-10 "Flammable" and "Combustible" placards and label.

Figure 25-11 Class 4 placards and labels.

Figure 25-12 Class 5 placards and labels.

Class 4, Flammable Solids (Figure 25-11)

- *Division 4.1.* Includes wetted explosives, self-reactive materials, and readily combustible solids. Examples include magnesium ribbons, picric acid, explosives wetted with water or alcohol, or plasticized explosives.
- *Division 4.2.* Composed of spontaneously combustible materials including pyrophoric materials or self-heating materials. An example is zirconium powder.
- *Division 4.3.* Dangerous-when-wet materials are those that when in contact with water can ignite or give off flammable or toxic gas. Calcium carbide when mixed with water makes acetylene gas, which is very flammable as well as unstable in this form. Sodium is another example of a material that when wet can ignite explosively. Lithium and magnesium are not as explosive as sodium but will react with water. Magnesium if on fire will react violently if water is used in an attempt to extinguish the fire.

Class 5, Oxidizers and Organic Peroxides (Figure 25-12)

- *Division 5.1.* The class assigned to materials that have the ability to produce oxygen, which in turn increases the chance of fire, and during fires make the fire burn more intensely. Ammonium nitrate and calcium hypochlorite are examples.
- *Division 5.2.* The organic peroxides, which have the ability to explode or polymerize, which if contained is an explosive reaction. These are further subdivided into seven types:

  Type A: Can explode upon packaging. These are DOT forbidden, which means they cannot be transported and must instead be produced on site.
  Type B: Can thermally explode, considered a very slow explosion.
  Type C: Neither detonates nor **deflagrates** rapidly, and will not thermally explode.
  Type D: Only detonates partially or deflagrates slowly, and has medium or no effect when heated and confined.
  Type E: Shows low or no effect when heated and confined.
  Type F: Shows low or no effect when heated and confined, and has low or no explosive power.
  Type G: Is thermally stable and is desensitized.

Class 6, Poisonous Materials (Figure 25-13)

- *Division 6.1.* Materials that are so toxic to humans that they would present a risk during transportation. Examples include arsenic and aniline.
- *Division 6.2.* Composed of microorganisms or their toxins, which can cause disease to humans or animals. Anthrax, rabies, tetanus, and botulism are examples.

Hazard zones are associated with Class 6 materials:

- *Hazard Zone A:* LC_{50} less than or equal to 200 ppm
- *Hazard Zone B:* LC_{50} greater than 200 ppm and less than or equal to 1,000 ppm.

Class 7, Radioactive Materials (Figure 25-14)

- Those materials determined to have radioactive activity at certain levels.
- Although there is only one placard, the labels shown in **Figure 25-14** are further subdivided

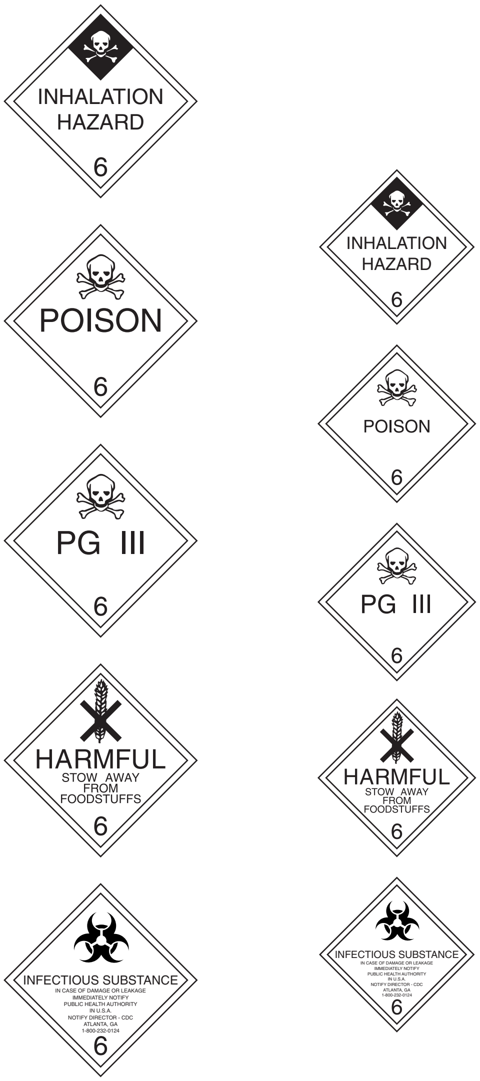


Figure 25-13 Class 6 placards and labels.

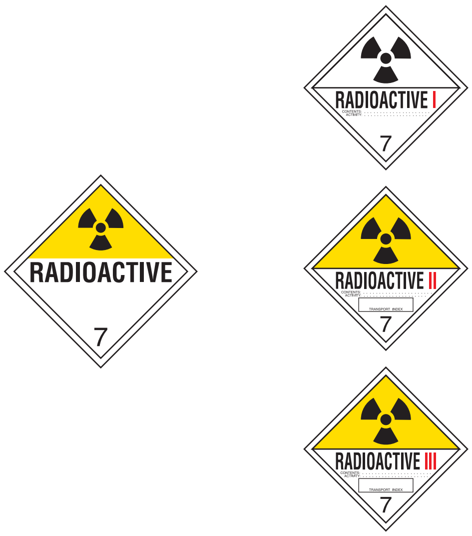


Figure 25-14 Class 7 placards and labels.

Figure 25-15 Class 8 placards and label.

into Radioactive I, II, and III, with level III being the highest hazard. The designation I, II, or III is dependent on two criteria: the transport index and the radiation level coming from the package. The transport index is the degree of control the shipper is to use and is based on a calculation of the radiation threat the package presents. Responders should understand that a package labeled radioactive may be emitting radiation. These emissions of radiation are legal within certain guidelines:

- Radioactive I label—less than 0.005 mSv/hr (0.5 mR/hr)
- Radioactive II label—more than Radioactive I and less than 0.5 mSv/hr (50 mR/hr)
- Radioactive III label—more than Radioactive II and less than 2 mSv/hr (200 mR/hr)

Packages emitting more than 2 mSv/hr require special handling and transportation and are subject to additional regulations.

Class 8, Corrosives (Figure 25-15)

- Includes both acids and bases, and is described by the DOT as a material capable of causing visible destruction in skin or corroding steel or aluminum. Examples include sulfuric acid and sodium hydroxide.

Class 9, Miscellaneous Hazardous Materials (Figure 25-16)

- A general grouping that is composed of mostly hazardous waste. Dry ice, molten sulfur, and polymeric beads are examples that would use a Class 9 placard.

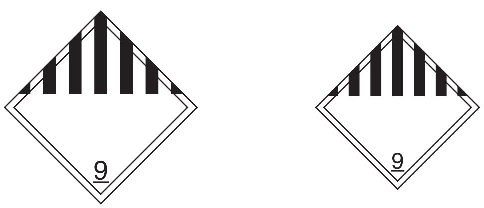


Figure 25-16 Class 9 placards and label.

Figure 25-17 "Dangerous" placard.

- This is known as a catch-all category. If a substance does not fit into any other category and presents a risk during transportation then it becomes Class 9.

Other Placards and Labels

- The Dangerous placard is used when the shipper is sending a mixed load of hazardous materials. If the shipper sends 2,000 pounds of corrosives and 2,000 pounds of a flammable liquid, then instead of displaying two placards the shipper can display a Dangerous placard, as shown in **Figure 25-17**. If any of the items exceeds 2,205 pounds and is picked up at one location, then in addition to the Dangerous placard the shipper is to display the placard for the material that exceeds the 2,205 pounds.
- The Stow Away from Foodstuffs placard indicates that a poisonous material is being transported, but it is not poisonous enough to meet the rules to be placarded as a poison; most are PG III. Chloroform is an example that would use a placard like the one shown in **Figure 25-18**.
- "Other Regulated Material—Class D" (ORM-D) is a classification that is left over from a previous DOT regulation. It is a subdivision that includes ammunition and consumer commodities, such as cases of hair spray. The package will have the printing "ORM-D" on the outside of the package. The previous regulation used to have ORM-A through ORM-E, but these are now grouped together in Class 9, Miscellaneous Hazardous Materials.

Figure 25-18 "Harmful" placard.

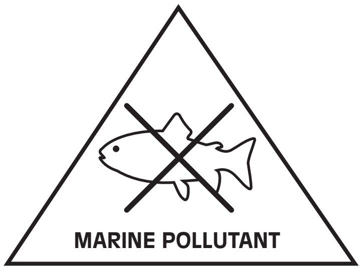


Figure 25-19 "Marine Pollutant" marking.

- "Marine Pollutant" is displayed on shipments that, if the material were released into a waterway, would damage the marine life, **Figure 25-19**.
- Elevated temperature material will have a "HOT" label either to the side of or on the placard, as shown in **Figure 25-20**, if it meets one of the following criteria:
  - Is a liquid above 212°F.
  - Is a liquid that is intentionally heated and has a flash point above 100°F.
  - Is a solid at 464°F or above.
  - "Infectious Substances" is a label like the one shown in **Figure 25-21** that is sometimes used on the outside of trucks. It is not required by the DOT but may be required by other agencies such as Health and Human Services or a state agency.
  - The Fumigated placard, like the one shown in **Figure 25-22**, is used when a trailer or railcar has been fumigated with a poisonous material. This placard is commonly found near ports where containers are frequently fumigated after arriving from a foreign port.

A white square background as shown in **Figure 25-23** is used in the following situations:

- On the highway for controlled Radioactive III shipments

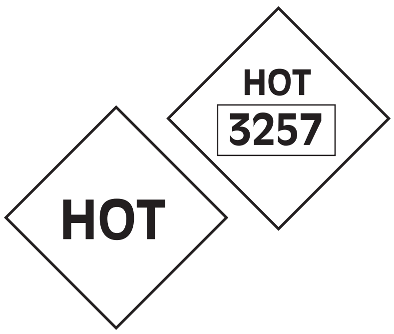


Figure 25-20 "Hot" placard.

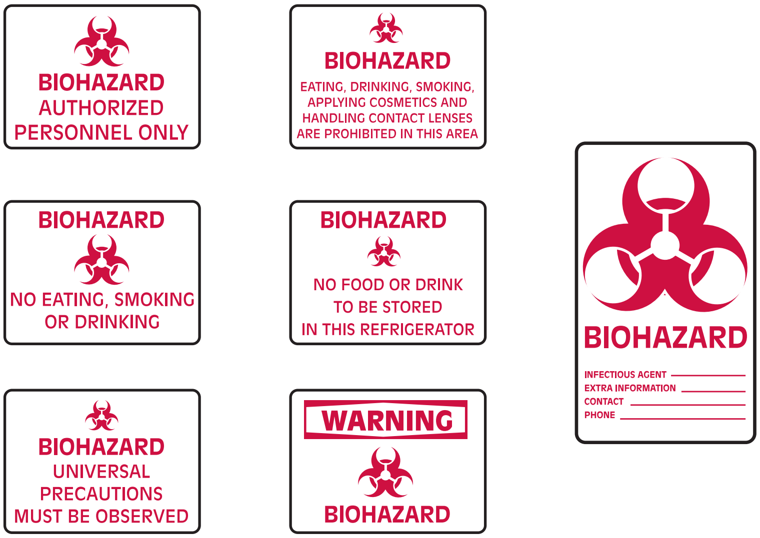


Figure 25-21 "Biohazard" labels.

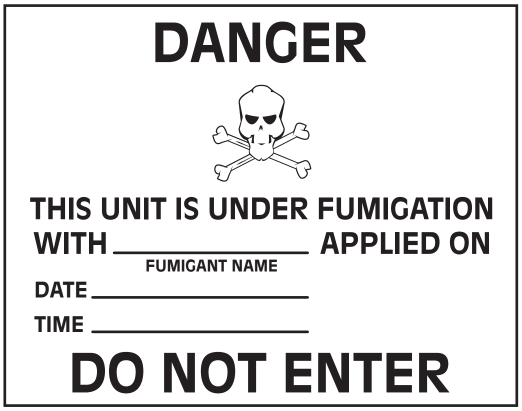


Figure 25-22 "Fumigation" marking.

Figure 25-23 White-squared "Flammable Gas" placard.

- On rail for:
  - Explosives 1.1 or 1.2
  - Division 2.3 Hazard Zone A (poison gas) materials
  - Division 6.1 Packing Group I Hazard Zone A (poison)
  - Division 2.1 (flammable gas) in a DOT 113 tank car
  - Division 1.1 or 1.2, which is chemical ammunition that also meets the definition of a material that is poisonous by inhalation

Problems with the Placarding System

The placarding system relies on a human to determine the extent of the load, determine the appropriate hazard classes, and interpret difficult regulations to determine if a placard is required. The placard then must be affixed to all four sides of the vehicle before shipment. Placards are only required for shipments that exceed 1,001 pounds, except for materials listed in **Table 25-1**, which require placarding at any amount. It is suspected that 10 to 20 percent of the trucks traveling the highway are not placarded at all or not placarded correctly.

> **Caution** Given the restrictions of many cities, bridges, and tunnels where hazardous materials are not allowed, many trucks are probably not carrying the proper designations.

A placard can come off during transport and legally may not have to be immediately replaced. The fact that an incident involves a truck or train should alert the first responder to the potential for hazardous materials, and when a placard is involved extra precautions should be taken.

Streetsmart Tip A tractor trailer was involved in an accident and had jackknifed in Baltimore County, Maryland. The HAZMAT team was called to assist with the fuel spill. Upon arrival the HAZMAT team inquired as to the contents of the truck and was told by the first responders that the truck was carrying rocking chairs. While working to control the fuel leak the HAZMAT team noticed a greenish blue liquid coming from the front of the trailer, where it had been damaged in the accident. They located the driver and asked him about the contents of the trailer, which did not display a placard. The driver stated he was carrying rocking chairs, which is what the shipping papers showed the load to be.

The crews opened the back of the trailer to inspect the cargo and found rocking chairs. Upon closer inspection of the front of the truck, several drums were noticed in the very front of the trailer. When the driver was confronted by the HAZMAT team and a state trooper, the driver confessed he had picked up a load of unknown waste from his first stop. He did not know the contents of the drums and it took several days to determine the exact contents of the drums. Beware—it is unlikely that someone trying to evade the law will mark the shipment appropriately.

Labels

Labeling and Marking Specifics

Package markings must include the shipping name of the material, the UN/NA identification number, and the shipping and receiving companies' names and addresses. Packages that contain more than a **reportable quantity (RQ)** of a material must also be marked with an RQ near the shipping name. Packages that are listed as ORM-D materials should be marked as such. Some packages with liquids in them must use orientation arrows. Materials that pose inhalation hazards must affix an Inhalation Hazard label next to the shipping name, as shown in **Figure 25-24**. Hazardous wastes will be marked "Waste" or will use the EPA labeling system to identify these packages.

Labels are identical to placards, other than their size.

Note Materials that have more than one hazard may be required to display a primary hazard label and a subsidiary label.

The primary label will have the class and division number in the bottom triangle, while the subsidiary label will not have the number at all, as shown in **Figure 25-25**. As an example, the material

Figure 25-24 The DOT adds the "Poison—Inhalation Hazard" label to those materials that present severe toxic hazards.

