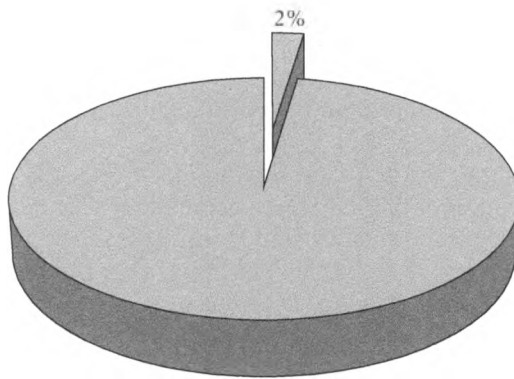


CHAPTER 11

Flammable and Explosive Materials



Percentage of OSHA General Industry citations addressing this subject

In Chapter 5, materials hazardous to the environment were considered. The health hazards of toxic materials have also been studied in Chapter 9. In this chapter, we examine a more traditional type of hazardous material, flammable and explosive substances, and their use in factory processes, such as spray finishing areas and dip tanks. We now know that most of these substances are dangerous from a health hazard perspective, but their safety hazards are the traditional concerns with flammable and explosive materials, and safety hazards take center stage in this chapter.

FLAMMABLE LIQUIDS

Flammable liquids such as gasoline are familiar to everyone, and the new safety and health manager might expect applicable standards for flammable liquids to be the easiest to learn and to apply. But, unfortunately, the standards are quite complicated as a natural result of the fact that flammable liquids occur in industry quite frequently and in such widely varying quantities and applications. To illustrate this point, procedures

for handling gasoline in a petroleum refinery in which gasoline is *manufactured* are vastly different from procedures for storing and handling flammable liquids in an ordinary factory or office. Therefore, no simple set of rules for flammable liquids is appropriate.

As familiar as flammable liquids are, most people do not really understand many of the commonly used terms, such as *flashpoint*, *Class I liquid*, *flammable*, *combustible*, and *volatile*. Much confusion surrounds the sources of ignition for flammable liquids also and the circumstances under which such substances will burn, explode, or not burn at all. This chapter will therefore focus first on definitions and principles of ignition of flammable liquids and then will discuss some of the problems in complying with appropriate standards.

Perhaps the most basic term should be defined first, and this is the term *liquid*. Almost everyone knows what a liquid is, but on the other hand, virtually every flammable substance exists as both a liquid and a gas, depending on temperature or pressure. A good practical rule to follow is that if the substance is normally a liquid, it is defined as a *liquid*. Where one can get into trouble is in classifying propane and butane, which are gases and are not intended to be considered flammable liquids, although they can be liquefied. The National Fire Protection Association's (NFPA) standard definition of flammable liquid excludes propane and butane by excluding all "liquids" having a vapor pressure in excess of 40 pounds.

The term *flashpoint* is very important to the safety and health manager because it is the principal basis for classification of flammable and combustible liquids. Therefore, it is primarily flashpoint that determines the various amounts of the liquid that are permitted to be stored in various types of containers. Flashpoint is the point to which a flammable liquid must be heated so that it will give off sufficient vapor to create a flash at the surface of the liquid when there has been a spark or flame applied to it. Flashpoint is not the same as *firepoint*; firepoint is a higher temperature and is the temperature at which a fire on top of the liquid is sustained.

Three principal testing methods are in use for determining flashpoint. The Cleveland open-cup test is simple, but is not often used because it is intended for heavy oils. The most frequently used method is the Tag closed tester method. The term *Tag* is simply an abbreviation for a French name *Tagliabue*. The third method is the Pensky-Martens closed tester method. This method uses a small stirring rod and is used for viscous liquids and liquids that form a film on the surface. This method is also rarer than the Tag test. The open-cup method best simulates the in-plant situation in which open vats are being utilized. The closed-cup situation best simulates the situation for flammable liquids in storage.

Classification of flammable liquids also depends on the *boiling point*, but even this can be confusing because liquid does not normally boil at only a single temperature point. This range is acknowledged in the standards by designating the 10% *point* as the key. The 10% point is the temperature at which 10% of the liquid has become gas. *IBP* refers to initial boiling point and is the temperature at which the first drop of liquid falls from the end of the distillation tube in a standard ASTM (American Society for Testing and Materials) test distillation.

Volatility refers to how readily a liquid will evaporate; it is closely related to boiling point. *Light* and *heavy* refer to high volatility and low volatility, respectively.

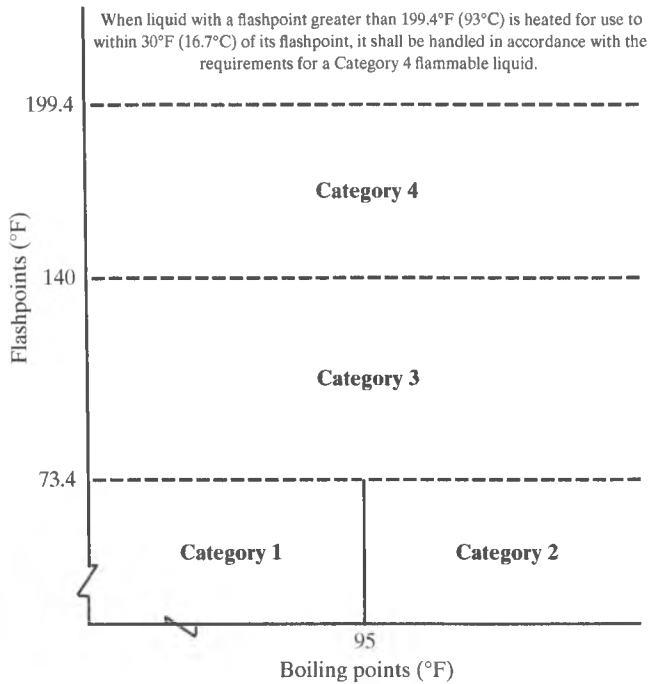


FIGURE 11.1

Classification of flammable and combustible liquids.

Previously flammable liquids were divided into classes with Class I being considered flammable liquids and Class II and Class III being considered combustible liquids. This has been changed to just flammable liquids with 4 categories. The entire classification scheme, which is based on flashpoint and boiling point, is explained in Figure 11.1.

Gasoline is the most widely used and plentiful flammable liquid. Because of its widespread use and because of horrible explosions and fires in its history, gasoline is blamed for a great deal of the fire hazards in workplaces and elsewhere. Some of the fears of gasoline hazards arise from ignorance rather than knowledge-based prudence, and this is detrimental to the cause of safety. In Chapter 3, it was explained that overzealous safety rules contribute to worker apathy for the rules and in turn work against the cause of safety rather than helping it. Operational and safety rules for working around gasoline and other flammable liquids are sometimes in this unfortunate category. Admittedly, gasoline can be extremely dangerous, but there is no substitute for knowledge of the mechanism of its hazards so that the worker can take sensible precautions.

