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Hazards of Chemicals and Gases

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CORROSIVES (ACIDS AND ALKALIES)

There are two basic groups of corrosives: acids and alkalies. These chemicals require precautions for safe handling. These precautions will be discussed in this chapter.

EO 1.1 STATE the hazards associated with the use of corrosives.

EO 1.2 STATE the general safety precautions necessary for the handling, storage, and disposal of corrosives.

Acids

Acids are compounds of hydrogen and one or more other elements (with the exception of carbon) that dissociate or break down to produce hydrogen ions (H^+) when dissolved in water or certain other solvents.

Acids are corrosive in any form, and in high concentrations destroy body tissue and cause severe burns on contact with the skin. The eyes are very susceptible, and permanent damage or loss of sight may result from contact with acids. The inhalation of excessive concentrations of vapor or mist is extremely irritating to the respiratory system and to mucous membranes in particular. Accidental swallowing of concentrated acids may result in severe irritation of, and damage to, the throat and stomach which, in some cases, may prove fatal. Some of these materials are specifically poisonous as well as irritating. In lower concentrations, repeated skin contact may result in inflammation.

Concentrated aqueous solutions of acids are not in themselves flammable. The potential hazard is the danger of their mixture with other chemicals or combustible materials which may result in fire or explosion. Acids also react with many metals resulting in the liberation of hydrogen, a highly flammable gas, which upon ignition in air may cause an explosion. Some of the acids are strong oxidizing agents and can react destructively and violently when in contact with organic or other oxidizable materials.

Personnel exposure requiring immediate action usually involves direct contact of the acid with the body or eyes of the individual, inhalation of acid vapors or decomposition products, and ingestion of acid. The initial treatment in all cases of local contact is immediate removal of the acid with a large amount of water. This treatment must be prolonged until all traces of acid have been removed, usually a minimum washing time of 15 minutes.

Alkalies

Alkalies (bases) are corrosive caustic substances that dissociate in water and yield hydroxyl ions (OH^-). Alkalies include: ammonia, ammonium hydroxide; calcium hydroxide and oxide; potassium, potassium hydroxide and carbonate; sodium, sodium hydroxide; carbonate, peroxide and silicate; and trisodium phosphate.

The alkalies, whether in solid form or concentrated liquid solution, are more destructive to tissue than most acids. Alkali dusts, mists, and sprays may cause irritation of the eyes and respiratory tract and lesions of the nasal septum. Strong alkalies combine with tissue, causing severe burns, frequently deep ulceration, and ultimate scarring. Severe burns result not only from contact with solid alkalies, but also from solutions of these compounds. Potassium and sodium hydroxide are the most active materials in this group. Even dilute solutions of the stronger alkalies tend to soften the epidermis (skin) and emulsify or dissolve the skin fats. Exposure to atmospheres contaminated with alkalies may result in damage to the upper respiratory tract and to lung tissue, depending upon the severity of the exposure. The effects of inhalation may vary from mild irritation of the nasal mucous membranes to severe inflammation of the lungs.

Ingestion causes severe damage to mucous membranes or deeper tissues with which contact is made. Perforation of these tissues may follow, or there may be severe and extensive scar formation. Death may result if penetration into vital areas occurs.

Even though alkalies are not flammable and will not support combustion, much heat is evolved when the solid material is dissolved in water. Therefore, cold water must be used to dissolve solid alkalies, otherwise the solution may boil, and splatter corrosive liquid over a wide area.

General Safety Precautions

Corrosives are available in numerous forms and varying concentrations. Some forms and concentrations are more hazardous than others, but the potential for serious accidents exists regardless of the substance in question.

Many of the safety precautions necessary for safe handling and storage are equally applicable to acids and alkalies. Some of the more common precautions are contained in this section. These precautions are not all inclusive, nor are they meant to be. Specific corrosives may require specific precautions, and Material Safety Data Sheets (MSDS) must be consulted in all cases. The MSDS will be discussed later in this module.

Safety in handling hazardous chemicals depends to a great extent upon effective employee education, proper safety practices, intelligent supervision, and the use of safe equipment. Workers should be thoroughly informed of the hazards that may result from improper handling. Each employee should know what to do in an emergency and should be fully informed about proper first-aid measures. Hazards from spills and leaks should be minimized by an adequate supply of water for washing-down. Drainage of hard-surfaced or diked areas should be directed to minimize the exposure of personnel and equipment. Adequate ventilation should be provided in areas where chemical mist or dust is present.

Alkalies are much more injurious to the eyes than acids because strong acids tend to precipitate a protein barrier, which prevents further penetration into the tissue. The alkalies do not do this. They continue to soak into the tissue as long as they are allowed to remain in contact with the eye. The end result of a corrosive burn to the eye (alkali or acid) is usually a scar on the cornea and possible permanent damage.