Figure 25-25 Primary and subsidiary placards.

acrylonitrile, inhibited, is required to be labeled "Flammable" with a subsidiary label of "Poison."

OTHER IDENTIFICATION SYSTEMS

There are several other identification systems that are used in private industry to mark facilities and containers. Military shipments and pipelines are also marked to provide a warning as to the potential for hazardous materials. Much like the transportation system the warnings are a clue to the potential presence of hazardous materials that could cause harm to the responders.

NFPA 704 System

One of the other more common systems used to identify the presence of hazardous materials is the NFPA 704 system. This system is designed for buildings, not transportation, and alerts the first responders to the potential hazards in and around a facility. The system is much like the placarding system and relies on a triangular sign that is divided into four areas, as shown in **Figure 25-26**. The four areas are divided by color as well, and use a ranking system to identify severity. The four areas and colors are:

- Health hazard—blue
- Fire hazard—red
- Reactivity hazard—yellow
- Special hazards—white

Figure 25-26 NFPA 704 system placard.

The system uses a ranking of 0–4 with 0 presenting no risk and a ranking of 4 indicating severe risk. The specific listings are discussed next.

Health

This listing is based on a limited exposure to the materials using standard firefighting protective clothing as the protective clothing for the exposure.

4—Severe health hazard
3—Serious health hazard
2—Moderate hazard
1—Slight hazard
0—No hazard

Flammability

This listing pertains to the ability of the material to burn or be ignited.

4—Flammable gases, volatile liquids, pyrophoric materials
3—Ignites at room temperature
2—Ignites when slightly heated
1—Needs to be preheated to burn
0—Will not burn

Reactivity

This listing is based on the material's ability to react, especially when shocked or placed under pressure.

4—Can detonate or explode at normal conditions
3—Can detonate or explode if strong initiating source is used
2—Violent chemical change if temperature and pressure are elevated
1—Unstable if heated
0—Normally stable

Special Hazards

This listing is used to indicate water reactivity and oxidizers, which are included in the NFPA 704 system. In some cases other symbols may be used such as the tri-foil for radiation hazards, "ALK" for alkalis, and "CORR" for corrosives. In the presence of the slashed W there is also an accompanying ranking structure for water reactivity in addition to the hazards listed in the other triangles:

4—Not used with the slashed W and a reactivity ranking of 4
3—Can react explosively with water
2—May react with water or form explosive mixtures with water
1—May react vigorously with water
0—Slashed W is not used with a reactivity ranking of 0

Some potential problems exist with the NFPA 704 system, because it groups all of the chemical hazards listed in a building into one sign. If the sign is placed on a tank that contains one material, the system does a good job of warning about the contents of the tank, but does not provide the name of the product. For a facility that has hundreds—if not thousands—of materials, the system will only warn of the worst-case scenario. As an example, dramatically different tactics are used to handle a flammable gas incident versus a flammable liquids incident, but both can be classified as fire hazard 4. The system is best used to alert the first responder to the presence of hazardous materials and to warn of the worst-case scenario.

Hazardous Materials Information System

Commonly referred to as HMIS, the Hazardous Materials Information System was designed to provide a mechanism to comply with the federal hazard communication regulation, which requires that all containers be marked with the appropriate hazard warnings and the ingredients be provided on the label, **Figure 25-27**. Many products that come into the workplace are missing adequate warning labels. The HMIS is not a uniform system. It can be developed by the facility or by the manufacturer of the labels, so one system may vary from another. Most systems are similar to the NFPA 704 system and use blue, red, and yellow colors with a numbering system that provides an indication of hazard. The colors may be used in a triangle format or, in most cases, as stacked bars. The numbers are usually 0–4, the same as the NFPA system, but in rare cases may differ from the NFPA system. The facility manager or other representative should have the key to the symbols, or a chart should be provided somewhere in the facility indicating what the symbols and the warning levels are. The chart is usually stored with the MSDS. In most cases, a central location should be chosen for the MSDS and other hazard communication information.

In some systems, a picture is provided of the level of PPE required for the substance. Each HMIS is different, and responders should not assume any particular hazard level until the warning levels can be determined.

Figure 25-27 HMIS label.

Military Warning System

The military uses the DOT placarding system when possible, but in some cases may use its own system. Within the DOT's *Emergency Response Guidebook,* an emergency contact number is given when responding to an incident involving a military shipment.

In most cases, for extremely hazardous materials, arms, explosives, or secret shipments, firefighters can assume prior to their arrival that the military is already aware of the incident and probably already responding. The higher the hazard the more likely there will be an escort for the shipment. There may be shipments in which the driver of the truck is not allowed to leave the cab of the truck and may provide warnings to stay away from the truck.

Safety For high-security shipments the driver is armed as are the personnel in the escort vehicle. If an incident occurs involving one of these vehicles, firefighters must obey the commands of the escorting personnel and determine if they have made the appropriate notifications.

If the driver and escort crew are killed or seriously injured in the accident, it would be advisable to notify the military about the incident, although with satellite tracking help is probably already on the way. The phone number to contact the military is in the DOT ERG, along with **Chemtrec's** and other emergency contact numbers.

Other incidents involving fuels, food, or military equipment may require notification of the military.

The military typically uses its own marking system at its facilities to mark the buildings. The military uses a series of symbols and a numerical ranking system as shown in **Figure 25-28**.

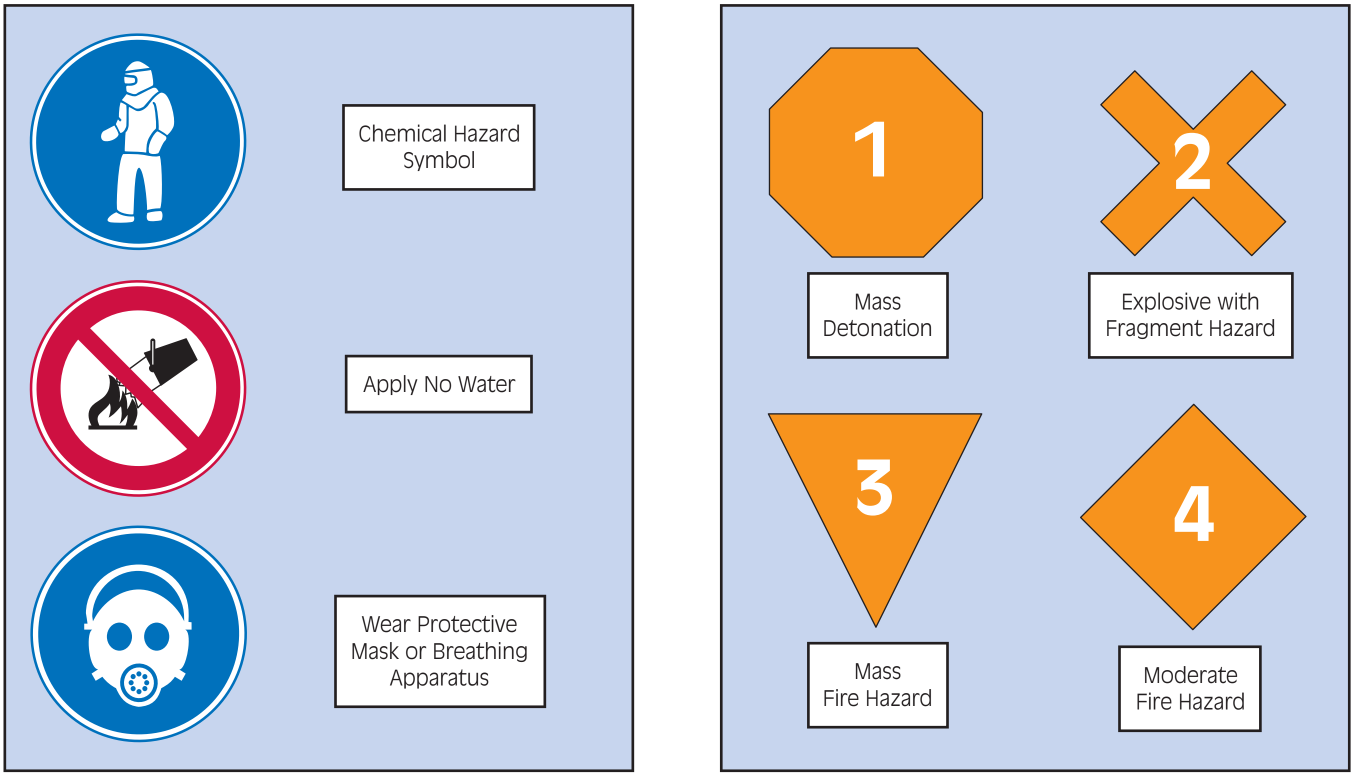


Figure 25-28 Military placards.

Pipeline Markings

Any place an underground pipeline crosses a mode of transportation the pipeline owner is required to place a sign like the one shown in **Figure 25-29** that indicates the pipeline contents, owner, and emergency contact number. The pipeline contents may be general, as in "petroleum products," because the same pipeline may be used to ship fuel oil, gasoline, motor oil, or other products. Dedicated pipelines that carry only one product will be marked with the specific product that it carries. The pipeline should be buried a minimum of 3 feet and should be adequately marked.

Figure 25-29 The owner of a pipeline is required to provide the contents of the pipe, the owner's name, and an emergency contact number.

Many of the larger pipelines, such as the Colonial pipeline that originates in Texas and ends in New York, are 26 inches in diameter along the main pipeline. In the event of a release involving the pipeline, the line will be shut down immediately. Even with this immediate shutdown, the potential exists to lose several hundred thousand gallons of hazardous materials because the distance between the shutoffs is substantial.

An incident involving a pipeline can be a serious event—firefighters should not underestimate the need for considerable local, state, and federal resources. Within the fire department alone, considerable resources may be required such as command staff, logistic support, communications, and tactical units. A fuel oil pipeline rupture in Reston, Virginia, resulted in the loss of more than 400,000 gallons of fuel, requiring considerable resources from several states to control the spill. The resources included emergency response organizations; local, state, and federal assistance; and a considerable number of private cleanup companies.

> **Note** Some pipelines move one type of product, while others move several different types each day.

The product in the pipelines varies from liquefied gases and petroleum products to slurried material. Pipeline companies are required to conduct in-service training and tours for the emergency responders in the communities their pipelines transverse. When firefighters have an incident on or near any pipeline, it is advisable to notify the pipeline owner of the incident, even if they are pretty sure the pipeline was not damaged. A train derailment in California caused a pipeline to shift, and the pipeline did not release any product until several days after the original derailment occurred. Most pipeline operators would like to have the opportunity to check the line as opposed to having a catastrophic release several days later because the line was not checked.

Container Markings

Most containers such as drums are marked with the contents of the drum, **Figure 25-30**, while cylinders have the name of the product stenciled on the side of the cylinder. In bulk shipments the bulk container will have the name of the product stenciled on the side.

Figure 25-30 The label describes the contents of the drum.

Figure 25-31 "Pesticide" placards.

Trucks that are dedicated haulers will also stencil or mark the product name on two sides of the vehicle.

Pesticide Container Markings

Due to their toxicity, pesticides are regulated by the EPA as to how they are to be marked. The label on a pesticide container, such as the one shown in **Figure 25-31**, will have the manufacturer's name for the pesticide, which is not usually the chemical name for the product. The label will also contain a signal word such as "Danger," "Warning," or "Caution."

In the United States the EPA issues an EPA registration number and in Canada the label will have a pest control number. The label will also include a precautionary statement and a hazard statement, examples of which include "Keep from Waterways," and "Keep Away from Children." The active ingredients will be listed by name and percentage; in most cases the active ingredients are usually a small percentage of the product. Inert ingredients are also listed but not specifically named. For liquid pesticides the "inert" ingredient is usually kerosene or diesel fuel, an item not normally considered "inert," except by the EPA.

CONTAINERS

Hazardous materials come in a variety of containers of many shapes and sizes, from 1-ounce bottles and larger bags to tanks and ships carrying hundreds of thousands of gallons. A survey of the materials in the average home will reveal a wide variety of storage containers. Compressed gas cylinders hold propane; steel containers hold flammable and combustible liquids; bottles, jars, and small drums hold various products. Plastic-lined cardboard boxes, and bags of various types are also used for chemical storage.

The type of material and the end use for the product determine the packaging. Packaging used to store household or consumer commodities is usually different than the industrial version. In some cases the industrial version may be full-strength undiluted product, whereas the household version is only a small percentage of that strength mixed with a less hazardous substance such as water. The type of container usually provides a good clue as to the contents of the package.

Streetsmart Tip The more substantial, durable, and fortified a container is, like the container shown in **Figure 25-32**, the more likely the material inside is dangerous.

On the other hand, materials transported in fiberboard drums usually have no significance with regard to human health, although they may pose a risk to the environment.

Figure 25-32 The type of container can provide some clues as to the contents of the container. Because this drum is reinforced, it has a high likelihood of containing an extremely hazardous material.

When looking at the recognition and identification process, **first responders** should be alert for anything unusual when arriving at an incident. When on an EMS call to a residential home, it would be unusual to find a 55-gallon drum in a bedroom along with glassware associated with a lab environment. These types of recognition and identification clues should alert the first responders that additional assistance may be required. Arriving at an auto repair garage and finding 55-gallon drums and compressed gas cylinders should not be unexpected, however.

General

Containers come in a variety of sizes and shapes and the general category of containers is not exceptional. Most of the general containers are designed for household use but will be carried in large quantities when moved in transportation. When moving to bags and into drums and cylinders the move is made from household to industrial use. All of these types can be used in the home, but a super sack which can hold thousands of pounds of materials is not usually considered household.

Cardboard Boxes

With the popularity of shopping clubs and discount warehouses, more and more homeowners are buying materials by the case, when in the past they bought in much smaller quantities. Cardboard boxes are used to ship and contain hazardous materials. They can hold glass, metal, or plastic bottles. In some cases they may have a plastic lining, such as the box shown in **Figure 25-33**, which holds sulfuric acid. Many household pesticides, insecticides, and fertilizers are contained in cardboard boxes. With the exception of these products and sulfuric acid, most products contained in boxes are usually not extremely toxic to humans, but may present an environmental threat. Materials in transport to suppliers may be transported in larger cardboard boxes and then broken down at the retail level. Responders should note any labels on these packages, but the absence of any labels does not indicate that hazardous materials are not present.

Bottles

From 1-ounce bottles to 1-gallon bottles, the variety of containers is endless and the types of products contained in them too numerous to mention. In recent times manufacturers have begun to take precautions when packaging their materials for transport and use, especially when glass bottles are used. Nowadays, when chemicals are shipped in glass

Figure 25-33 Typically, chemicals that can cause harm are not packaged in cardboard. This sulfuric acid is one example of a material that can cause harm, but unfortunately is packaged in cardboard.

bottles, the bottles are usually packed in cardboard boxes and insulated from potential damage. One-gallon glass containers are usually shipped in what is known as carboys, like the one shown in **Figure 25-34**. Carboys provide a protective cover to

Figure 25-34 To protect the glass bottle, which has a corrosive in it, a carboy is used in case the bottle is dropped.

protect against potential damage during transportation. If the container is dropped, the bottle should survive the fall. Carboys are usually seen in laboratories and in smaller chemical production facilities.