Knowledge begins with exposing the falsehood of the many myths surrounding the subject. Gasoline and other flammable liquids have their share of such myths, and this book will attempt to dispel some of them here.

Perhaps the wildest myth about gasoline is the one discussed next.

Flammable Liquid Myth 1

A lighted cigarette when brought into contact with the surface of a container of gasoline is sure to ignite it.

On the contrary, it is almost impossible to ignite a tank of gasoline at the surface with a lighted cigarette. As with any ordinary fire, three ingredients are essential to support combustion:

1. Fuel
2. Oxygen (usually from the air)
3. Sufficient heat

There is plenty of fuel at the surface of a container of gasoline, but the other two ingredients are generally insufficient to support combustion. A concentration of gasoline vapors in excess of 7.6% is too rich and will not burn. At the surface of gasoline standing in still air, the concentration is much higher than 7.6%. In addition, a glowing cigarette is not hot enough in most cases to permit ignition.¹ In fact, dramatic demonstrations have been performed in which a lighted cigarette is extinguished by drowning it in a cup of gasoline! Incidentally, there are hazards involved in such demonstrations, and experimentation is not recommended. Things can go wrong, such as tiny flame on the cigarette paper being hot enough for ignition. In addition, there is the problem of getting the cigarette *through* the region in which the vapors are not too rich and causing ignition before the rich area near the surface can be reached. In addition, small quantities of gasoline in the surrounding area can cause vapor-air mixtures just right for combustion. These are the reasons for “no smoking” rules around gasoline.

Gasoline has a burnability range of 1.4 to 7.6% gasoline vapors in dry air. Some other flammable liquids have wider burnability ranges and are more easily ignited than gasoline. Burnabilities for some commonly used highly flammable liquids are shown in Figure 11.2. Note that though gasoline is easier to ignite at “lean” concentrations than alcohol is, alcohol will ignite at much richer concentrations. Also note the extremely

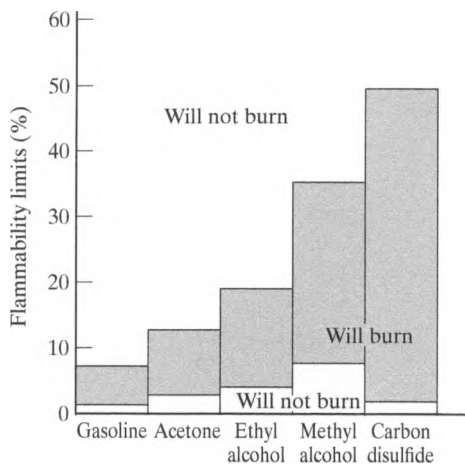


FIGURE 11.2

Burnability ranges of some popular flammable liquids.

¹The ignition temperature for gasoline (536–853°F) is higher than that for wood (approximately 400°F)!

broad and dangerous burnability range of carbon disulfide. The upper limit, above which concentrations of flammable vapors are too rich to ignite, is designated as the *upper explosive limit* (UEL). The corresponding lower limit, below which concentrations of flammable vapors are too lean to ignite, is the lower explosive limit (LEL).

Another myth regarding gasoline has to do with service station fires and other fires around underground tanks.

Flammable Liquid Myth 2

Fires in underground gasoline tanks burn or explode with such intensity as to destroy much life and property around service stations.

Actually, fires do not burn in underground tanks of gasoline, even when a serious fire occurs above the ground. John A. Ainlay² states that in a 45-year-long study of petroleum-fire reporting by the National Fire Protection Association (NFPA) and the American Petroleum Institute (API), there has never been a fire reported in an underground tank of gasoline currently in use. The vapor mixture in the tank is too rich to support combustion.

An abandoned empty tank is, curiously, more dangerous than a full or nearly full tank in use. The abandoned empty tank has had a chance to dry out, and vapors have gradually dispersed until the mixture may have become lean enough to result in an explosive mixture. The same is true of any *empty* gasoline drum. But a drum that is full or partially filled with gasoline will normally have a vapor-air ratio that is too rich to support combustion. Figure 11.2 shows that fire has a much greater hazard potential inside drums of alcohol or carbon disulfide.

With aboveground tanks, the hazard takes on a different dimension. The aboveground tank is exposed to intense heat and possible rupture during a service station fire. When a tank ruptures or explodes, tremendous quantities of fuel are suddenly added to the fire in the presence of abundant supplies of oxygen and heat.

The preceding paragraph describes ample reason for the standards that prohibit aboveground tanks for service stations, except when special conditions are met. There is, however, still another hazard for aboveground tanks. The vapor density³ of gasoline is higher than 3 to 1. This means that unlike natural gas or other lighter-than-air materials, gasoline vapors will settle in low places. An aboveground tank is an invitation for gasoline vapors to settle in low areas of the service station, such as in service pits. The vapor density of gasoline is the reason that basements in service stations are now illegal.

Despite these hazards, a large number of violations of the standard that prohibits aboveground tanks have been found. Small independent service stations and private, in-plant service stations are the most frequent violators. Many of these installations were made prior to the writing of the standard, and some feel that such a standard was intended to act as a "building code" and apply to all future installations—not requiring all existing noncomplying stations to remodel.

Misconceptions about *octane rating* are at the root of the third myth.

²John A. Ainlay of Evanston, Illinois is a nationally recognized authority on the chemistry of petroleum fires.

³Vapor density is the ratio of the weight of the vapor to the weight of the same volume of air.

Flammable Liquid Myth 3

High-octane “aviation gasoline” or “premium gasoline” is much more hazardous than regular gasoline.

Octane rating has to do with the preignition characteristics of gasoline within internal combustion engines and has nothing to do with fire safety. High-octane gasoline should be given the same fire precautions as regular gasoline—no more, no less.

SOURCES OF IGNITION

Dispelling myths about flammable liquids should make personnel more cautious. The chemistry of a petroleum fire explains some of the seemingly peculiar instances of non-occurrence of such fires. But at the same time, this understanding can highlight the extreme hazard involved when conditions are right for a fire. A broken light bulb seems innocent, but can result in a disastrous fire. In the instant before a hot light bulb filament burns out after the glass breaks, that filament is hot enough to ignite gasoline vapors. This is why it is important to protect light bulbs in the presence of flammable vapors as required in both the *National Electrical Code*® and further references in federal standards.

Welding sparks are another important ignition hazard for flammable vapors. The usual temptation is to speed up a repair operation, and welding is often commenced before sources of flammable vapors are removed from the area and existing vapors purged. Welding around flammable vapors has cost the lives of many inexperienced personnel who were not aware of the hazards involved.

Associated with welding is the grinding of the finished weld. Sparks generated are not to be trusted. It is true that many grinding sparks do not reach the required ignition temperature for gasoline vapors, but some sparks do. Therefore, spark-producing grinding should not be performed in the presence of flammable vapors.