Ensuring the material's compatibility with the container it will be stored in is important, but the one area that usually results in a release is the use of an improper cap. The chemical must not only be compatible with the glass, it must also be compatible with the material the lid is composed of. A variety of materials are used in the manufacturing of lids. Many new glass containers, like the one shown in **Figure 25-35**, are coated with plastic to avoid the bottle being broken when dropped. Even if the bottle is cracked, the contents are supposed to remain sealed within the plastic coating.

Bags

Bags are also commonly used as containers for chemicals. Bags can be as simple as paper bags or plastic-lined paper bags to fiber bags, plastic bags, and the reinforced super sacks or tote bags. It might be a surprise to open the back of a trailer and find four super sacks like those shown in **Figure 25-36** carrying a material that is classified as a poison. Bags

Figure 25-35 This glass jar is coated with a plastic coating that will not allow the liquid to spill out if the glass is broken or dropped.

Figure 25-36 It can be quite surprising to open the back of a tractor trailer and find these super sacks. They can hold solid materials, some of which can be toxic.

carry anything from food items to poisonous pesticides, and the method of transportation varies widely.

Drums

When discussing hazardous materials, drums are the containers with which most responders are familiar. They vary from 1-gallon sizes up to a 95-gallon overpack drum. The construction varies from fiberboard to stainless steel. The typical drum holds 55 gallons and weighs 400 to 1,000 pounds. It is possible to get an idea of what a drum may contain by the construction of the drum. **Table 25-7** provides an indication of potential drum contents, but this is not an absolute listing; contents can and do vary from drum to drum.

Cylinders

Cylinders, like those shown in **Figure 25-37**, come in 1-pound sizes up to several thousand pounds and carry a variety of chemical products. The product and its chemical and physical properties will determine in what type of container the product is stored.

Caution Other than the hazard of the chemical itself, the big hazard of all cylinders is that they are pressurized.

The pressures range from a low of 200 psi to a high of 5,000 psi. One of the most common cylinders firefighters run across is the propane tank, which range from 1 pound up to millions of gallons. In residential homes, firefighters will find everything from the 20-gallon cylinder for barbecues to the 100- to 250-pound cylinders used as a fuel source for the home. In some areas it is not uncommon to find 1,000-pound cylinders and often they are buried underground.

Specialized cylinders that hold cryogenic gases (extremely cold) appear to be high pressure, but in reality are low pressure. The bulkiness of the cylinders is a result of the large amount of insulation required to keep the material cold. Cylinders usually have **relief valves** or **frangible disks** in the event they are overpressurized or are involved in a fire. Most communities, regardless of their size, have

Drum Contents

TYPE OF DRUM	POSSIBLE CONTENTS (IN ORDER OF LIKELIHOOD)
Fiberboard (cardboard), unlined	Dry, granular material such as floor sweep, sawdust, fertilizers, plastic pellets, grain, etc.
Fiberboard, plastic lined	Wetted material, slurries, foodstuffs, material that may affect cardboard or could permeate the cardboard
Plastic (poly)	Corrosives such as hydrochloric acid and sodium hydroxide, some combustibles, foodstuffs such as pig intestines
Steel	Flammable materials such as methyl alcohol, combustible materials such as fuel oil, motor oil, mild corrosives, and liquid materials used in food production
Stainless steel	More hazardous corrosives such as oleum (concentrated sulfuric acid)
Aluminum	Pesticides or materials that react with steel and cannot be shipped in a poly drum

TABLE 25-7

Figure 25-37 Cylinders present additional risks to responders because not only can the contents be hazardous, but if the cylinder is involved in a fire it may explode.

cylinders of chlorine and sulfur dioxide used in water treatment. These cylinders come in 100- to 150-pound and 1-ton cylinders, which could create a major incident if they were ruptured or suffered a release.

> **Note** The area affected by a 100-pound chlorine cylinder release can be several miles, **Figure 25-38**, causing serious injuries if not fatal effects.

Totes and Bulk Tanks

Both **totes** and **bulk tanks** are becoming more common, sized as they are between drums and tank trucks, and are used for a variety of purposes. Used in industrial and food applications, they hold flammable, combustible, toxic, and corrosive materials. They are constructed of steel, aluminum, stainless steel, lined materials, poly tanks, and other products, **Figure 25-39**. They can carry up to 500 gallons, but the usual capacity is 300 gallons. They are transported on flatbed tractor trailers or in box-type tractor trailers.

A common incident with totes can occur during offloading. Tanks are offloaded from the bottom through a swinging valve, such as the one shown in **Figure 25-40**. It is a common occurrence for this valve to swing out during transport and get knocked off during movement.

One unusual tote is made to transport calcium carbide, a material that when it gets wet forms acetylene gas, which is reactive and very flammable.

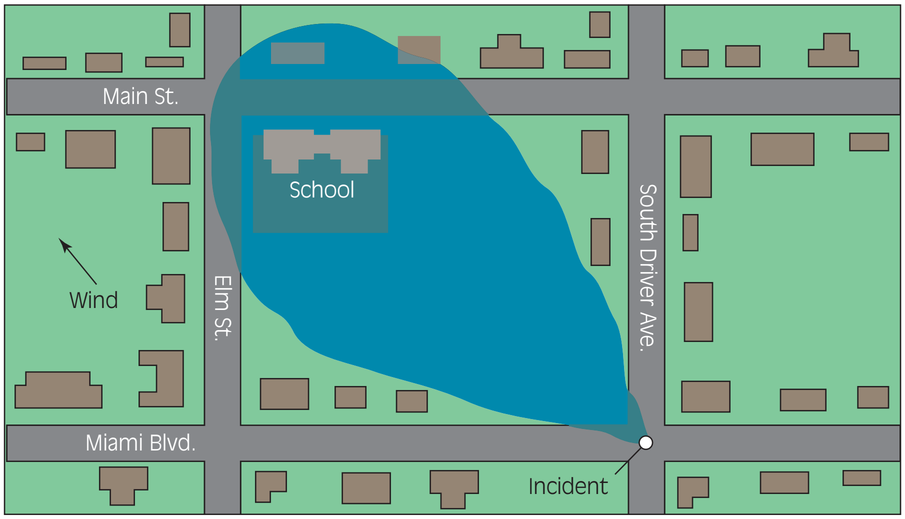


Figure 25-38 The type of vapor cloud commonly referred to as a plume varies with the terrain and buildings in the vicinity. The plume here represents one of the most common types.

Figure 25-39 The use of 55-gallon drums is decreasing and the use of these portable bulk tanks is increasing. Like the super sacks these can be hidden away in the back of a trailer.

Figure 25-40 The most common type of spill occurs when a valve is knocked off, releasing the contents.

Pipelines

Pipelines vary in size and pressure, but can be sized between 1/2 inch and more than 6 feet. They are commonly buried underground. The most common products they carry are natural gas, propane, and assorted liquid petroleum products. The larger petroleum pipelines originate in Texas and Louisiana and then proceed up throughout the East Coast. The West Coast also has its share of large pipelines, with Alaska having a majority. Pipelines can originate from any bulk storage facility and can cross many states, and some type of pipeline system is found in every state. Because the amount in the pipelines varies it is important that first responders know the location of the pipelines and emergency contact names and phone numbers so if there is a suspected problem they can notify the pipeline owner immediately.

Highway Transportation Containers

The type of vehicle provides some important clues as to the possible contents of the vehicle. The most common truck is a tractor trailer or a box truck. There are four basic tank truck types that carry hazardous materials, with some additional specialized containers. Tractor trailers carry the whole variety of hazardous materials and portable containers. They can carry loose material that is not contained in any fashion other than by the truck itself. They can carry portable tanks that hold 500 gallons or bulk bags that weigh several tons.

> **Caution** When dealing with tractor trailers the rule is to expect the unexpected.

Nothing is routine. Until the driver has been interviewed, the shipping papers looked at, and the cargo actually examined, a firefighter cannot confirm or deny the presence of hazardous materials. Sometimes the signage on the trailer is an indication of the possible contents, and a trailer that has several placard holders is a likely candidate for hazardous materials transport. If a tractor trailer is refrigerated like the one shown in **Figure 25-41** and is carrying hazardous materials, extra precautions must be taken because the materials may require the cold temperature to remain stable.

Leakage is often found in containers known as **intermodal containers** or, more commonly, **sea containers**. These types of containers are typically used on ships, then offloaded onto a tractor trailer or loaded directly onto a flatbed railcar. These containers come from all over the world and can contain any imaginable commodity.

> **Note** The types of containers that are shipped in these trailers vary from bags, boxes, and drums to bulk tanks and cylinders.

Although the driver is supposed to have the shipping papers for the contents, on occasion the paperwork is missing or is sealed in the back of the

Figure 25-41 Although in most cases refrigerated trailers are carrying food, there exists the possibility that they may have chemicals that require refrigeration to remain stable.

trailer. Determining the contents of a trailer can be very difficult and frustrating.

Tank trucks carry several hundred gallons up to a maximum of 10,000 gallons. The DOT allows maximum loads by weight not by gallons, so the actual capacity varies state to state. The most common tank truck is the gasoline tank truck, which usually carries 5,000 to 10,000 gallons. In September 1995 the DOT changed the regulations covering tank trucks, so two systems are used for identifying tank trucks, **Figure 25-42**. In the past the DOT wrote specifications as to how the manufacturer should build a tank truck. Today, they have established performance-based standards for the construction. The DOT allows trucks that were manufactured before the new regulation to remain on the road, as long as they meet the applicable inspection requirements. The four basic types of tank trucks are:

- DOT-406/MC-306 gasoline tank truck
- DOT-407/MC-307 chemical hauler
- DOT-412/MC-312 corrosive tanker
- MC-331 pressurized tanker

Figure 25-42 Many of the differences between a 306 and a 406 tank truck are internal. The biggest difference is that the dome covers on a 406 are less likely to open during a rollover, although the skin of the tank is thinner. *(Photo courtesy of Maryland Department of the Environment)*

The DOT numbers are the more recently manufactured tanks, and the MC (motor carrier) numbers identify those tanks manufactured prior to September 1995. There are some differences in construction of the two types—some of which favor the emergency responders, others favor the shipping company—but overall the newer tanks hold up better during accidents and rollovers. If unsure of the type of tank, all tank trucks have **specification (spec) plates**, which list all the pertinent information regarding that tank. The spec plate in many cases is located on the passenger side of the tank near the front of the tank. In some cases, shipping papers or MSDS are located in a paper holder as shown in **Figure 25-43** (tube).

Figure 25-43 In most cases the shipping papers will be with the driver in the cab of the truck, but they may be in a special tube located on the trailer.

Figure 25-44 The DOT-406/MC-306 is the most common truck on the highway today and is referred to as a gasoline tanker. It can and frequently does carry other types of flammable and combustible liquids. *(Photo courtesy of Maryland Department of the Environment)*

DOT-406/MC-306

This is the most common tank truck on the road today, **Figure 25-44**, and for that reason, along with the large number of shipments, suffers the most accidents. Although the most common products carried on these trucks are gasoline and diesel fuel, almost any flammable or combustible liquid can be found on these types of trucks. This truck is known for its elliptical shape and is usually made of aluminum. Older style tanks used to be made of steel, which presented an explosive situation known as a BLEVE. The tanks generally have three or four separate compartments, but two to five compartments are not uncommon. Newer style tanks have considerable vapor recovery systems as well as rollover protection, and in some cases these features are combined. The valving and piping are contained on the bottom of the tank, as shown in **Figure 25-45**, and the number of pots is indicated by the number of outlets as well as the number of manhole assemblies located on top of the tank. The maximum pressure that this truck can hold is 3 psi. The compartments are separated by bulkheads, which usually fail during a rollover situation. Although in most states the shipper is not allowed to ship a mixed load of flammable and combustible materials, widely differing loads can be encountered from compartment to compartment.

Figure 25-45 Most 406/306 trucks have more than one tank (pots) and the number of tanks is indicated by the number of valves or the number of dome covers on top of the truck. *(Photo courtesy of Maryland Department of the Environment)*

Caution During a rollover, the bulkheads may shift, allowing all products to mix.

On initial examination it may appear that only one tank has ruptured and is leaking, but it is possible to lose the entire contents of the tank through a leak in one compartment, like that shown in **Figure 25-46**. In the majority of rollovers experience has shown that at least one bulkhead has separated in almost every accident, resulting in product mixing. In most cases this is not a big problem because it may only be the mixing of different grades of gasoline. Within the individual tanks themselves, baffles limit the movement of the product within the tank. The emergency shutoff valves, **Figure 25-47**, are located on the driver's side near the front of the tank and near the piping on the passenger side.

DOT-407/MC-307

The DOT-407/MC-307 tankers are the workhorses of the chemical industry, **Figure 25-48**. They carry a variety of materials including flammable, combustible, corrosive, poisonous, and food products.

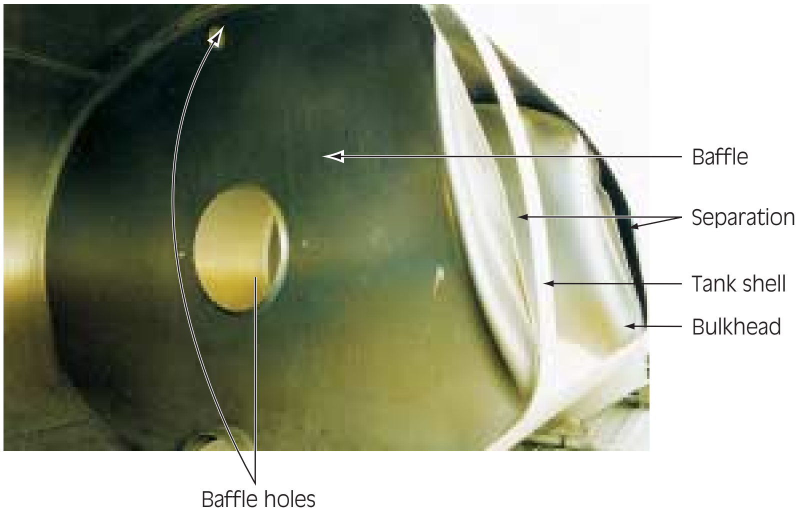


Figure 25-46 When a truck rolls over on its side, the internal baffles and bulkheads may shift. The internal baffles reduce the amount of sloshing the liquid will do when the truck starts and stops. The baffles will allow product to move through the holes in the baffle wall. A bulkhead separates the compartments and does not allow the products to mix. Shown in the photograph is an MC-306 that rolled on its side. The side wall of the tank has been cut away, revealing a baffle and a bulkhead. Also shown is the separation that took place between the tank shell and the baffles/bulkhead. When the tank wall was cut away, strips of the tank shell were left where they should have connected to a baffle or bulkhead.

The two basic types of chemical tanks are insulated and uninsulated. The insulated tank can have a number of additional concerns that do not apply to an uninsulated tank. These tanks usually hold 2,000 to 7,000 gallons, lower amounts than the 406/306 because most of the products they carry are heavier than petroleum products. The average amount found in these tanks is 5,000 gallons.