The hazards of static electrical discharge around flammable vapors are well publicized. After all, it is electrical discharge that ignites gasoline vapors with precise reliability in most internal combustion engines. Electrical arcing or static electrical discharge is easily a source of ignition.

To prevent ignition hazards, electrical interconnection is required between nozzle and container when dispensing Category 1 or 2 flammable liquids, or Category 3 flammable liquids with a flashpoint below 100°F. The first part of Figure 11.3 shows two conducting containers, neither of which are bonded or grounded. The second part shows two conducting containers which are both bonded, that is, they share the same electrical charge. The final part shows the best way to dispense these liquids into containers made of conducting material. The two containers are both bonded, and are grounded, meaning they have no charge. But this raises questions regarding dispensing these liquids into containers made of plastic or other nonconductive material. It makes no sense to bond a plastic container to the nozzle because such a bond would be ineffective in equalizing the static charge (see Figure 11.4). The NFPA recognized this fact when it exempted nonconducting containers from electrical bonding requirements in NFPA standards.

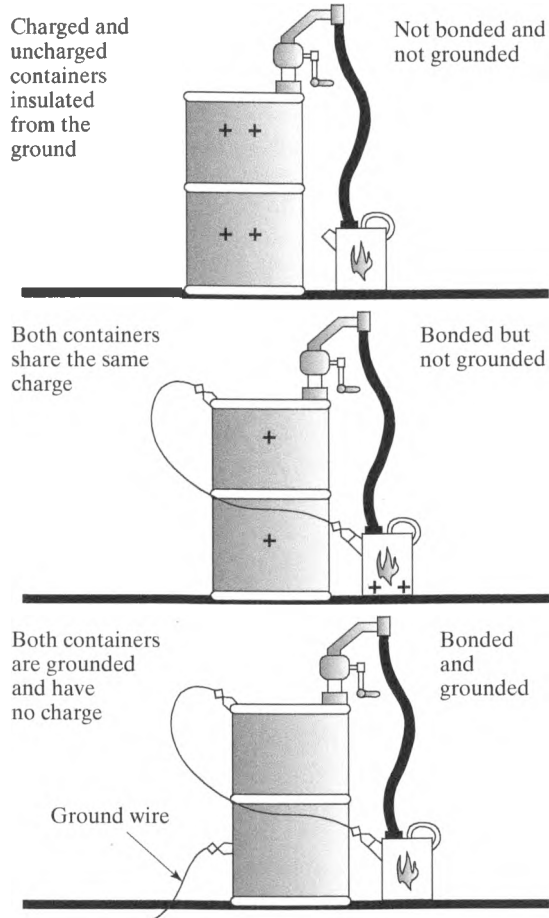
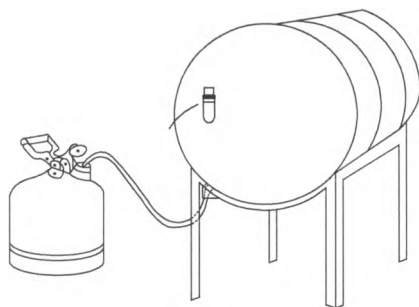


FIGURE 11.3

Dispensing Class I liquids into conducting container (*Source: Flammable and Combustible Liquids Fact Sheet, 2005*).



Nonmetallic safety can needs no bonding wire during filling operation

FIGURE 11.4

Bonding not necessary for nonconducting container.

Some readers may wonder why there is so much fuss about static electricity during dispensing operations. But filling tanks or containers *generates* static electricity because of the flow of the liquid—a little known phenomenon regarding fluid flow. The rapid flow of carbon dioxide from a fire extinguisher in use can cause static electrical shocks that make the extinguisher very uncomfortable to hold. During the loading of fuel oil into tank trucks at night, an astonishing phenomenon has been observed in which “lightning displays” are seen flashing around inside the tank!

To prevent buildup of static electricity during loading operations, the flow should be kept as quiet and smooth as possible. Filters are big static generators and are best placed as far back in the line as possible, remote from the fill spout. Another measure that can be taken to reduce static electricity is to retard the flow. In addition, *splash loading* should be avoided; that is, the fill spout should extend down to a point close to the bottom of the compartment to avoid excessive splashing, which generates static electricity. When loading multicompartment trucks, the front and rear compartments are the most likely to present problems from splash loading because of the arrangement of some types of loading apparatus. The reason for this can be seen in Figure 11.5. Another way to eliminate static is to place a rest area in the delivery line, as shown in Figure 11.6. The rest area is an expansion area in the pipe that allows static charge to bleed off the liquid before rapid flow continues.

STANDARDS COMPLIANCE

An understanding of the principles underlying the hazards with flammable liquids is useful when applying appropriate standards. Having covered some of the basic definitions and principles, we now turn to a direct analysis of the standards and helpful procedures to be followed by safety and health managers to bring their facilities into compliance.

In many facilities, small quantities of flammable materials are required for processes or operations. Section 1910.106 specifies that no more than 25 total gallons of incidental use in separate containers are allowed in a given area. This is not the limit

FIGURE 11.5

Splash loading occurs more often while loading front and rear compartments than while loading a middle compartment.

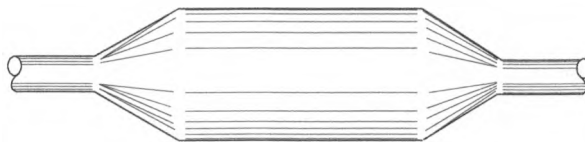
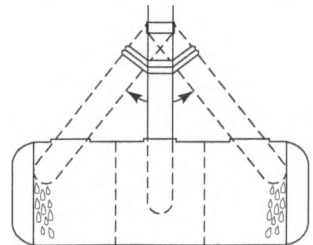


FIGURE 11.6

Static eliminator rest area.

TABLE 11.1 Container Limits from Table H-12 of Section 1910.106

Container type	Category 1	Category 2	Category 3	Category 4
Glass or approved plastic	1 pint	1 quart	1 gallon	1 gallon
Metal (other than DOT drums)	1 gallon	5 gallons	5 gallons	5 gallons
Safety cans	2 gallons	5 gallons	5 gallons	5 gallons
Metal drums (DOT specifications)	60 gallons	60 gallons	60 gallons	60 gallons
Approved portable tanks	660 gallons	660 gallons	660 gallons	660 gallons

DOT, Department of Transportation

Source: Flammable and Combustible Liquids Fact Sheet, 2005.

for storage in flammable storage cabinets or in specially built storage rooms. The standard is also specific in the quantity of flammable material kept in the various types of portable use containers. These quantities can be found in Table 11.1.

Federal codes for tank storage are quite complicated and are mostly the concern of layout designers of petroleum tank farms, bulk plants, dikes and drainage schemes, refineries, and service stations. The codes also cover such elements of design as tank construction and proper venting. Most safety managers do not need to concern themselves with mastering the details of tank construction. It is sufficient to know where to find the requirements and to alert designers and other planners that strict codes must be followed in specifying tanks for flammable liquids.