The uninsulated tank is round and has stiffening rings around the tank. The offloading piping is located on the bottom or off the rear of the tank. These tanks are composed of only one compartment, and its loading piping and manhole are usually on the top in the middle. These tanks generally do not hold up as well during rollovers

Figure 25-47 On most trucks there is a minimum of one emergency shutoff, and with most there are two. The most common location is near the driver's door; the other is usually located near the valve area.

Figure 25-48 On the right is an insulated MC-307/DOT-407, and on the left is an uninsulated MC-307/DOT-407. Both trucks hold comparable products, but the insulated one holds products that are heated or may require heating to offload.

Figure 25-49 This insulated version is identical to the uninsulated tank but has an aluminum cover and insulation. Note the differences in these two trucks. The one on the right has safety railings around the manhole. Although not an absolute rule, the truck on the right would carry more dangerous products and would have other added safety features. Most of these items are not required but were added by the trucking company.

and accidents as the insulated version. The shell is made of stainless steel and can hold pressures up to 40 psi.

The insulated tank, **Figure 25-49**, is a covered version of the uninsulated tank, although in some cases it has a slightly smaller inner tank. The inner tank is made of stainless steel with about 6 inches of insulation, and the outer shell is made of aluminum. The inner tank may also be lined with a fiberglass or other liner depending on the chemical that is carried. Due to the aluminum and insulation these tanks hold up remarkably well during rollovers.

Safety One of the major problems with this insulated tank is that in the event of a leak, the location where the material leaks out of the outer shell is usually nowhere near the leak on the inner shell.

Within the insulation there can be heating and cooling lines depending on the product being carried, **Figure 25-50**. Products such as paint are shipped at 170°F and need to be heated to that temperature for offloading. Some products need to remain at certain temperatures to remain stable, and first responders need to be aware of any special requirements.

In general, both types of tanks have rollover protection, similar piping, and relief valves that serve two purposes: overpressurization and vacuum protection. The emergency shutoffs are located near the front of the tank on the driver's side and near the offloading piping.

Figure 25-50 Products carried in an insulated 407/307 need to remain either heated or cooled. Some products may need to be heated for offloading. The heater coils that run around the tank heat the product up, allowing it to be offloaded.

DOT-412/MC-312

These tankers, **Figure 25-51**, carry a wide variety of corrosives, both acids and bases. These tankers are round and are smaller than the 306s and 307s due to the weight of the corrosives they carry. Most petroleum products weigh about 8 pounds per gallon while some corrosives weigh up to 15 pounds per gallon. Because of the weight, the stiffening rings used are generally bulkier than the ones used on DOT-407 tanks. These tankers are constructed of a single tank that carries up to 7,000 gallons, with most tanks holding 5,000 or fewer gallons. The tanks are made of stainless steel and are usually lined to protect against corrosion. The piping can be on top of the tank located in the middle, but

Figure 25-51 The DOT-412/MC-312 is designed to carry corrosives and is similar in design to the uninsulated 307, although smaller. The inner tank may be lined with a variety of materials to prevent the corrosive from attacking the tank.

Figure 25-52 The black coating around the manhole indicates that a corrosive is being carried. It is used to protect the tank from spillage. It is not required nor will it be found on all corrosive tanks.

is usually located on the end of the tanker. The piping is usually contained within a housing that includes the manhole and offload piping. This housing protects the piping in the event of a rollover, **Figure 25-52**. The area around the manhole is usually coated with a material that resists the chemical being carried and is usually a black, tar-like coating.

MC-331

MC-331 tanks look like bullets and are noted for their rounded ends and smooth exterior, as shown in **Figure 25-53**. They carry liquefied gases that are liquefied by pressure. One of the most common products carried in this type of tank is propane. They also carry ammonia, butane, and other flammable and corrosive gases. These tanks carry up to 11,500 gallons and have a general pressure of 200 psi, although it can be as high as 500 psi. The relief valves are located on top of the tank at the rear of the trailer, and they sometimes malfunction during a rollover. The tanks are made of steel, are uninsulated, and are heavily fortified with heavy bolts used in the piping and manholes. The tanks are usually painted white or silver to reduce the potential heating by sunlight.

The tanks contain a liquid along with a certain amount of vapor. The most liquid the tank is supposed to have is 80 percent to allow for expansion when heated. The liquid in the tanks is at atmospheric temperature but on release can go below 0°F (propane is −90°F) and could cause frostbite upon contact. The pressure in these tanks is of concern when responding to incidents involving these tanks.

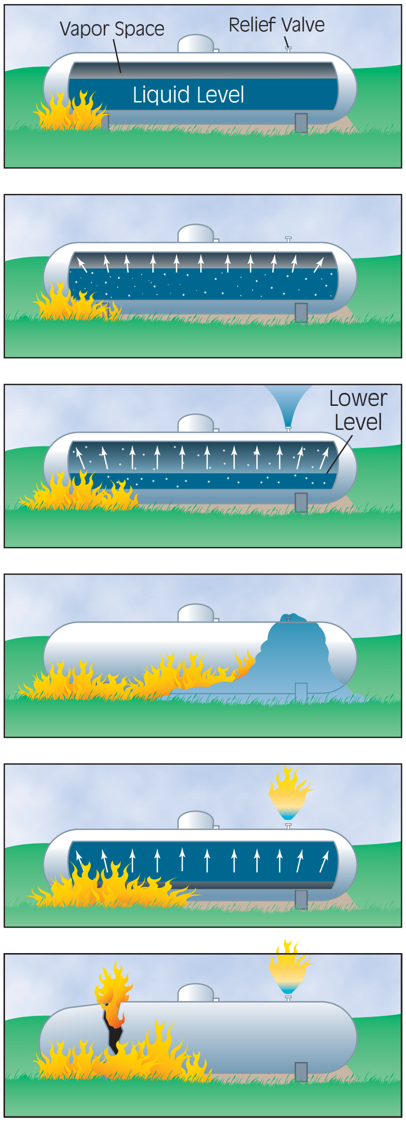
Figure 25-53 MC-331 tanks carry liquefied compressed gases such as propane and ammonia. They are made of steel and are designed to carry a variety of products.

Firefighter Fact **Temperatures and Pressurized Container** When a propane tank is emptied and, hence, the pressure reduced, the temperature of the propane drops below 0°F. Temperature, pressure, and volume are interrelated. Think of an SCBA bottle. When it gets filled it becomes hot because the pressure and volume are increasing. When the SCBA bottle is used, it becomes cold because it is losing pressure and volume. Any time one of the parameters is changed, there is a corresponding change in the other properties. When a pressurized gas is pressurized to a point that it becomes a liquid, as is the case with propane, it allows for a lot of propane to be stored in a small container. When released, however, the temperature will drop because the pressure is decreasing in the container. This is known as autorefrigeration.

Boiling Liquid Expanding Vapor Explosion (BLEVE)

Safety If the pressure increases at a rate higher than the relief valve can handle, the tank will explode. These explosions have been known to send pieces of the tank up to a mile, with the ends of the tank typically traveling the farthest, although any part is subject to become a projectile.

When tanks, trucks, tank cars, or other containers are involved in a fire situation there are a number of hazards. One very deadly hazard is known as a boiling liquid expanding vapor explosion (BLEVE), **Figure 25-54.** A large number of firefighters have been killed by propane tank BLEVEs, and when a BLEVE



Fire impinging on a propane tank.

As heat increases inside of tank, the pressure also increases. The liquid will begin to boil.

As the pressure increases, the relief valve will open, releasing propane. The propane, being heavier than air, will sink.

The vapor will reach the fire and ignite.

The relief valve will ignite, also causing heat to be on the tank by that flame. The pressure will increase in the tank.

As the pressure in the tank is increasing, the tank may discolor and the pitch of the relief valve will get higher. Eventually the tank will rupture. This is known as a BLEVE.

Figure 25-54 Diagram of a BLEVE.

occurs it usually results in more than one firefighter being killed at a single incident. The type of container and the product within the container will dictate how severe a BLEVE may be. The basis of a BLEVE is the fact that the pressure inside the container increases and cannot be held by the container. The contents are violently released, and if the material is flammable, an explosion or large fireball occurs. In the recent past there have been several incidents involving BLEVEs that resulted in emergency responder deaths and injuries, thus emphasizing the need to recognize and prevent this event before it occurs.

Another phenomenon that transpires with containers is known as violent tank rupture (VTR), which occurs with nonflammable materials. The concept is the same as a BLEVE, but there is not a characteristic fireball and explosion. With both a BLEVE and a VTR there is some form of heat increase inside the container, typically from a nearby fire. The fire heats the container, which heats the contents. The contents will boil, which creates expanding vapors, which in turn increase the pressure inside the container. In some containers the relief valve will activate, relieving the pressure. In some cases the pressure inside the tank is greater than the relief valve can handle and the pressure continues to increase. One of two possibilities can occur with a BLEVE or a VTR. One possibility is that the relief valve will not be able to handle the increase in pressure and the tank will fail. The other possibility is that the fire or heat source that is creating the problem will weaken the container shell, and the resulting increasing pressure will vent at this weakened portion of the container. If the heat source is a fire and the container product is flammable, when the relief valve activates the raw product coming out of the container typically ignites. This may increase the temperature of the tank, increasing the pressure. It is never advisable to extinguish the fire coming from a relief valve, as that is a safety mechanism. It is possible to cool the top of the tank near the relief valve with an unstaffed hose stream. The difference between a BLEVE and a VTR occurs when the container fails. A BLEVE occurs with flammable liquids, such as propane. When the container fails, the vapors of the flammable liquid ignite, creating the explosion. How the container ruptures and the amount of product released will determine how severe the explosion will be. With a VTR the container will fail. Since the product is nonflammable, the product will not ignite. The only event is a rupture of the container, spilling its contents. The container can still rocket, and the resulting release of pressure can be violent. A VTR can occur with a container of water or other "nonhazardous" material. As an example a 55-gallon steel drum of water, when heated, can travel several hundred feet depending on where the release point is on the container. In most cases the bungs (screw-top caps) will release, flying a considerable distance, and the container will remain mostly intact.

The failure of the container when impinged from a fire usually occurs as the fire is impacting the tank in the vapor space. When heat is applied to a section of the tank that has no internal mechanism to provide cooling, failure of the steel can occur. When fire impinges on the liquid portion of the tank, the liquid will distribute the heat spread internally and the steel tank typically will not weaken. The problem is that responding firefighters do not usually know the liquid level, and one cannot easily predict when a tank may fail. Any fire impingement on a tank is a serious problem, and withdrawing from the scene may be the best course of action. This brings up another interesting note: A casual observation of BLEVEs indicates that most BLEVEs and firefighter deaths occur within the first few minutes of arrival. The clock starts ticking on the BLEVE time bomb from the first minute heat is applied to the tank. The clock does not start with the 9-1-1 call or the arrival of firefighters. The critical time for safety may have already passed before firefighters arrive on the scene. If firefighters arrive at an incident involving a propane tank on fire or being impinged by fire, they are in extreme danger. If the relief valve is not operating, the danger is even more pronounced. Operating in close proximity to a tank in this situation can be a fatal mistake. Firefighters should follow this risk/benefit analysis: Risk a lot to save a lot, and risk a little to save a little.

One recent event involved the death of two firefighters and injuries to seven other emergency responders. The location was a farm, at which a propane tank was on fire. The relief valve on the tank was operating and the vapors from the relief valve were on fire. About eight minutes after the firefighters had arrived, the tank exploded into four separate parts. The four parts went in four different directions. The two firefighters who died were 105 feet away and were struck by one piece of the tank, dying instantly.

In two other farm incidents, firefighters lost their lives. In 1993 a fire and BLEVE in Ste. Elisabeth de Warwick, Quebec, Canada, killed three firefighters. In 1997 in Burnside, Illinois, two firefighters lost their lives in a fire and BLEVE. In all three of these fatal BLEVE events, the relief valves were operating upon arrival of the fire department.

One other event worth noting is the 1984 PEMEX LPG Terminal fire in Mexico City, Mexico. An 8-inch pipeline broke while filling a tank at the terminal. The resulting vapor cloud, which was 650 feet by 572 feet by 8 feet, ignited. This resulted in an explosion, which included a ground shock, and a major fire. The terminal had two large spheres, four small spheres, and forty-eight horizontal tanks. About fifteen minutes into the fire the first BLEVE occurred, and for the next ninety minutes tanks continued to BLEVE. Tanks and liquid propane rained down on the adjacent community. The death toll exceeded 500 people, and thousands were injured.

In 1983 five Buffalo, New York, firefighters lost their lives when a three-story building collapsed. Nine other firefighters were injured in the massive explosion. The force of the explosion caused the first arriving apparatus, including a ladder truck, to be blown across the street. A propane tank inside the building had been struck and was leaking. An unknown ignition source sparked the explosion minutes after fire crews arrived.

In January 2003 a propane truck (MC-331) went over a guardrail and fell to the ground 35 feet below. The tank ruptured and the leaking propane ignited, resulting in a 600-foot-high fireball. The resulting explosion moved the truck several hundred feet away from the first impact area. The driver of the truck was killed in the accident.

As can be noted in the stories above, BLEVEs and VTRs can result in injuries and fatalities. Any time containers are under stress, such as during a fire, they can fail. Many times they fail violently and with severe consequences. Some containers have relief valves, while others do not. Materials that are highly poisonous such as chlorine will not have a relief valve; they will have a fusible metal plug that vents the pressure of the tank. This fusible metal plug is not like a relief valve that shuts off when the pressure inside the tank is decreased. Once a fusible metal plug melts, the contents of the tank come out, no matter the pressure. When a tank is on fire or is being impinged by fire, the tank is being weakened and the contents are being heated, creating increased pressure. Some of the general rules of firefighting and propane tanks (or other containers under pressure) are as follows:

- Firefighters should withdraw immediately in the case of rising sound from venting relief valves or discoloration of the tank.
- Fire must be fought from a distance with unstaffed hose holders or monitor nozzles.
- The tank should be cooled with flooding quantities long after the fire is out. A minimum of 500 gpm at the point of flame impingement is recommended by the NFPA.
  - If the water is vaporizing on contact, firefighters are not putting enough water on the tank. Water should be running off the tank if it is being cooled.
- Firefighters should not direct water at relief valves or safety devices, as icing may occur. Icing would block the venting material, which could cause an increase in pressure inside the tank.
- The tank may fail from any direction, but firefighters should avoid the ends of the tank.
- For massive fire, it is recommended to use unmanned hose holders or monitor nozzles. If this is impossible, firefighters should withdraw from the area and let the fire burn.
- The dangers associated with a BLEVE are:
  - The fireball can engulf responders and exposures.
  - Metal parts of the tank can fly considerable distances.
  - Liquid propane can be released into the surrounding area and be ignited.
  - The shock wave, air blast, or flying metal parts created by a BLEVE can collapse buildings or move responders and equipment.

Specialized Tank Trucks

These types of tank trucks are used to carry unique chemicals or chemicals that have to be transported in a certain fashion. When gases are transported, they are transported as liquefied gases, as was described with the MC-331 tank trucks. They can also be transported as refrigerated gases or as compressed gases as will be described in this section. Other trucks are dry bulk which can carry a variety of products from grain to explosives. Materials that required high temperatures are transported in special vehicles to keep them hot. The intermodal series of tanks are cousins to their full size highway tanks but carry the chemicals in a comparable fashion.

MC-338 Cryogenic Tankers

MC-338 tankers are uniquely constructed like the one shown in **Figure 25-55**. They have a tank with an outer shell. The inner container is steel or nickel, with a substantial layer of insulation; the exterior is aluminum or mild steel. The space between the shells is placed under a vacuum to assist in the cooling process. The ends of the tank are flat, and the piping is contained usually at the end of the tanker in a double door box. Relief valves are located on top of the tank, to the rear of the tank. The best way to describe this tanker is to compare it to a Thermos bottle on wheels. Cryogenic materials are gases that have been refrigerated to a temperature that converts them to liquids. Unlike liquefied gases, which use pressure to reduce them to liquids, these are cooled to the point of becoming liquid. To remain

Figure 25-55 The MC-338 carries cynogenic liquefied gases. The tank resembles a rolling Thermos bottle.

liquids, the material must be kept cool. To be a cryogenic material the liquid has to be at least −150°F and can be as cold as −456°F.

The most common products are nitrogen, carbon dioxide, oxygen (liquid oxygen or LOX), argon, and hydrogen. The material inside is kept liquid by vacuum, and when on the road the tank will have a maximum of 25 psi. As the truck travels the sun will heat the material, and the pressure will increase. As the pressure increases the relief valve will open up, relieving any access pressure into the atmosphere.

> **Note** It is not uncommon to see a white vapor cloud like that shown in **Figure 25-56** coming from the relief valves while the truck is traveling on the highway or sitting alongside the road. This is a normal occurrence and is not cause for alarm.

When the truck makes a delivery, the pressure needs to be increased to push the liquid out of the tank. The driver opens the piping and allows the material to flow into an evaporator which is located just in front of the rear wheels of the tank. Once in the evaporator the material will heat up, increasing the pressure in the tank and forcing the liquid into the receiving tank. During transportation and offloading, a large amount of ice will build up on the piping and valves.

Tube Trailers

Tube trailers, **Figure 25-57**, contain several pressurized vessels, constructed much like the MC-331 tank. They are constructed of steel and have pressures ranging from 2,000 to 6,000 psi. They hold pressurized gases such as air, helium, and oxygen. The piping and controls are usually located on the

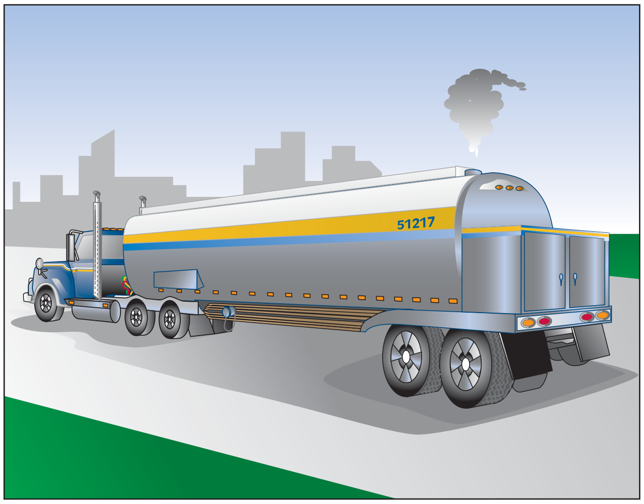


Figure 25-56 When transporting liquids it is not uncommon to see vapors coming from the relief valves. The truck can only travel with the tank at 25 psi or less. As it heats, the pressure increases, triggering the relief valve. This is a normal situation, and the tank will vent until below the 25 psi. When offloading the pressure can be increased to assist with the offloading procedure.

Figure 25-57 The tubes on this trailer contain pressurized gases. The pressure can vary from 2,000 to 6,000 psi.

Figure 25-58 Dry bulk tanks carry a variety of products. Some examples include fertilizers, explosives, and concrete.

rear of the trailer, but could be in the front. The typical delivery mode is that the driver will drop a full trailer off at a facility and pick up an empty one for refilling. Although they are not subject to BLEVEs because they only contain a gas, if involved in a fire, tube trailers can experience a VTR and rocket in the same fashion as a BLEVE.

Dry Bulk Tanks

Dry bulk tanks resemble large uninsulated MC-307s in shape with bottom hoppers to unload the product, as shown in **Figure 25-58**. The tanks hold dry products and sometimes a slurry, like concrete. The most common products are fertilizers, lime, flour, grain, and other food products. The potential hazard when dealing with these tankers is predominantly environmental but at times these tankers contain toxic materials. They are usually offloaded using air pressure either from the truck itself or at the facility.

Hot Materials Tanker

Hot materials tankers vary in that they can be modified MC-306s, 307s, or dry bulk containers, **Figure 25-59**. They may have a mechanism to keep the material hot or it may be loaded hot. It may require heating prior to offloading. Common products are tar, asphalt, and molten sulfur, fuel oil #7 and #8.

> **Safety** The major problem with these tankers is the heated material itself. Anyone coming into contact with the material could be seriously burned. The molten material could ignite the truck or other combustibles.

Figure 25-59 These trucks carry molten products and can be heating the product while driving. This practice is illegal but is found on occasion. The fuels used to heat the product are either diesel/kerosene or propane.

IMO Containers

CONTAINER	MAXIMUM CAPACITY (GAL)	PRESSURES (PSIG)	PRODUCTS
IM-101 or IMO Type 1	6,340	25.4–100	Nonflammable liquids, mild corrosives, foods, and other products
IM-102 or IMO Type 2	6,340	14.5–25.4	Flammable materials, corrosives, and other industrial materials
Spec 51 or IMO Type 5	6,418	100–500	Liquefied gases, much like an MC-331
Specialized tanks	Varies	Varies	Includes cryogenic tanks and tube banks (small tube trailers) that carry the same products as their highway counterparts

TABLE 25-8

If the material is allowed to cool, it can cause problems for the responders or the shipping company. Tar trucks may be transported with a propane or fuel oil flame ignited to heat the product en route to the job site, although this is illegal in most states.

Intermodal Tanks

Intermodal tanks are increasing in use and carry the same types of products as their highway and rail companions, **Table 25-8** and **Figures 25-60, 25-61,** and **25-62**. They are called *intermodal* (IM) because they can be used on ships, railways, or highways.

> **Note** Smaller intermodal tanks may be found inside of box-type tractor trailers.

Figure 25-60 This is an IMO-101 tank. Like the totes, these are bulk tanks capable of carrying a large quantity of product. These are normally placed on ships, then delivered locally by a truck, although trains can also be used.

Figure 25-61 This is an intermodal tank, commonly referred to as an IM or IMO. This is a bulk tank that carries an average of 3,000 to 5,000 gallons. This tank is an IMO-101, which it is an atmospheric tank. The orange panel indicates that it has a United Nations (UN) hazard code of 60 and a UN number of 2572. The code of 60 indicates that the product is a toxic material. The UN number indicates that the product is phenylhydrazine. The name is also stenciled on the sides of the container, and there are toxic placards.

Figure 25-62 This is another IMO-101, and the photo shows that the orange panel indicates a hazard code of 66 and a UN number of 2810. The hazard code indicates that the product is a highly toxic material, and there are fifty-two different materials listed for UN 2810. One would have to look at the shipping papers to figure out what is being carried in this tank. The tank is marked "foodstuff only," which means that it is holding a product used in food. It is interesting to note that many of the chemicals listed for UN 2810 are chemical warfare agents such as sarin nerve agent and comparable materials. The most likely candidate, considering the "foodstuff only" label, would be a medical-type product

Intermodals follow three basic types: nonpressurized, pressurized, and highly pressurized. They are built in two ways. In one, they sit inside a steel frame, called a box-type framework; in the other, the tank is part of the framework, called a beam-type intermodal. Like tank trucks they are assigned specification numbers, IM-101, IM-102, Spec 51 (specification 51). When used internationally they are called IMOs. They are made to be dropped off at a facility and when empty picked up for refilling.

Rail Transportation

As with highway transportation there are only a few types of railcars, and they are similar to their highway counterparts. The piping and shape may be the same but that is the extent of the similarities.

> **Note** In rail transportation the quantities are greatly increased—up to 30,000 gallons for hazardous materials and up to 45,000 gallons for nonhazardous materials.

Rail incidents usually involve multiple railcars, whereas highway incidents usually involve one or two trucks. The incidents may occur in rural areas, away from water supplies and easy access. Rail incidents will involve multiple agencies, and the local community can expect a large contingent of assistance coming from the state and federal government, which in itself will be difficult to manage.

Railcars come in three basic types: nonpressurized, pressurized, and specialized cars. Although they are categorized in this fashion, the commodities they carry will determine the ultimate use of the car. As with highway transportation there are dedicated railcars that will be marked with the products they carry.

> **Caution** The term *nonpressurized car* is actually misapplied because it can have up to 100 psi in the tank.

It carries chemicals, combustible and flammable liquids, corrosives, and slurries. The easiest way to determine if the car is nonpressurized, such as the one shown in **Figure 25-63**, is to observe whether the valves, piping, and other appliances are located outside of a protective housing. In some cases, the car will be bottom unloaded, with the ability to load the car through the top, or the car may be top loaded and unloaded. The cars will usually have a small dome cover, but the relief valves and other piping are located outside of this dome. Most of the piping is located on the catwalk on top of the car.

Some cars have unique paint schemes such as those shown in **Figure 25-64.** Nonpressurized cars can be insulated and may have heating and cooling lines around the tank. Prior to offloading, the tank may need to be heated to ease the offloading process. Some nonpressurized railcars have an expansion dome. The piping valves and fittings sit on top of this dome, which was constructed to hold

Figure 25-63 The indication that this is a nonpressurized railcar is given by the fact that all of the valves are on the outside of the tank and not contained within any protective housing.

Figure 25-64 This railcar is white with a red stripe, which is used to indicate hydrogen cyanide but on occasion is used to indicate dangerous materials. This car holds hydrogen fluoride anhydrous, which is a severe inhalation hazard and is corrosive. The term *anhydrous* indicates "no water" and means the hydrogen fluoride is pure.

any potential expansion. These cars are not in regular service but may be seen in larger industrial facilities that have their own railroad service on site.

Pressurized tank cars, **Figure 25-65**, also carry a wide variety of products, including flammable gases like propane, and poisonous gases like chlorine and sulfur dioxide. The pressurized cars will have pressures in excess of 100 psi up to 600 psi. Most pressure cars that carry flammable materials will be insulated with a spray-on insulation or may be thermally insulated. This insulation is 1 to 2 inches thick and helps reduce the chance of a BLEVE during a fire situation. To determine if the railcar is a pressurized car the firefighter can look at the spec plate, which will have all of the valves, piping, and fittings located under the protective housing, on top of the railcar. A catwalk around the protective housing provides relatively easy access.

Figure 25-65 The pressurized car is indicated by the valves being contained within the protective housing of the railcar.

Figure 25-66 This specialized railcar holds liquefied carbon dioxide, a cryogenic material.

Specialized Railcars

Specialized railcars have the same characteristics as highway vehicles, and, in fact, in some cases highway box trailers are loaded onto flatbed railcars. When transported in this fashion they are referred to as trailers on flat cars (TOFC). Regular box trailers as well as refrigerated trailers can be found on flat cars. Much like highway trailers, there are freight boxcars that haul the same products as their highway trailers, with the exception of carrying much larger quantities. Examples of these cars are shown in **Figure 25-66**. The boxcars can carry boxes, cylinders, bulk tanks, totes, and super sacks. Refrigerated railcars are similar to highway and intermodal boxes and are referred to as reefers. They contain their own fuel source. Dry bulk closed railcars are common, and open hopper cars can also be found. Tube trailers for rail are also found, but they are rarely used; the most common is a highway tube trailer set on a flat car. Cryogenics are also carried in railcars and have the same low pressure (25 psi) as in highway transportation, with the characteristic venting when the pressure increases.

Markings on Railcars

Railroads use the same placarding system used on highways, with the exceptions noted in the placard section. Railcars, however, are usually marked better than their counterparts on the highway; at the very least, the information is printed larger. In addition to a placard, the name of the hazardous material is stenciled on two sides of the car. In addition, by looking at the sides of a railcar, a firefighter can learn the specification type, maximum quantities, test pressures, relief valve settings, and other pertinent information. These types of markings are shown in **Figure 25-67**.

Figure 25-67 A railcar has a lot of information stenciled on the side. The FMLX indentifies who owns the car. The X at the end indicates that the car is privately owned, that is, the railroad does not own the car. The 15020 is the car number and can be used to cross-reference the shipping papers. The photo on the left is the certification and testing data. The top line DOT 111 A 100 W 1 provides most of the information. The tank is a DOT 111 specification, which means that it is a non-pressure car. The A indicates the type of couplers, and the 100 is the maximum pressure for the car. The W and the 1 indicate the type of welds and other tank construction information. The last line is also important, and it shows that the tank was lined on 3-94, which means that it has an internal lining. In a derailment the lining could separate from the tank and the chemical could react with the tank metal.

Note Certain railcars may be painted in a certain configuration to identify their hazardous loads.

It used to be common practice to paint a car carrying hydrogen cyanide white with a red stripe running around the middle, hence the name "candy-striper."

Bulk Storage Tanks

Bulk storage tanks range in size from 250 gallons up to millions of gallons and store a variety of products, the most common being petroleum products. These tanks are seen in residential homes and rural areas, and are common at an industrial facility, such as the one shown in **Figure 25-68**. In residential homes the most common tank is a 250-gallon home heating oil tank, and some homes or small businesses may have gasoline or diesel fuel tanks that vary from 250 to 500 gallons.

The two basic groupings of tanks are in-ground and aboveground. Since the passage of the EPA underground storage regulations, there has been considerable movement to remove **underground storage tanks (USTs)** and replace them with **aboveground storage tanks (ASTs)**. If the facility

Figure 25-68 The sizes of tanks vary from a few hundred gallons up to several million gallons. A catastrophic failure of the tank may overwhelm the responders' ability to handle the incident.

owner elects to keep its tanks underground then additional requirements are placed on them for testing, containment, and leak prevention.

Caution Leaks from these types of tanks can be overwhelming because the leak may not be detected for a period of time, giving it a chance to spread throughout the area, contaminating a large area.

A substantial release from a million-gallon tank of gasoline that escapes a facility would require an enormous response from the emergency responders and environmental contractors.

Underground tanks are usually constructed of steel and are coated with an anticorrosion material. New tanks are usually double walled, that is, a tank within a tank, to prevent any spillage into the environment. The piping comes up through the ground and its use will determine its route. The offload piping for an UST at a gasoline station comes up through the pump, which **Figure 25-69** demonstrates. The piping is manufactured so that in the event that a car knocks off the pump it will shut off the flow of gasoline and will snap the piping off at or near the ground level. The only spillage of gasoline would be from the amount in the piping aboveground and in the hose, if everything works properly. (See boxed text for more information.)