One criterion for distance requirements between tanks is whether the tank roof is fixed or floating. The general public does not usually realize that the roofs of many petroleum tanks rise and fall with the level of the liquid inside (see Figure 11.7). A tank with a fixed roof will not fill unless it is vented, and such venting causes a costly loss of vapors. But the safety and health manager should understand that the floating roof also protects against the fire hazards of releasing vapors to the atmosphere. The vapor-air space inside an empty or nearly empty tank with a fixed roof is also more hazardous than for the floating-roof tank, which has little or no vapor-air space. The floating-roof tank is a dramatic example of an industrial improvement that saves production cost while promoting a safer workplace.⁴

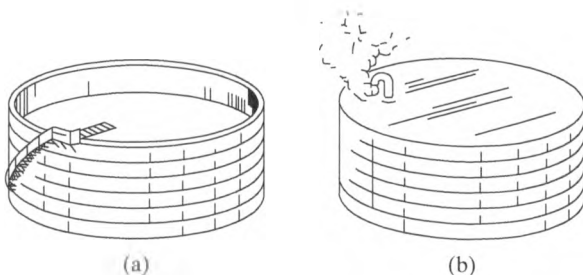


FIGURE 11.7

Two types of storage tanks: (a) floating-roof type; (b) conventional vented type. The floating roof rises and falls with the level of the liquid inside the tank, eliminating the necessity of costly and dangerous venting.

⁴The disastrous effects of improper design of flammable liquid tanks are illustrated in Exercise 11.45 at the end of this chapter.

One curious provision of appropriate safety standards requires accurate *inventory records* for flammable liquid storage tanks. Inventory records are usually for accounting and cost control, so what business does a *safety* standard have in dealing with accurate inventory records? The answer is that accurate inventory records can be used to detect dangerous leaks. Unfortunately, inventory discrepancies are often attributed to “clerical error” or “unexplained loss” and are simply ignored. After a serious fire has occurred, an investigating team sometimes probes the past inventory records only to discover that the evidence of a dangerous leak had been in the records for many days. It may seem incredible that a leaking underground tank of gasoline would go undetected, but it happens, as will be seen in Case Study 11.1.

CASE STUDY 11.1

SERVICE STATION UNDERGROUND LEAK

In the 1980s, a resident of Fayetteville, Arkansas, complained of the odor of gasoline vapors in the basement of his home. The local fire department investigated and found that flammable gasoline vapors did indeed exist there. Other homes in the same block were also found to have traces of gasoline vapors. Further investigation revealed that a service station in the neighborhood (but not adjacent to the house) had a leaking underground gasoline tank. It was necessary that the residents of the unsafe homes be evacuated until necessary repairs could be made. The repair required an extensive excavation to resolve the problem.

With respect to the hazards of leaking tanks, the safety and health manager must follow the regulations of two federal agencies: OSHA and EPA. The EPA cracked down on underground storage tanks in late 1988 (Cross, 1988) and required systems for monitoring tank and pipe leaks, automatic shutoffs for pressurized systems, specified tank and pipe construction, spill protection, and systems to prevent overflow. In addition, there are reporting requirements to notify local or state authorities whenever a new tank is installed, an old one is closed permanently, or a leak is discovered. A notable exemption to EPA's tank rule is *above* ground tanks, provided that less than 10% of the product is stored in subsystem piping.

In summary, the safety and health manager should approach the flammable liquids problem with a knowledge of the principles of ignition. Any new facility should be designed and constructed with recognition of the hazards of flammable liquids. After construction and installation, commonsense rules for eliminating sources of ignition and preventing dangerous leaks should be established and enforced by the safety and health manager. Training of personnel to understand the underlying principles of the hazards will help a great deal with the problem of safety around flammable liquids.

COMBUSTIBLE LIQUIDS

The reclassification of flammable/combustible liquids as Category 1, 2, 3, and 4 flammable liquids is relatively new, and the concept of “flammable” versus “combustible” is still familiar in industrial usage. The higher flashpoints of Category 3 and 4 flammable liquids make them less hazardous to use in industrial settings. Most of these Category 3

and 4 liquids are associated with the common industrial term "combustible liquid." Even though combustible liquids have a higher flashpoint and the hazard of ignition is much lower, a false sense of security is often engendered by commonplace association with these liquids at room temperatures. In the event that temperatures are elevated by some exceptional circumstance or even by normal process operations, the gravity of the hazard can shift dramatically. Ordinary kerosene, a combustible liquid, can become even more dangerous and ignitable at elevated temperatures than is gasoline at room temperature.

Another way in which combustible liquids can present an unexpected hazard is in *switch loading*, when transport trucks are used for hauling gasoline, a flammable liquid, and fuel oil, a combustible liquid, interchangeably. Switch loading is a danger from the standpoint of ignition by static electricity. With gasoline, static electricity is not as serious a problem in loading because the vapor concentration is generally far too rich to permit ignition. Even when loading gasoline into a tank that previously contained fuel oil, the vapor concentration becomes too rich as soon as loading commences. The real danger is when fuel oil is loaded into a compartment that previously contained gasoline. This is switch loading and is very hazardous. The vapor concentration in such an operation is just right for ignition and a static discharge or any other source of ignition can result in an explosion that will rip the truck apart. Remedies for the problem when switch loading is necessary are to (1) fill the tank with carbon dioxide (the cardox method); (2) use vacuum cleaners to purge the tank of gasoline; or (3) cut the loading speed down to about 30% until the tank is about one-third full.

When a choice is to be made between a flammable and a combustible liquid for a given application, the difference in costs of electrical equipment installations can be dramatic. When the normal operation of a process produces ignitable concentrations of flammable liquids in the atmosphere, explosion-proof electrical equipment approved for Class I, Division 1 hazardous locations is specified for the area in which the vapors are present. Providing explosion-proof electrical equipment is a costly undertaking and is discussed in detail in Chapter 17. Case Study 11.2 is used to illustrate the valuable impact a knowledgeable safety and health manager can have on a company when a decision is to be made regarding flammable and combustible liquids.

CASE STUDY 11.2

FLAMMABLE VERSUS COMBUSTIBLE LIQUIDS

A process engineer has a new idea to cut costs in an operation that strips organic coatings from metal parts before they are plated. The process currently uses Enthone Stripper S-300, but the engineer has discovered in the laboratory that Enthone Stripper S-15 is much more effective in removing the organic coatings than S-300 and can save the company both production time and money by reducing the volume of stripper required to be purchased from the vendor. How would this new idea affect fire safety?