The loading piping is located separately and all of the fill pipes are located in the same area for easy transfer from a tank truck. The fill pipes are usually color coded and marked so that the driver can differentiate between unleaded, unleaded super, and diesel fuel, although the color coding is not standard across the country and varies from company to company. At some location on the property there will be vent pipes for the tanks, generally away from the pumps and near the property line. There will also be other manhole covers approximately 6 to 8 inches in diameter that have a triangle on the top of the cover. These are inspection wells and typically surround the tank. The holes are drilled at various depths so that leaks can be easily detected by air monitoring of the well, or if water is in the well, by taking a sample. If a facility has had a leak, there may be a large number of these wells on and around the property. Most gas station tanks are 10,000 to 25,000 gallons in size and, if not properly monitored, can slowly release a substantial amount of product over a short period of time.

Note It is not uncommon to find gasoline bubbling up in a basement miles away from the gas station and to find that the release occurred several years ago.

Another common problem arises when farms are redeveloped into housing developments. If unknown USTs are located on the property, they may or may not be discovered during the construction and can eventually leak, causing problems. The tank and environmental industry refers to a **leaking underground storage tank** as a **LUST**.

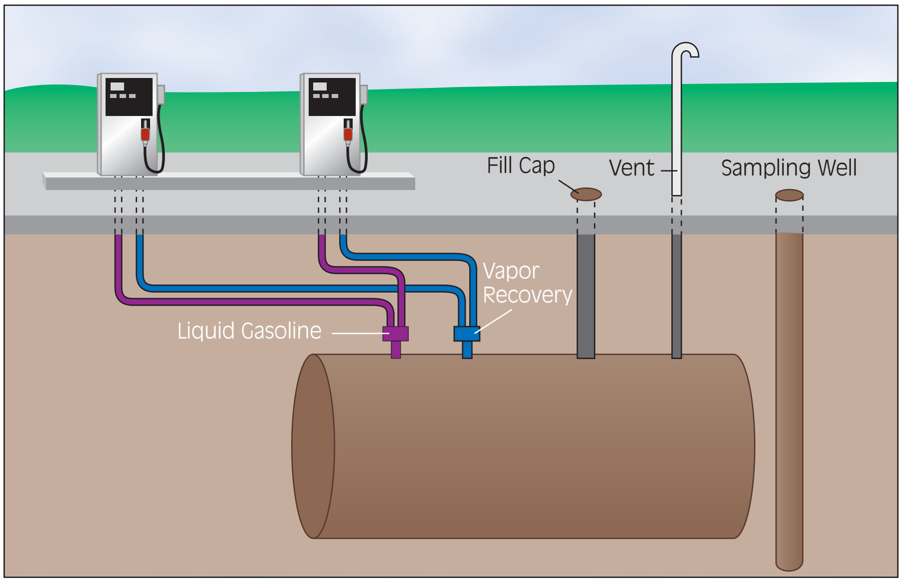


Figure 25-69 Piping system of a gas station.

Safety A recent incident in Baltimore County, Maryland, demonstrates that regardless of how many protection systems may be in place, a release off the property is still possible.

One afternoon a gas station was getting a tank filled with fuel, as per normal procedure, and the tank filling went as expected with no problems. The gas station had installed a state-of-the-art alarm system that would indicate a fault in the system and alert the owners to any potential releases. The system goes through a system check after each sale, if no pump is operated for a period of thirty seconds. If a pump is on, or the period between sales is less than thirty seconds, then the system check does not begin to work. During a busy afternoon, it could be estimated that the system check would not function for a long period of time, because at least one of the pumps is operating all the time.

In addition to the system check of each of the storage tank locations, some piping and the pumps all have electronic monitors that detect the presence of a liquid. When a liquid is detected, an alarm activates—the same type of alarm as if the system check fails the system. One of the potential problems with many self-service gas stations is that there is only one attendant, who for many reasons cannot leave the work area to either check on a problem outside or, depending on the alarm panel location, cannot check any alarms. In some gas stations the alarms are in other rooms and cannot be seen or heard by the only attendant. Another problem is that the liquid alarms will activate when it rains, tripping for rainwater.

The pumps that sit on top of the storage tanks have the ability to supply upward of 80 psi of pressure to all pump station nozzles, although this is governed down to an actual working pressure of 10 psi at all pumps. In this particular incident, a flange that comes out of the tank pump failed and separated from the tank pump. From the pump discharge there is a 2-inch-diameter opening, which at 10 to 80 psi could pump a considerable amount of fuel in a short time. One theory is that a customer may have set a nozzle down after not being able to pump fuel, or the amount of fuel being pumped was inadequate. This action would have resulted in the tank pump continuing to pump. A liquid alarm sounded for a number of areas at the gas station. The attendant notified the pump repair company as per protocol, but a response was delayed due to a number of extenuating circumstances.

Once the repair company arrived they found the tank empty; it was at this time the clerk informed them of the recent delivery. It was later found that an estimated 4,500 gallons were lost and were causing flammable vapor readings in a several-block area, although all the gasoline was later recovered. Within the gas delivery system, this station had the best protection in place, and had just retrofitted the station with a new piping system, but it shows that no matter how many protection systems are in place, it is still possible to have a release.

Aboveground tanks are becoming more and more common, although they have been used for many years, **Figure 25-70**. They are of two basic construction types—upright and horizontal—and some are nonpressurized or atmospheric tanks and some are pressurized tanks. ASTs hold a wider variety of chemicals as opposed to their UST counterparts, but petroleum products are still a leading commodity stored in these type of tanks. They vary in size from the 250-gallon home heating oil tank to the several million gallon oil tank. In industrial and commercial applications, a containment area is required around the tank. The containment area must be able to hold the contents of the largest tank within the containment. Regular inspection of these areas is required to ensure that rainwater, snow, or ice does not cause a buildup of liquid in the containment area, which would reduce the containment's ability to hold its intended amount. Depending on the weather conditions, the containment area's gate valve may be left in an open position,

Figure 25-70 Due to increased environmental concerns, many tanks are being placed aboveground and are called aboveground storage tanks or ASTs.

which leaves the facility at risk for product to escape the facility through the open drain or gate valve.

Upright storage tanks come in three basic construction types: **ordinary tank**, **external floating roof tank**, and **internal floating roof tank**. The ordinary tank, **Figure 25-71**, is constructed of steel and typically has a sloped or cone roof to shed rainwater, snow, and ice. The roof and tank shell seam is purposely made weak so that in the event of an explosion, only the top of the tank is relocated. One of the major problems with this type of tank is that when the tank is not full, there is room for vapors to accumulate.

Caution Any time vapors are allowed to accumulate, the potential exists for a fire or explosion.

Some ordinary tanks are purposely constructed without a roof in place. These are typically used in safety vent situations and water treatment areas where a roof may cause additional problems. It is important to identify these tanks during pre-incident surveys so as not to misjudge the severity of an incident. In many chemical processes it is not uncommon to have a storage tank with piping into the tank just to catch overflow or the contents of a system in the event of overpressurization or failure. The materials can be hot and produce large amount of vapors, which, if a roof were present, would allow a buildup of pressure, causing a catastrophic failure of the tank and roof.

External floating roof tanks are used to eliminate the buildup of vapors. They ride on top of the liquid, **Figure 25-72**, and since there is no space between the roof and the liquid, vapors cannot accumulate and create problems. External floaters can be seen from the top of the tanks, and a ladder is affixed to the roof to allow access. A common incident with these types of tanks results from a lightning strike, which can cause a fire in the roof/shell interface area. *This type of fire is difficult to extinguish and can result in roof/tank failure if not controlled quickly.* It is also possible that water used for firefighting could also sink the roof, causing further problems.

Internal floaters are constructed in the same manner as external floaters but have an additional roof over the top of the tank. An example is shown in **Figure 25-73**. The type of roof varies, but is usually a slightly coned roof with vent holes along the outer edge of the tank shell, or a geodesic type of roof that is usually made of fiberglass. The internal floater suffers from the same type of fire problem as the external, although it is a reduced risk. If a fire were to start in the roof/shell interface, the roof makes it more difficult to extinguish.

Figure 25-71 This is a cone roof tank. It has a weak roof-to-shell seam so that in the event of an explosion the roof will come off, but the tank should remain intact.

Figure 25-72 This is an open floating roof tank, in which the roof floats on top of the product. This reduces the release of vapors, as there is no vapor space, and reduces the fire potential.

Figure 25-73 This is a covered floating roof tank, which is the same as an open floating roof tank but has a cover to keep out snow, rain, and debris. Another term for this type of tank is *geodesic domed tank.*

Figure 25-74 The specialized tank such as the propane tank shown here has some of the same properties as its transportation equivalents.

Figure 25-75 This tank holds cryogenic liquid oxygen and is typical of a cryogenic upright tank.

Specialized Tanks

Specialized tanks are a combination of the tank types discussed earlier in this section and include pressurized tanks and cryogenic tanks. The larger pressurized vessels are divided into two categories: low-pressure and high-pressure tanks. The low-pressure tanks hold flammable liquids, corrosive liquids, and some gases, up to 15 psig. Common high-pressure commodities are liquefied propane, liquefied natural gas, or other gaseous or liquefied petroleum gases. An acid like hydrochloric acid, which has a high vapor pressure, would not be uncommon in a tank like this.

These types of tanks may have an external cover, which appears to be a tank within a tank. The pressurized tanks are larger versions of the propane tanks discussed earlier and can have a capacity of up to 9 million gallons although less than 40,000 gallons is typical. Liquefied petroleum gases are not only stored in pressurized tanks such as the one shown in **Figure 25-74**; these types of gases are also stored in other locations such as caves carved out of mountains, although this is rare. Because these facilities are not required to report under the SARA Title III regulations, firefighters will have to contact their local gas suppliers to find out how they store their gas products.

Upright cryogenic storage tanks, **Figure 25-75**, are located in almost every community, especially if the community has a hospital or medical center. Most hospitals are supplied with liquid oxygen (LOX) through the cryogenic tank. Facilities that sell or distribute compressed gases are likely to have cryogenic tanks. Fast-food restaurants and convenience stores are now using cryogenic tanks to supply carbon dioxide to the soda dispensing machines.

SENSES

Vision and hearing are acceptable senses to use while investigating potential chemical releases. The use of touch, smell, and taste, however, is a dangerous use of the senses.

> **Caution** The lack of an odor cannot be equated with a lack of toxicity. Many severely toxic materials are colorless and odorless.

Sensory clues gained from other persons are useful to help identify the spilled material. The smell of materials is an important clue when trying to identify a spilled material, so if bystanders or evacuated persons can assist by describing an odor, firefighters should take advantage of this clue, but they should not endanger their lives to determine an odor. Many toxic materials can be harmful if touched because the material can be absorbed through the skin. Any-time a person handles a chemical, appropriate chemical protective clothing should be worn.

CHEMICAL AND PHYSICAL PROPERTIES

Although not intended to be a full chemistry lesson, the material in this section is a key component of safety. The chemical and physical properties outlined here are appropriate for a firefighter's level of response. The identification and use of these key terms can determine the outcome of an incident and firefighter well-being. As a firefighter progresses up through the response levels the need for additional chemistry also increases. When in doubt, the firefighter should consult with a HAZMAT team or other resources such as Chemtrec or a local specialist. A lot of the terms to be discussed next can be applied throughout the entire firefighter text. The basis of a fire is a chemical reaction. The better that firefighters understand this chemical reaction, the better off they will be, which will also benefit the citizens of their communities.

States of Matter

The basic chemical and physical properties that are important to understand are the **states of matter**: **solid, liquid**, and **gas** as shown in **Figure 25-76**. The severity of an incident can be determined by knowing if the material is a solid chunk of stuff, a pool of liquid, or an invisible gas.

Note The level of concern rises with each change of state; relatively speaking, a release of a solid material is much easier to handle than a liquid release, and it is nearly impossible to control a gas.

The control methodology for each state increases in difficulty from simple controls with a solid, to difficult with a gas. Evacuations have to be larger for releases involving gases, whereas a minimal evacuation would be required for most solid materials.

How the chemicals can hurt someone also varies with the state of material. Solids usually can only enter the body through contact or ingestion, although inhalation of dusts is possible. Liquids can be ingested, absorbed through the skin, and, if evaporating, inhaled. Gases on the other hand can be absorbed through the skin, and inhaled, and to some extent ingested.

Adjoining the states of matter are melting point, freezing point, **Figure 25-77**, boiling point, **Figure 25-78**, and condensation point. All of these are related because they are the points at which a material changes its state. The **melting point** is the temperature at which solid must be heated to transform the solid to the liquid state. Ice, for instance, has a melting point of 32°F. The **freezing point** is the temperature of a liquid when it is transformed into a solid. For water, the freezing point is 32°F. The actual temperatures vary by the tenths of a degree, but are very close. The **boiling point** is reached when the liquid is heated to the point at which evaporization takes place, that is, the liquid

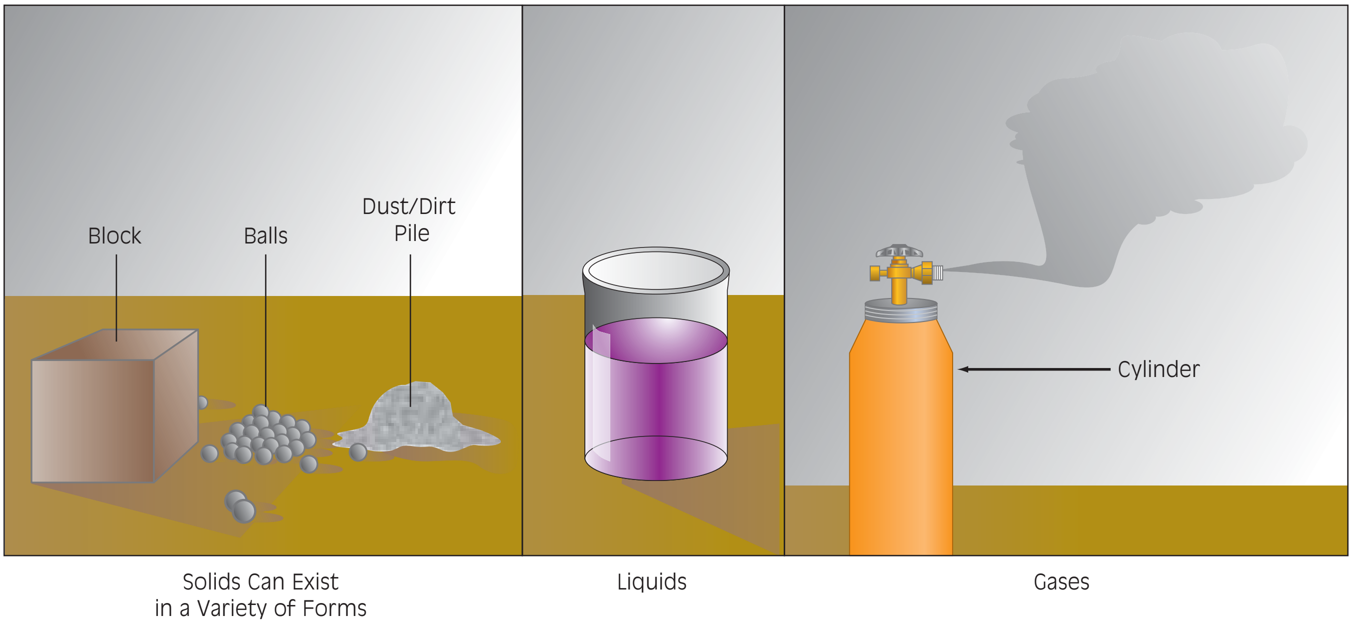


Figure 25-76 States of matter.