Solution

The safety and health manager would wisely take a keen interest in a comparison of the flammability characteristics of the two strippers under consideration. Checking

the NFPA's *Flashpoint Index of Trade Name Liquids* (Flashpoint Index of Trade Name Liquids, 1978) the safety and health manager notes that Stripper S-300 has a flashpoint of 155°F, whereas S-15 has a flashpoint of 34°F. From Figure 11.1, it can be seen that these data mark S-300 as a moderately safe Category 4 flammable liquid, whereas S-15 is identified as a very hazardous Category 1 or 2 flammable liquid. Choosing Stripper S-15 would definitely affect fire safety and perhaps increase insurance rates. If electrical equipment, such as conveyors and switches, is required around the stripping operation, the requirement to provide Class I, Division 1 explosion-proof equipment could make the S-15 alternative prohibitively expensive, even considering the cost savings that the process engineer is claiming.

In Case Study 11.2, the idea generator was a process engineer. The case study should serve as a model, however, for ways in which the safety and health manager, armed with knowledge of the contrasting properties of flammable and combustible liquids, can be the idea generator to make processes safer and perhaps much cheaper. This is the kind of impact on the company's bottom line that corporate management has not customarily expected from the safety and health manager, but that will certainly get top management's attention. We now turn our attention to one of the most important industrial applications of flammable and combustible liquids: spray finishing.

SPRAY FINISHING

A direct concern of safety and health managers, especially in manufacturing plants, is the installation of facilities and proper procedures for spray painting areas or booths. The subject is important not only from a compliance standpoint, but it also greatly affects insurance rates and basic insurability.

The construction and operation of a spray painting area that meets applicable code is a quite costly undertaking, and an unethical safety and health manager sometimes attempts to circumvent the rules to appease top management. The most common example of such circumvention of the rules is to call the paint facility a "small portable spraying apparatus not used repeatedly in the same location" and thus achieve exemption from spray painting standards. But if the small "temporary" setup becomes a more or less permanent arrangement, a continuing and serious fire hazard will result. Furthermore, neither the insurance company inspector nor an experienced government inspector will be fooled by a so-called temporary arrangement that has eventually become permanent, because spray paint residues will accumulate throughout the area in large quantities.

There are both health and safety considerations in spray finishing operations, but standards for spray finishing principally concern safety aspects, particularly fire. The most frequent violations of spray finishing standards are in the following categories:

- Improper wiring type for hazardous location
- Exhaust air filter deficiencies

- Cleaning and residue disposal
- Quantities of materials in storage
- Grounding of containers
- “No Smoking” signs

In addition, frequently violated but of somewhat less emphasis are the physical construction requirements for spray booths and their mechanical ventilation requirements.

Applying the rule of attacking the easiest problems first, the safety and health manager should take steps to immediately install “No Smoking” signs in spraying areas and in paint storage rooms. This advice may sound superficial, but thousands of firms have received OSHA citations simply for failure to post such signs. The cost of complying with this rule is almost negligible.

After ensuring that “No Smoking” signs are installed, the safety and health manager should investigate the wiring in the spray area to determine whether it conforms with *National Electrical Code*® specifications for hazardous areas. A competent electrician, knowledgeable in the provisions of the *National Electrical Code*, is useful for this phase of the problem.

Appropriate wiring and electrical equipment classification in and around spray areas may be simplified to some extent by using a decision diagram like the one shown in Figure 11.8. A great deal of controversy has arisen regarding the enforcement of electrical requirements around spray areas, particularly regarding the interpretation of the legendary “20-foot distance” from the spray area. It is interesting to note that the *National Electrical Code*, 1975 edition, reduced the required distance from 20 feet to 5 feet from the spray area. The federal standard for this distance, however, was left unchanged—another example of how the legal promulgation process slows the standards revision process.

Besides distance of travel, another issue is the *direction* of travel of the flammable vapors after they leave the paint spray booth. Since flammable vapors can travel in any direction, it is recommended that the safety and health manager take the cautious rule of using Class I, Division 2 wiring in all directions from the open face of the spray area or booth, including vertically and around the corners alongside the booth. Additional guidance on the various classifications for electrical wiring is contained in Chapter 17.

Some people construe the standards to require automatic sprinkler systems for all paint spray areas, but the standards do not really specify this. If an automatic sprinkler system is used, however, it must meet NFPA requirements. The vendor who installs the sprinkler system should be required to ensure that the system conforms to all applicable codes for the installation to which it will be applied. If the system is installed inside the ducts, sprinklers are needed on both sides of the filter system.

Combustible residues contribute to the largest proportion of spray booth fires. Reactions between different materials can add to this hazard, especially when peroxides are used. The control of overspray residues involves both engineering and administrative controls and is an item that deserves the attention of the safety and health manager. Residue accumulation is easy to recognize and is an embarrassing testament to poor maintenance and lack of hazard control. Once removed, the residue and debris must be

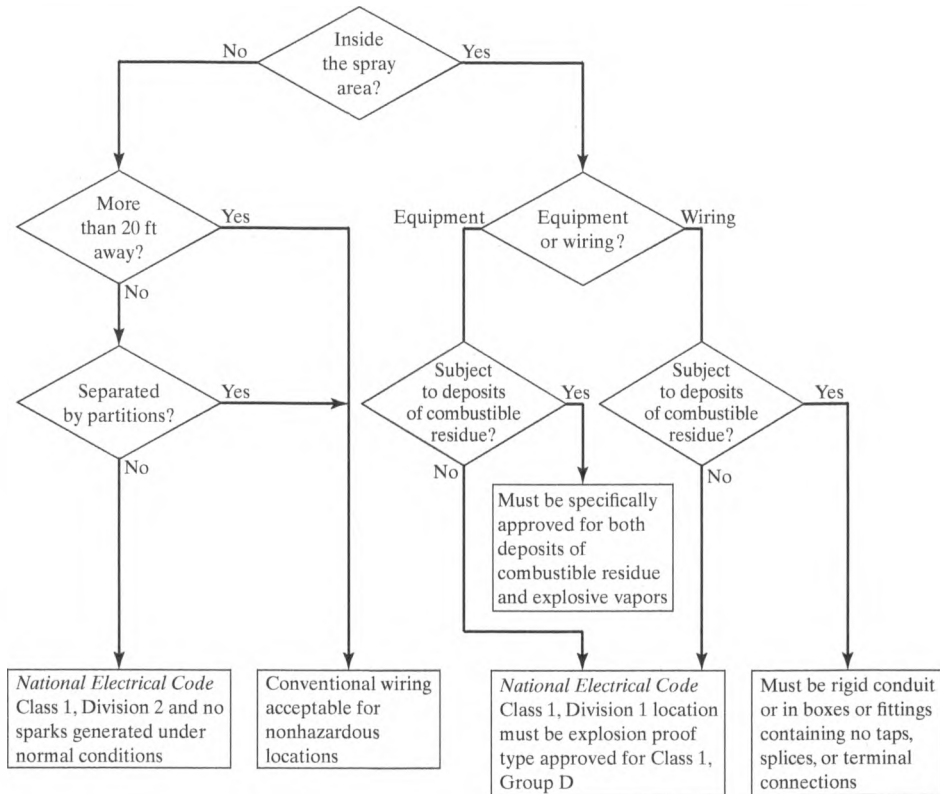


FIGURE 11.8

Decision diagram: How to follow OSHA Standard 1910.107(c)(5) and (c)(6) specifications for spray area wiring and electrical equipment.

properly disposed of to prevent spontaneous combustion and other fire hazards from oily rags and residue debris.