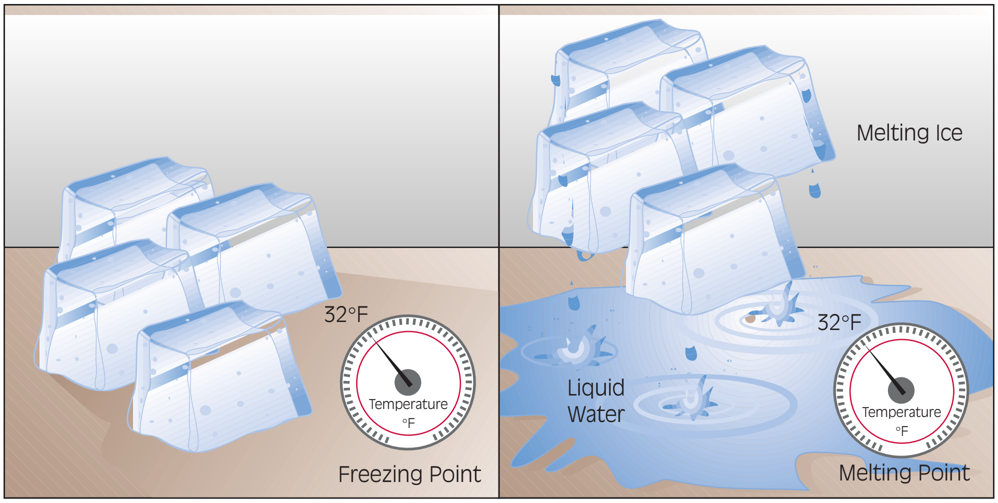


Figure 25-77 Melting and freezing points.

is being changed into a gas. Another way of defining boiling point is the temperature of a liquid when the vapor pressure exceeds the atmospheric pressure and a gas is produced. Water boils at 212°F and changes into a gaseous state. The important thing to remember about boiling points is the fact that when the liquid approaches this temperature, vapors are being produced that can cause larger problems.

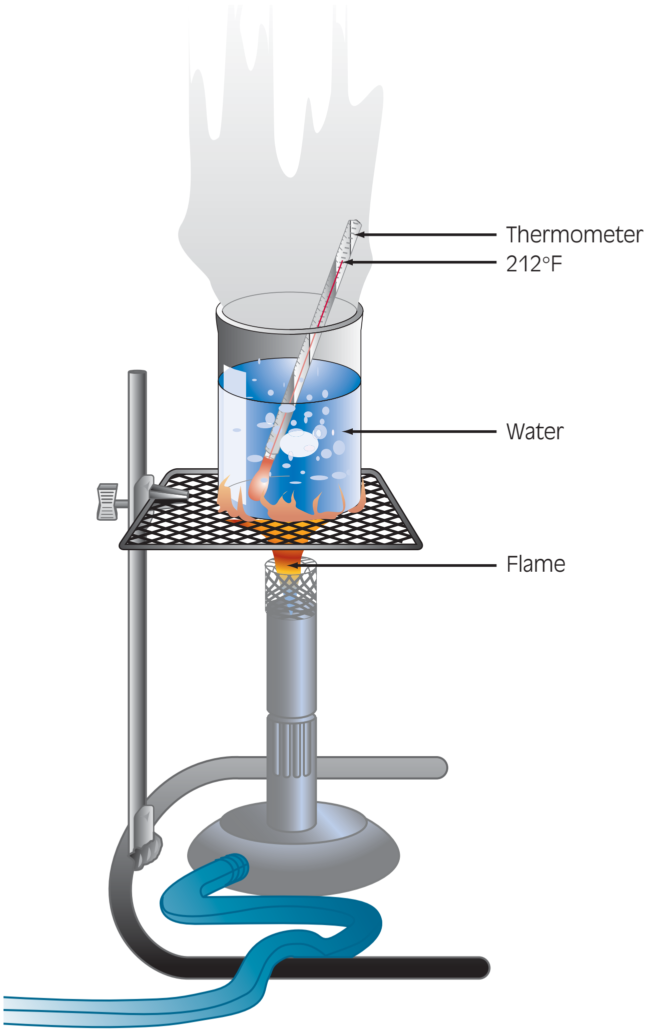


Figure 25-78 Boiling point.

Vapor Pressure

Out of all of the chemical and physical properties, vapor pressure is one of the most important to a hazardous materials responder. If a product has a high **vapor pressure**, it can be very dangerous. A material with a low vapor pressure is typically not a major concern. Vapor pressure has to do with the amount of vapors released from a liquid or a solid, **Figure 25-79**. The true definition is the pressure that is exerted on a closed container by the vapors coming from the liquid or solid. Vapor pressure can be related with the ability of a material to evaporate, in that the material is not really disappearing, it is just moving to another state of matter. Chemicals like gasoline, acetone, and alcohol all have high vapor pressures, whereas diesel fuel, motor oil, and water all have low vapor pressures.

Vapor pressures are measured in three ways: millimeters of mercury (mm Hg), pounds per square inch (psi), and atmospheres (atm). Normal or aver-

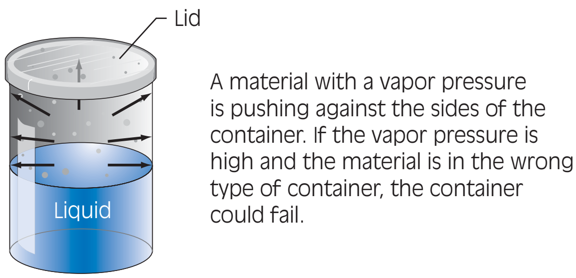


Figure 25-79 Vapor pressure.

Common Products and Their Vapor Pressures

NAME	VAPOR PRESSURE @ 68°F (MM HG)	BOILING POINT (°F)
Water	25*	212
Acetone	180	134
Gasoline	300–400	399
Diesel fuel	2–5	304–574
Methyl alcohol	100	149
Ethion (pesticide)	0.0000015	304 (decomposes)
Sarin nerve agent	2.1	316

*The vapor pressure of water has been reported in various texts as between 17 and 25 mm Hg. This text uses 25, as it is the highest reported vapor pressure for water.

TABLE 25-9

age vapor pressures are 760 mm Hg, 14.7 psi, and 1 atm. Although these figures are used to describe normal vapor pressure, they best describe atmospheric pressure. The temperature which is used is 68°F (20°C), which is the standard temperature. If a temperature is not provided, then it can be assumed it is 68°F. Chemicals that have a true vapor hazard are those in excess of 40 mm Hg, and they are considered volatile. Chemicals with a vapor pressure of less than 40 mm Hg do not present much inhalation hazard even though they can still present extreme toxicity through skin absorption. Chemicals with a vapor pressure above 40 mm Hg can be considered inhalation hazards in addition to any other route of exposure they may possess. **Table 25-9** lists vapor pressures for some common products.

A unique chemical phenomenon called **sublimation** occurs when a chemical goes from a solid state of matter to a gas. The material never enters the liquid phase. The sublimation ability means that some solids have a vapor pressure and can move directly to the gaseous stage. Some solids such as dry ice (carbon dioxide) move quickly to the gaseous stage, while others, such as mothballs (naphthalene or paradichlorobenzene), move slowly.

Vapor Density

It is easy to confuse vapor pressure with vapor density, but they have two entirely different meanings. Vapor density determines whether the vapors will rise or fall, **Figure 25-80**. When deciding on potential evacuations and other tactical objectives (e.g., sampling and monitoring) this is an important consideration. One of the primary reasons that natural gas leaks do not ignite or flash back more often is the vapor density of natural gas. Air is given a value of 1, and all other gases are compared to air. Gases that have a vapor density of less than 1 will rise in air and will dissipate, whereas gases with a vapor density greater than 1 will stay low to the ground. Natural gas has a vapor density of 0.5, while propane has a vapor density of 1.56, which causes it to seek out any low spots, like gullies or sewers. Propane is more likely to ignite or flash back because it has a greater potential of finding an ignition source.

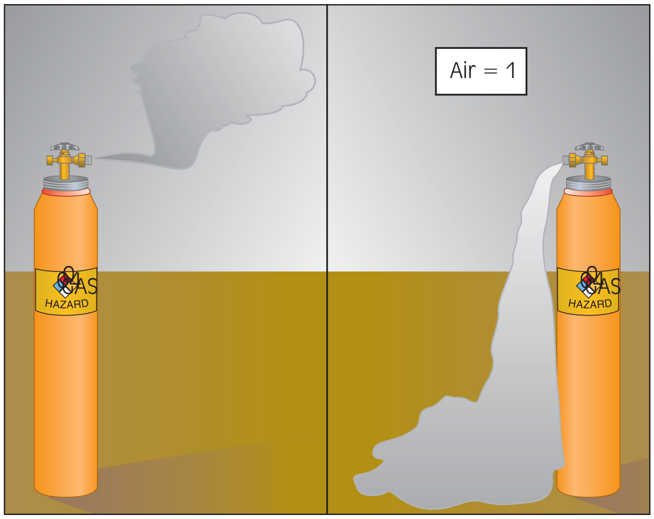


Figure 25-80 Vapor density.

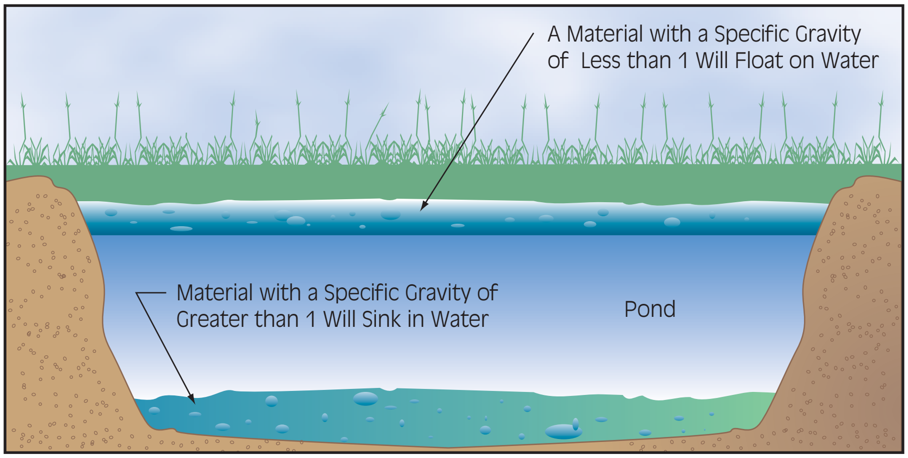


Figure 25-81 Specific gravity.

Specific Gravity

This chemical property is similar to vapor density in that it determines whether a material sinks or floats in water, **Figure 25-81**. Specific gravity is of prime concern when efforts are being taken to limit the spread of a spill by the use of booms or absorbent material. Water is given a value of 1, and chemicals that have a specific gravity of less than 1 will float on water. Fuels, oils, and other common hydrocarbons (chemicals composed of hydrogen and carbon, typically combustible and flammable liquids) have a specific gravity of less than 1 and, hence, will float on water.

Materials that have a specific gravity of greater than 1 will sink in water. It is much easier to recover materials floating on top of the water as opposed to those underwater. Carbon disulfide and 1,1,1-trichloroethane are two common materials that sink in water. Any material that sinks in water is especially troublesome if it has the potential to reach any groundwater, because remediation (cleanup) efforts are difficult and expensive.

Also of concern are materials that are water soluble, that is, have the ability to mix with water, not sink or float. Corrosives and many poisons are water soluble and are difficult to remove from a water source. Examples are provided in the following Firefighter Fact. Alcohol is also water soluble. Materials that are water soluble are difficult to extinguish.

Corrosivity

This text has already discussed tanks and containers that hold corrosives, as well as the concerns of dealing with corrosives. *Corrosive* is a term that is

Firefighter Fact When dealing with water-soluble materials it is important to protect bodies of water, because the cleanup can be difficult or impossible if the material enters the water. In one incident more than 10,000 gallons of sodium hydroxide, a very corrosive material, entered a small stream. The creek had to be dammed, and a neutralizing agent was put into the stream. Any life existing in this mile of stream was killed by the sodium hydroxide, but the environmental damage could have spread for many more miles if it had not been neutralized. Once neutral, the water was released, which eventually led to a larger body of water, where no damage occurred. This took considerable resources and time to accomplish, and luckily the necessary neutralizing agent was located at the site of the spill.

In another incident a very small amount of a pesticide was sprayed near a pond. After a rainfall the pesticide ran into the pond, killing all of the fish. The only method of removing this pesticide is the addition of other chemicals that are also hazardous. It will be years before the pond is able to sustain life.

In another incident in Baltimore City a railcar was involved in an accident and released 18,000 gallons of hydrochloric acid, which eventually ran into a local stream. The addition of the acid actually raised the pH level of the stream to near acceptable levels, because this stream was already heavily contaminated from a number of other sources.

Note that nothing should be flushed into any body of water without the express permission of the local or state environmental agencies.

pH of Common Materials

MATERIAL	pH	MATERIAL	pH
Water*	7	Sulfuric acid	1
Stomach acid	2	Gasoline	7
Orange juice†	2	Hydrochloric acid	0
Drain cleaner**	14	Pepsi‡	2
Potassium hydroxide	14	Household ammonia***	14

*Tap water is usually a 7, while rainwater in the Northeast can be 3–6 (acid rain).

†Citric acid is the main ingredient.

**The main ingredient is sodium hydroxide (lye).

‡Phosphoric acid is the main ingredient.

***This is a 5 percent solution of ammonium hydroxide and water.

TABLE 25-10

applied to both acids and bases, and is used to describe a material that has the potential to corrode or eat away skin or metal. Some examples are shown in **Table 25-10.** People deal with corrosives every day in that the human body is naturally acidic and they use many corrosive materials in their everyday lives. Acids are sometimes referred to as corrosives, whereas bases are also known as alkalis or caustics. The accurate way to describe a corrosive is to identify the material's pH, which provides some measure of corrosiveness. pH is an abbreviation for positive hydronium ions. It is used to designate the corrosive nature of a material. Acids have hydronium ions, and bases have hydroxide ions. It is the percent (ratio) of these ions that makes up the pH number. Materials having a pH of 0 to 6.9 are considered acids, and materials with a pH of 7.1 to 14 are considered bases. A material having a pH of 7 is considered neutral. The pH scale is a logarithmic scale, meaning the movement from 0 to 1 is an increase of 10. The movement from 0 to 2 is an increase of 100.

When dealing with a corrosive response, one of the common methods to mitigate the release is to neutralize the corrosive. One thought is that water can be used to dilute and thereby neutralize the spill. This presents two major issues: one, the mixing of water (chemical reaction), and two, the runoff from the reaction. Corrosives and water can be a dangerous combination. One should never add a corrosive to water, as it presents great risk. There may be some spattering and heat generation.

If 1 gallon of an acid had a pH of 0, it would take 10 gallons of water to move the material to a pH of 1. To move it to a pH of 2 would take 100 gallons of water, and to change the pH to 6 would require 1 million gallons of water—all for a 1-gallon spill. Chemically neutralizing a corrosive spill is the better choice, but even that can present some issues. When neutralizing a strong acid, a weak base should be used to perform the neutralization. A street method of calculation for neutralization is that it takes more than 8,800 pounds of potash to bring 1,000 gallons of 50 percent sulfuric acid to neutral, which is more realistic than controlling 1 million gallons of runoff. These examples are provided for information only; the neutralization of corrosives is a technician-level skill and can be very dangerous.

If the skin or eyes are exposed to a corrosive material, they should be immediately flushed with large quantities of water. This flushing should continue for at least twenty minutes uninterrupted. Some corrosive materials will cause immediate blindness and skin burns, and water should be used to prevent further injury.

Chemical Reactivity

Chemicals when they mix will have one of three types of reactions: exothermic, endothermic, or no reaction. The most common is the **exothermic reaction**, meaning the release of heat.

As discussed in Chapter 4, fire is a rapid oxidation reaction (exothermic) accompanied by heat and light. When most chemicals mix and provide an exothermic reaction there usually is not a lot of light but there can be substantial heat. By mixing one tablespoon each of vinegar (acetic acid) and ammonia (base) at the same temperature, an immediate rise in temperature of 10°F will occur. When handling oleum (concentrated sulfuric acid) and applying water to a spill, the resulting mixture will bubble,

Flash Points of Some Common Materials

MATERIAL	FLASH POINT (°F)	MATERIAL	FLASH POINT (°F)
Gasoline	−45	Diesel fuel	>100
Isopropyl alcohol	53	Motor oil	300–450
Acetone	−4	Xylene	90

TABLE 25-11

fume, boil, and heat to over 300°F the instant the water hits the acid. An **endothermic reaction** is one in which the energy created by the reaction is absorbed and cooling occurs.

Flash Point

A flash point is described as the temperature of a liquid at which, when heated by an ignition source, a flash fire occurs, **Table 25-11**. This resulting flash fire will ignite just the vapors and self-extinguish once those vapors are burned up. The liquid itself does not burn; it is the mixture of vapors and air that ignites. Following closely behind the flash point is the fire point of a liquid. The fire point is the temperature of the liquid at which, when heated, vapors are produced that when ignited will sustain burning. In the laboratory, scientists can replicate flash points and fire points; on the street, however, they are usually one and the same.

Autoignition Temperature

Sometimes referred to as **ignition temperature**, the autoignition temperature is the temperature at which a material will ignite on its own without an ignition source. Ignition temperatures are much higher than flash points and represent a potential hazard level depending on the temperature. Depending on the context, the term **self-accelerating decomposition temperature (SADT)** may be used, which is essentially the same thing as the autoignition temperature. Regardless of what it is called, it is a level to avoid.

Flammable Range

The two main areas within a flammable range are the lower explosive limit and upper explosive limit. The flammable range is the difference between the two extremes. A fire or explosion needs an ignition source, a fuel (vapors), and air. The proper vapor-to-air ratio is also required or ignition cannot occur. The **lower explosive** (flammable) **limit (LEL)** is the lowest amount of vapor mixed with air that can provide the proper mixture for a fire or explosion. The air monitor that is used to detect combustible gases is designed to read this level. The **upper explosive** (flammable) **limit (UEL)** is the highest amount of vapor mixed with air that will sustain a fire or explosion.

Each year many natural gas explosions occur throughout the United States. The LEL of natural gas is 5 percent, so if it is mixed with 95 percent air with an ignition source present an explosion or fire is possible, as shown in **Figure 25-82**. The UEL for natural gas is 15 percent, so 85 percent air is required to result in a fire or explosion. The flammable range for natural gas is 5 to 15 percent, and a fire or explosion can occur at any point in that range, as long as there is enough air to complete the mixture. With 4 percent methane and 96 percent air, there would not be any fire or explosion nor would there be at 16 percent natural gas and 84 percent air. Acetylene, which is a common gas, has a LEL of 2.5 percent and UEL of 100 percent, which means that when 2.5 percent LEL is reached, the potential for a fire exists. Having less than the LEL is referred to as *too lean,* and amounts in excess of the UEL are called *too rich.* Levels less than the LEL are much safer than levels above the UEL.

> **Safety** When confronted with a situation that has a level higher than the UEL, the situation is very dangerous.

Ventilation should be carried out using non-spark-inducing devices, and great care should be taken to minimize any potential electrical arcs such as not using light switches or doorbells.

Toxic Products of Combustion

This is the one area in which firefighters suffer considerable chemical exposures. Any time a person is in smoke or breathes smoke, the body is being bombarded with toxic chemicals. Many toxic chemicals, such as carbon monoxide, carbon dioxide, hydrogen cyanide, hydrochloric acid, and phosgene, are produced in a fire. The worst type

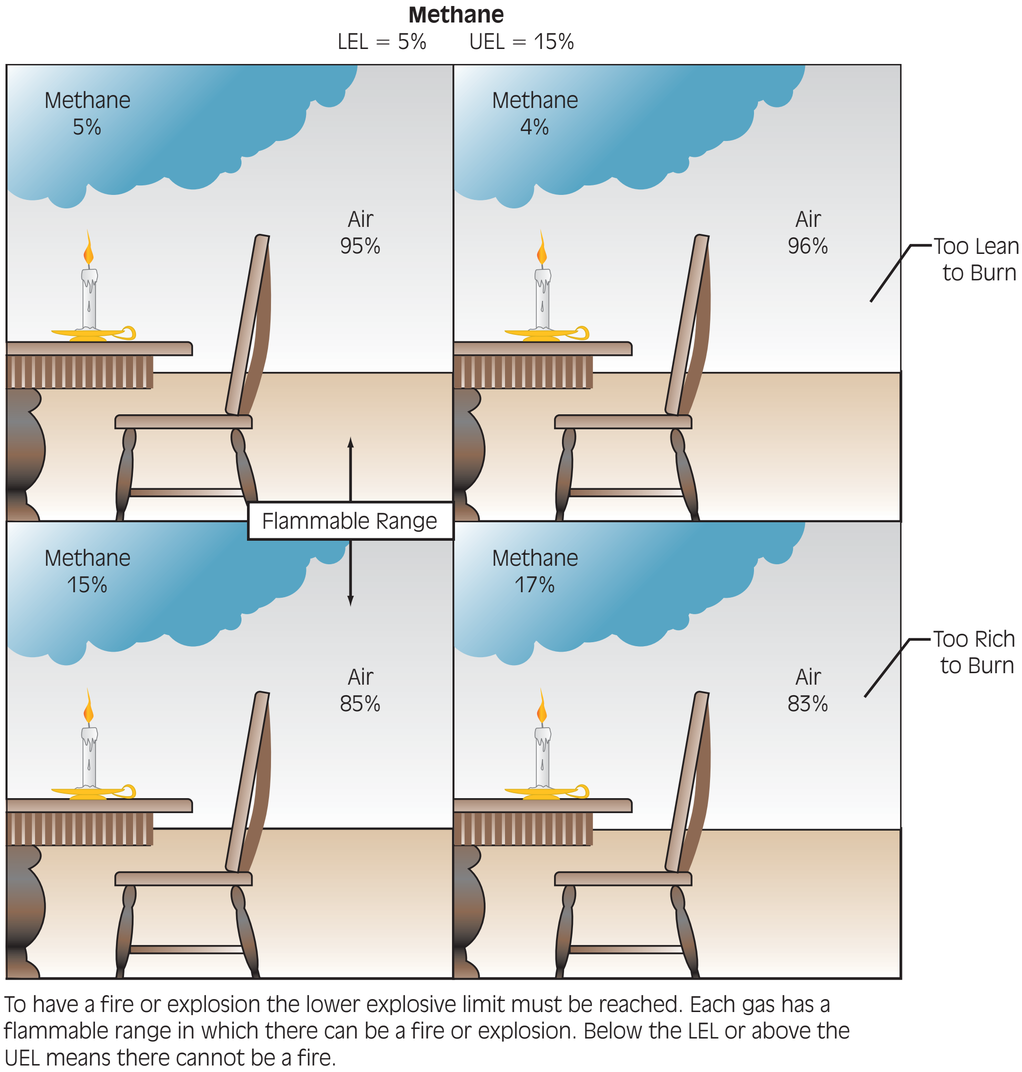


Figure 25-82 Flammable range.

of chemical accident a firefighter can respond to is a house, car, or Dumpster fire. Even brush fires are not exempt from the toxic products of combustion, because the field may have been sprayed with pesticides, herbicides, or other chemicals. Even burning wool or hay produces extremely toxic gases. Due to this constant exposure to these and other materials, it is important for firefighters to wear all of their protective clothing, especially the SCBA.

Lessons Learned

The ability to recognize and identify the potential for hazardous materials to be present at an incident is important for the first responder. The numbers of tank trucks, tank cars, and containers can easily overwhelm the beginning student. At any incident there is always a factor that relates to the recognition and identification process, whether it is the location, placards, container type, or physical senses. It could even be that sixth sense that alerts people to a potential problem. When that occurs, it is important to proceed with caution.

One of the important lessons for responders to remember is that they do not have to commit everything to memory, but they should know where to access hazardous materials information. It is not expected that each community have a railcar expert in their fire department. What is expected is that each fire department have a contact person available around the clock to obtain that resource. It is possible that every material on this earth has the ability to cause harm in some fashion, but the chemical and physical properties play a factor in the type of harm that can be caused.

Materials that have low vapor pressures present little risk to the responders unless touched or eaten. Materials that have high vapor pressures do present a great risk to responders and to the community and should be treated with caution. Vapor pressure is only one of the terms with which responders should become familiar. Local HAZMAT responders are a good resource and should be contacted early in an incident and whenever assistance dealing with hazardous materials is needed.

KEY TERMS

Aboveground Storage Tank (AST) Tank that is stored above the ground in a horizontal or vertical position. Smaller quantities of fuels are often stored in this fashion.

Boiling Point The temperature to which a liquid must be heated in order to turn into a gas.

Building Officials Conference Association (BOCA) A group that establishes minimum building and fire safety standards.

Bulk Tank A large transportable tank, comparable to a tote, but considered to be the larger of the two.

Chemtrec The Chemical Transportation Emergency Center, which provides technical assistance and guidance in the event of a chemical emergency; a network of chemical manufacturers that provide emergency information and response teams if necessary.

Cryogenic Gas Any gas that exists as a liquid at a very cold temperature, always below −150°F.

Deflagrates Rapid burning, which in reality with regard to explosions can be considered a slow explosion, but is traveling at a lesser speed than a detonation.

Emergency Response Guidebook (ERG) Book provided by the DOT that assists the first responder in making decisions at a transportation-related chemical incident.

Endothermic Reaction A chemical reaction in which heat is absorbed, and the resulting mixture is cold.

Exothermic Reaction A chemical reaction that releases heat, such as when two chemicals are mixed and the resulting mixture is hot.

External Floating Roof Tank Tank with the roof exposed on the outside that covers the liquid within the tank. The roof floats on the top of the liquid, which does not allow for vapors to build up.

First Responders A group designated by the community as those who may be the first to arrive at a chemical incident. This group is usually composed of police officers, EMS providers, and firefighters.

Frangible Disk A type of pressure-relieving device that actually ruptures in order to vent the excess pressure. Once opened the disk remains open; it does not close after the pressure is released.

Freezing Point The temperature at which liquids become solids.

Gas A state of matter that describes the material in a form that moves freely about and is difficult to control. Steam is an example.

Ignition Temperature The temperature of a liquid at which it will ignite on its own without an ignition source. Can be compared to SADT.

Intermodal Containers These are constructed in a fashion so that they can be transported by highway, rail, or ship. Intermodal containers exist for solids, liquids, and gases.

Internal Floating Roof Tank Tank with a roof that floats on the surface of the stored liquid, but also has a cover on top of the tank, so as to protect the top of the floating roof.

Leaking Underground Storage Tank (LUST) Describes a leaking tank that is underground.

Liquid A state of matter that implies fluidity, which means a material has the ability to move as water would. There are varying states of being a liquid from moving very quickly to very slowly. Water is an example.

Lower Explosive Limit (LEL) The lower part of the flammable range, and is the minimum required to have a fire or explosion.

Melting Point The temperature at which solids become liquids.

Ordinary Tank A horizontal or vertical tank that usually contains combustible or other less hazardous chemicals. Flammable materials and other hazardous chemicals may be stored in smaller quantities in these types of tanks.

Relief Valve A device designed to vent pressure in a tank, so that the tank itself does not rupture due to an increase in pressure. In most cases these devices are spring loaded so that when the pressure decreases the valve shuts, keeping the chemical inside the tank.

Reportable Quantity (RQ) Both the EPA and DOT use the term. It is a quantity of chemicals that may require some type of action, such as reporting an inventory or reporting an accident involving a certain amount of the chemical.

Sea Containers Shipping boxes that were designed to be stacked on a ship, then placed onto a truck or railcar.

Self-Accelerating Decomposition Temperature (SADT) Temperature at which a material will ignite itself without an ignition source present. Can be compared to ignition temperature.

Solid A state of matter that describes materials that may exist in chunks, blocks, chips, crystals, powders, dusts, and other types. Ice is an example.

Specification (Spec) Plates All trucks and tanks have a specification plate that outlines the type of tank, capacity, construction, and testing information.

States of Matter Describe in what form matter exists, such as solids, liquids, or gases.

Sublimation The ability of a solid to go to the gas phase without being liquid.

Tote A large tank usually 250 to 500 gallons, constructed to be transported to a facility and dropped for use.

Underground Storage Tank (UST) Tank that is buried under the ground. The most common are gasoline and other fuel tanks.

Upper Explosive Limit (UEL) The upper part of the flammable range. Above the UEL, fire or an explosion cannot occur because there is too much fuel and not enough oxygen.

Vapor Pressure The amount of force that is pushing vapors from a liquid. The higher the force the more vapors (gas) being put into the air.

REVIEW QUESTIONS

1. What are the nine hazard classes as defined by DOT?
2. An explosive placard is what color?
3. What three things on a placard indicate the potential hazards?
4. A DOT-406/MC-306 tank truck commonly carries what product?
5. A DOT-406 tank truck has a characteristic shape from the rear. What is it?
6. An MC-331 carries what type of gases?
7. What does the blue section of the NFPA 704 system refer to?
8. What are the locations of emergency shutoffs on an MC-331?
9. What are the four basic clues to recognition and identification?
10. The **Table 25-1** placards are required for what quantities?
11. A tractor trailer carrying Division 1.1 materials is well involved in fire. What should be the firefighter's initial tactics?
12. When propane tanks are involved in a fire, what is a potential consequence?

Endnotes

1. A tank truck placarded for gasoline could also haul diesel fuel or fuel oil without having to change placards.
2. The requirements for the subdivisions are presented in general. Other requirements may need to be met for a material to be assigned to a subdivision. Refer to 49 CFR 170–180 for more information.

Additional Resources

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