It was stated earlier that automatic sprinkler systems are not required for *all* areas. However, for fixed electrostatic systems, automatic sprinklers are required “where this protection is available.” Automatic sprinkler systems are preferred, and if such a system is already available close by (within approximately 50 feet), it should be extended to the electrostatic spraying area. In the absence of “available” automatic sprinkler systems, the standard requires “other approved automatic extinguishing equipment” for electrostatic spray areas. Such alternate systems would include fixed carbon dioxide or dry chemical systems, and these systems will be discussed further in Chapter 13.

The use of heating devices for drying in the spray area increases the hazard by raising the temperature of overspray residues and also by increasing the vapor level in the air. In addition, the standards are not very clear concerning the use of the spray area for a drying area. The use of the spray area as a drying area is prohibited unless the arrangement does not “cause a material increase in the surface temperature of the spray booth, room, or enclosure.”

DIP TANKS

Dip tanks often contain hazardous materials and are treated separately in federal standards. However, care must be exercised when consulting the standard because it applies only to those dip tanks containing flammable and combustible liquids. Plating dip tanks containing hazardous acids are *not* covered by the dip tank standard unless the acid is flammable or combustible.

The following are the principal problems with dip tanks:

- Automatic extinguishing facilities
- "No Smoking" signs
- Dip tank covers

The lack of dip tank covers is the most frequent violation of the three. One problem with covers is that they must be "kept closed when tanks are not in use." It is unreasonable to expect dip tank covers to be closed during short intervals of nonuse, such as coffee breaks and other short interruptions. However, an idle period as long as one-half shift would be considered a "not in use" period. In addition, if the dip tank is discovered to be idle for any period during which the work crew and supervisor have left the area, the dip tank should be considered "not in use." Automatic closure devices for actuation in event of fire are desirable, but are not specifically required. Such closure devices "shall be actuated by approved automatic devices and shall also be arranged for manual operation." Automatically closing dip tank covers are considered among the most appropriate means of automatic extinguishing facilities specified under conditions described in Figure 11.9.

EXPLOSIVES

Everyone knows that explosives are dangerous, and the general public completely avoids contact with them. Only the well-trained professional knows which procedures are safe and what to do in each situation. The body of existing codes governing explosives pertains almost entirely to storage or to the construction of the magazines in which the explosives are stored.

As in flammable liquids, explosives are classified according to degree of hazard. The most explosive are "unstable explosives" which are thermally unstable and/or too sensitive for normal handling. They then are categorized by division 1.1 through 1.6 with division 1.1 being chemicals with a mass explosion hazard all the way down to division 1.6 which are extremely insensitive items that do not have an explosive hazard. The safety and health manager should take advantage of manufacturers' labeling to determine explosive classes when a questionable item is concerned.

The storage magazines for explosives are divided into two groups, also called *classes*, but in the case of magazines, the class designation is a Roman numeral instead of a letter of the alphabet. The magazine class depends chiefly on quantity (weight) of explosives stored, not on the explosives class. Class I magazines are for quantities more than 50 pounds, and Class II magazines are for 50 pounds or less.

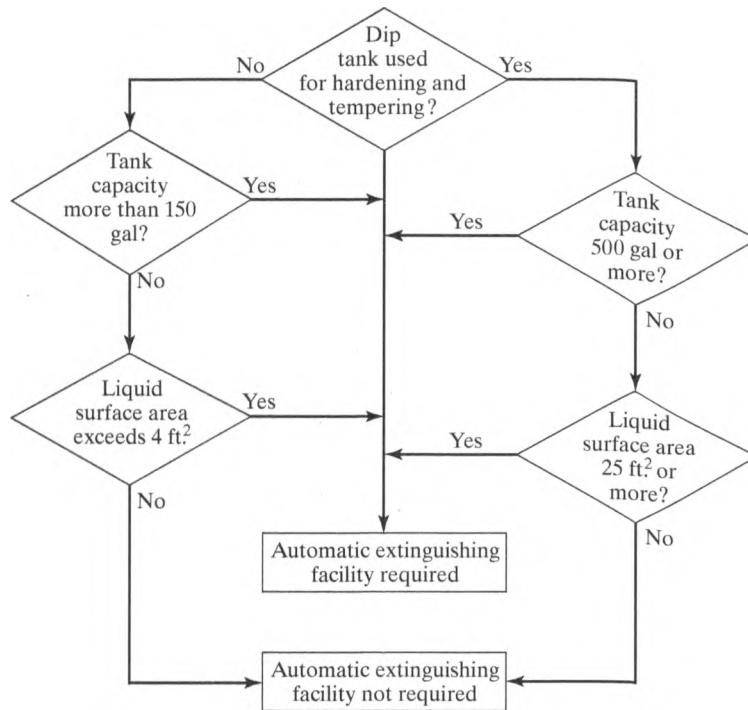


FIGURE 11.9

Decision chart: Automatic extinguishing facilities for dip tanks.

The transportation of explosives is considered particularly hazardous and entails detailed procedures specified by the U.S. Department of Transportation to protect the public. Transportation of a new explosive requires prior approval through a five-step process and the assignment of an “EX number” to the explosive to be transported. The details of the five-step process go beyond the scope of this book, but the safety and health manager should be aware of the need to pursue the five-step process with the U.S. Department of Transportation should a new explosive be developed by the firm.

Most facilities do not use explosives, and most safety and health managers can ignore the standard if they do not have explosives. But those who do have explosives within their facilities should take the precaution of assuring that handling and especially storage procedures are in compliance with applicable code.

LIQUEFIED PETROLEUM GAS

Liquefied petroleum gas (LPG) is a commonly used fuel gas, especially in areas remote from piped natural gas utilities. All petroleum gases can be liquefied if the temperature is lowered sufficiently, but natural gas, which is chiefly methane, is very difficult to liquefy, although it is otherwise cheaper than LPG. LPG is principally a mixture

of propane and butane, both of which can be liquefied more easily than methane and therefore can be transported more compactly. The expansion ratio is approximately 1:270, that is, 1 gallon of liquid converts to 270 gallons of gas at normal temperature and pressure.

The choice between propane and butane is a matter of climate and economics. Butane has a higher boiling point and is unsuitable for cold climates because it will not convert to a gas at low temperatures. Butane has historically been cheaper, however, so it has been used in climates such as those in the southern United States. In the twenty-first century, propane has been used almost exclusively because butane prices have increased because of butane's application in the manufacture of artificial fabrics.

Propane is a product of the refinery cracking⁵ process and is odorless in the natural state. For safety's sake, the odorant ethyl mercaptan is added as a stenching agent before delivery to the customer. This stenching agent facilitates leak detection. However, as was emphasized for hydrogen sulfide in Chapter 9, a heavy exposure to a strong odor can overcome the olfactory system, and consequently the victim simply can no longer smell it.

One of the safety hazards of propane is that it is heavier than air (approximately $1\frac{1}{2}$ times the density of air). This contrasts with natural gas (methane), which is lighter than air. This difference in properties can lead to problems when one attempts to convert a piece of equipment from natural gas powered to propane powered.

Another hazard with propane is that the extreme cold of its liquid state can burn the flesh. In fact, the treatment is the same as for third-degree burns. One way such a burn can occur is by opening the valve too quickly and placing the hand over the valve to feel the flow. Injury from liquid propane while opening the valve does not indicate a defective valve.

Unlike gasoline and other atmospheric vented tanks, LPG tanks are closed, and there is no opportunity for water vapor to accumulate inside the tank. Therefore, no "bleed-off" valve for moisture is used. If water should happen to be introduced into the system, it would probably freeze the valve during expansion of the gas. The closed tank of LPG then contains no air and is a mixture of liquid and gaseous propane. The vapor pressure inside the tank depends on temperature. At 0°F, the pressure is 28 pounds per square inch (psi), and at 100°F, the pressure is almost 200 psi. The pressure relief valve for tank trucks is set at 250 psi and for cylinders at 375 psi.

Although flesh burn from the extreme cold is a hazard to be considered, the principal hazard with LPG is fire, and when an LPG fire occurs, it is usually a disaster. The fire expands quickly, and portable fire extinguishers are generally useless, although they may be useful in extinguishing other burning materials threatening LPG facilities. Once a tank itself ignites, however, it is strictly a matter for professional firefighters and special techniques using large volumes of high-pressure water spray to protect firefighters who must approach the tank to close valves or otherwise control the fire. Large tanks, such as railroad cars, have resulted in spectacular fires, including the phenomenon called *BLEVE* (rhymes with "heavy"), which means "boiling liquid expanding vapor explosion."

⁵Large molecules are "cracked" into simpler molecules of more economically useful products.

The federal standard requiring the use of laboratory-approved equipment (“listed” by an approved testing laboratory) seems like so much red tape. But without this requirement, people would try all kinds of makeshift arrangements. One individual decided to use an old hot-water tank for storage of LPG. The tank exploded, killing one person and injuring another. Another temptation is to use ordinary water hose instead of approved piping. The insidious nature of this hazard is that the water hose will often withstand the LPG pressures and will seemingly work, but the LPG will attack the rubber in the hose and will eventually result in a rupture. Similar problems result from using ordinary plumbing fittings and valves that have rubber seals.

Another frequent misuse of equipment is the interchange of tanks for storage of anhydrous ammonia and LPG. Anhydrous ammonia attacks brass and copper fittings in LPG tanks, making them unsafe. Particularly dangerous is damage to the tank relief valve.

Fire, welding operations, and other sources of intense heat can weaken LPG cylinders and make them no longer capable of meeting laboratory test standards. The safety and health manager should be on the alert for this danger and have LPG equipment recertified after a plant fire or other exposure to heat. As for welding, no welding should be permitted directly to the tank shell; it is permissible, however, to weld to existing brackets, plates, and lugs, which in turn were already welded to the tank in its original manufacture in the configuration that has laboratory approval.

Fire control for LPG tanks is quite different from fire control for flammable liquid tanks. Dikes are built around flammable liquid tanks to contain the burning liquid in the event of tank rupture. But such dikes are hazardous to LPG tanks because they can cause burning near or beneath the tank, which might result in explosive rupture.

In any high-pressure cylinder with a valve on the end, there is danger should the valve be accidentally ruptured or even broken off. Like a torpedo in size and shape, the cylinder becomes a dangerous missile. The most dangerous are the very high pressure oxygen cylinders used in welding (see Chapter 16). However, LPG cylinders at 200 psi can also be quite dangerous. This danger is in addition to the fact that the gas liberated in the rupture can ignite explosively. Therefore, valves must be protected, and there are two acceptable methods for this: by recessing the valve into the tank or by a ventilated cap or collar.

Safety and health managers often misinterpret the provision of the federal standard for LPG, which reads as follows:

Engines on vehicles shall be shut down while fueling if the fueling operation involves venting to the atmosphere.

In-plant refueling of forklift trucks that operate on LPG normally does not involve venting to the atmosphere. It is not required that the engines be shut down in such refueling operations.

COMBUSTIBLE DUST

Since 2009, OSHA has been working to create a standard to address the hazard of combustible dusts. OSHA identifies the hazard of combustible dust in its proposed rule. “Any combustible material can burn rapidly when in a finely divided form. Materials

that may form combustible dust include, but are not limited to, wood, coal, plastics, biosolids, candy, sugar, spice, starch, flour, feed, grain, fertilizer, tobacco, paper, soap, rubber, drugs, dried blood, dyes, certain textiles, and metals (such as aluminum and magnesium).” (Federal Register, Docket Number. OSHA-2009-0023, 2009).

Once a fire starts, the difference between combustible dust explosions and regular fire danger is the addition of two components: dispersal of the dust cloud at the proper concentration and the confinement of the dust. The dispersion of the dust cloud creates an explosion when the pressure developed by the flaming dust cloud bursts its enclosure (Federal Register, Docket Number. OSHA-2009-0023, 2009). From 1980 to 2008, there were 422 such explosions. The most notable was the Imperial Sugar Refinery explosion in 2008 referenced in Chapter 13. While there are many standards that cover various aspects of requirements necessary for safe operation, OSHA intends to address additional ignition sources, control of hazardous dust, and additional engineering controls for the design of facilities. As an intermediate step during the standard making process, OSHA has introduced a national emphasis program to guide their education, consultation, and enforcement efforts.

CONCLUSION

A final suggestion for safety and health managers is to take advantage of community resources, public and private, for advice and assistance in dealing with hazardous materials. Local fire departments and state fire marshals can be of assistance, particularly with regard to flammable liquids, spray finishing, and codes. Some fire or police departments have explosives experts on hand. Compressed gases, LPG, and anhydrous ammonia problems can sometimes be alleviated by consulting the local distributor for these materials. Some of these distributors are backstopped by extensive training resource centers at their company headquarters and can supply booklets, guides, warning labels, and audiovisual programs for in-house training to combat hazards.

EXERCISES AND STUDY QUESTIONS

- 11.1 What is a floating roof? What are its benefits?
- 11.2 Would it be proper to use a Class II magazine for storage of Division 1.1 explosives? Explain.
- 11.3 What is a BLEVE?
- 11.4 What is the difference between “light” and “heavy” oils? Which evaporate more readily?
- 11.5 Compare the flammability hazards of gasoline with those of ethyl alcohol.
- 11.6 A manufacturing process uses the powerful solvent acetone. One phase of the process is to dry out the acetone in a *drying area*. The drying area evaporates 2 gallons of acetone per hour. Every gallon of liquid acetone produces 41 cubic feet of vapor. Calculate the amount of ventilation (cubic feet/hour) needed to maintain vapor concentration below the burnable level. How many times per hour would the ventilation system exhaust a room 9 feet by 12 feet with a ceiling height of 10 feet?
- 11.7 In a one-time inspection of a facility, how will an insurance representative be able to determine that a temporary spraying area or a so-called “touch-up area” is really a more permanent arrangement?

- 11.8** Under what circumstances are automatic sprinkler systems required for paint spraying areas?
- 11.9** When are dip tank covers required to be closed? Must they close automatically in the event of fire?
- 11.10** Compare liquefied petroleum gas (LPG) with natural gas in terms of safety hazards.
- 11.11** Are fire extinguishers appropriate for LPG facilities? Why or why not?
- 11.12** What is the hazard of using a paint spray area as a drying area? Under what conditions is it acceptable to use a paint spray area as a drying area?
- 11.13** Carbon disulfide has the following physical properties:

Flashpoint	-22°F
Boiling point	46.5°C
Density	1.261
Vapor density	2.64
Lower flammable limit	1.3%
Upper flammable limit	50%
8-hour TWA PEL	20 ppm

An industrial process liberates 3 cubic feet of carbon disulfide per hour into a room that measures 10 feet by 20 feet and has a ceiling height of 8 feet.

- (a) Calculate the minimum general exhaust ventilation (cubic feet/hour) necessary to prevent a general safety hazard for the process.
- (b) Calculate the minimum general exhaust ventilation (cubic feet/hour) necessary to prevent a general health hazard for the process.
- (c) Carbon disulfide is which of the following:
1. Category 1 Flammable Liquid
 2. Category 2 Flammable Liquid
 3. Category 3 Flammable Liquid
 4. Category 4 Flammable Liquid
- 11.14** What are the two classifying characteristics of flammable liquids?
- 11.15** Explain why an empty gasoline drum can be more dangerous than a full one. Why is a drum containing carbon disulfide more likely to ignite than a drum containing gasoline?
- 11.16** Explain the hazard mechanism that has led to a ban on basements in service stations.
- 11.17** Under what circumstances can kerosene become even more dangerous and ignitable than gasoline?
- 11.18** Why is ethyl mercaptan added to propane? Why might this not work as planned?
- 11.19** Sometimes forklift trucks powered by LPG are fueled with the engines still running. Is this a violation of safety standards? Why or why not?
- 11.20** Generally speaking, which is more hazardous, flammable or combustible liquids? Why?
- 11.21** What is switch loading? Why is it dangerous?
- 11.22** Identify a cost-saving principle that a safety and health manager might bring to a design team for a process needing a solvent.
- 11.23** Explain the hazard of using water hose for LPG.

- 11.24 Why are dikes built around gasoline storage tanks, but not around LPG tanks?
- 11.25 What three ingredients are essential to support combustion? Fortunately, one of these three is usually missing in gasoline storage tanks. Identify which of these three ingredients is usually missing?
- 11.26 Which is easier to ignite at lean concentrations, gasoline or alcohol? Which has a wider “burnability range?”
- 11.27 What is the significance of the UEL? What about the LEL?
- 11.28 Most service stations have underground tanks for gasoline storage. Why do they rarely cause fires?
- 11.29 Process engineers are trying to decide between ethyl alcohol and methyl alcohol for a new process. They have already considered cost and other factors and have come to you as a safety consultant to seek your advice. What would you recommend and why?
- 11.30 What is a good source of audiovisual programs for LPG training?
- 11.31 Where might a safety and health manager seek advice and assistance with hazardous materials?
- 11.32 Can an ordinary hot water tank be used to store LPG?
- 11.33 Why are moisture “bleed-off” valves not seen on LPG tanks?
- 11.34 Historically, butane has been a popular fuel gas, but it has been largely replaced by propane. Why?
- 11.35 What might make a natural gas odorant ineffective in the detection of leaks?
- 11.36 What is the “EX number” for an explosive?
- 11.37 Where should a safety and health manager look for expert assistance with preparing for explosions?
- 11.38 How can climate affect the choice between butane and propane as a fuel gas?

RESEARCH EXERCISES

- 11.39 Use the Internet to research LPG disasters.
- 11.40 Research the San Juanico, Mexico, LPG disaster.
- 11.41 Small LPG bottles can be purchased at small convenience stores. Can this be dangerous? Cite actual incidence of explosion.
- 11.42 Research the advantages of LPG in dealing with large national disasters such as earthquakes, floods, and hurricanes.
- 11.43 Use the Internet to find special firefighting materials for use in petroleum fires.
- 11.44 Examine facts about the train accident near Shepherdsville, Kentucky in 2007. Describe the concern about a potential BLEVE in this accident.
- 11.45 **Design Case Study.** Study the design of the tanks shown in Figure 11.10 and attempt to determine the cause of an accident, described as follows. The tank arrangement shown was intended to store tetrahydrofuran liquid on the second-story level of a building in Chicago. The first day the tanks were loaded, the following events took place: A tanker delivery truck hooked up at the receiving valve at ground level and proceeded to deliver 500 gallons. About halfway through the filling operation, a company employee inside the building yelled out of the window that the tank was overflowing. Soon after a tremendous explosion and fire killed both the company employee and the tank truck driver. What faults do you see in the system, and how would you redesign the system to prevent this type of accident? Look up the characteristics of tetrahydrofuran, including the flashpoint. To what flammability classification does tetrahydrofuran belong?

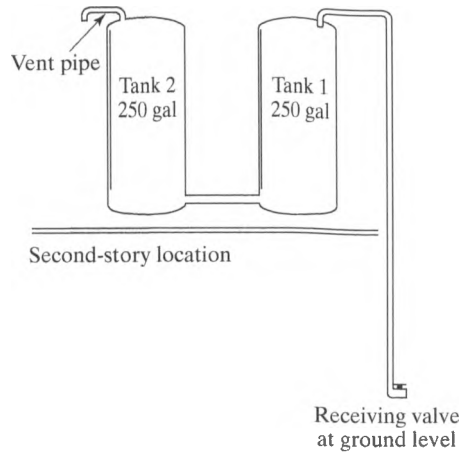


FIGURE 11.10
Tank configuration.

STANDARDS RESEARCH QUESTIONS

- 11.46 Do a General Industry standards search to identify the numerical designation of the spray finishing standard. Use the Companion Website database to determine the frequency of citation of this standard. Check average penalty levels.
- 11.47 Identify the provisions of the General Industry OSHA standards that deal with dip tanks using flammable and combustible materials. Use the Companion Website database to determine whether these provisions are cited by OSHA.
- 11.48 Find the OSHA General Industry standard for liquefied petroleum gas. Use the Companion Website database to examine the citation statistics for the provisions of this standard.