Speed in removing corrosives is of primary importance. If the chemical enters the eyes, they should be copiously irrigated with water for at least 15 minutes, and a physician should be consulted immediately. In case of contact with skin or mucous membranes, the safety shower should be used immediately. Clothing can be removed under the shower. Contaminated skin areas should be washed with very large quantities of water for 1 to 2 hours, or until medical help arrives. The ready availability of water, particularly safety showers and eye-washing baths, greatly minimizes the possibility of severe, extensive damage. Contaminated clothing and shoes should be thoroughly washed and decontaminated before re-use.

The use of personal protective equipment is not intended as a substitute for adequate control measures, but because corrosives can cause extensive damage to the body this equipment must be available as needed. During handling operations where spills or splashes are possible, whole body protection (eyes, head, body, hands, and feet) may be necessary. All personal protective equipment should be carefully cleaned and stored following use, and any equipment that cannot be decontaminated should be discarded.

For the protection of the eyes, chemical safety goggles should be worn. Face shields should be worn if complete face protection is necessary. Eyewash fountains and safety showers must be available at any location where eye and/or skin contact may occur. Protection against mist or dust can be provided by proper respiratory protective equipment. The wearing of protective clothing is also advisable to avoid skin contact. This may consist of rubber gloves, aprons, shoes or boots, and cotton coveralls which fit snugly. Safety shoes or boots made of rubber, chlorobutadiene, or other chemical-resistant materials with built-in steel toecaps are recommended for workers handling drums or in process areas where leakage may occur. Containers should be stored in rooms with trapped floor drains. Curbs or a drained gutter, covered with an appropriate grill, should be constructed at door openings where floor drains are not provided.

Tanks should be entered for cleaning or repairing only after these have been drained, flushed thoroughly with water, ventilated, and sampled. Workers entering tanks should be monitored by someone on the outside of the tank. A supplied-air respirator or self-contained breathing apparatus, together with rescue harness and lifeline, should be on hand for rescue purposes.

Removal from exposure is the primary, and most important, step where exposure by inhalation is involved. The individual should be made as warm and comfortable as possible, and a physician should be called immediately.

Ingestion, the least common mode of contamination, requires immediate medical attention. Any attempt at first aid beyond drinking large quantities of water should be made only upon the advice of a physician.

If body burns are severe or extensive, or if the eyes are in any way involved, a physician should be consulted as soon as possible after first aid is rendered. No attempt should be made to neutralize the corrosive prior to treatment with water. Any treatment, in addition to the use of water, should be undertaken only with the advice of the physician.

When corrosives are shipped in small containers such as glass or polyethylene bottles, they should be well protected, whether individually packaged or several are packaged in a single case. After careful inspection, the corrosives may be stored in these containers if the containers are maintained in an upright position and under cover. The containers should be kept off the floor on materials that are corrosive resistant, or protected with corrosive-resistant coverings, to facilitate flushing and other cleanup procedures in the event of leakage or spills.

All drums should be stored on individual racks or securely blocked on skids, with the closure (plug) up to prevent leakage. Drums containing corrosives in liquid form should be vented when received, and at least weekly thereafter, to relieve accumulated internal pressure.

Cylinders should be stored in an upright position, preferably in individual racks and with the valve protective cap in place. In all cases, to avoid error, empty and full containers should be stored in different locations.

Under no circumstance should corrosives be transferred from the original labeled container to an unmarked container. All containers must be labeled clearly, concisely, and in simple, easily understood terms. Inspection of containers before handling will disclose conditions such as breakage, leakage, and improperly positioned closures which could readily cause a leak or spill.

In handling bottles, barrels, or drums containing corrosives, the following guidelines must be followed.

1. Carefully inspect containers prior to handling.
2. Use personal protective equipment.
3. Use equipment specifically designed for the purpose of transporting and dispensing the chemical in question.
4. Label all containers into which the chemical is transferred.

Properties of corrosives make several considerations mandatory in the selection of a storage site.

1. The building, or area within the building selected, should be of fire-resistant construction.
2. The floors should be composed of chemical-resistant brick or treated concrete, be washable, and be provided with adequate drainage.
3. A well-lit and ventilated area in which there are adequate outlets for water should be provided.
4. A relatively cool and dry environment should be maintained, preventing extremes of temperature and humidity.
5. Electrical fixtures should be protected against corrosive mists, and wiring should be enclosed and covered with corrosive-resistant material.

The nature of the corrosive will determine the manner in which it is stored. Most acids should, to some extent, be isolated, some from all other chemicals, some from certain other acids and oxidizable materials such as oil and grease, and some from combustible materials.

Generally, adequate natural ventilation is sufficient in areas where corrosives are stored, that is, where the containers remain unopened. Where acid is used in work areas where dust or mists may arise (such as in processing equipment or tanks), some form of mechanical exhaust system must be provided.

Transporting containers within the plant and dispensing at various points throughout the plant are two high-risk procedures that may cause an accident. Proper equipment can be readily obtained, which precludes the necessity of using makeshift or otherwise dangerous methods of transportation.

Handtrucks or power trucks used for transporting containers should have lifting parts, or clamps specially designed for that purpose. If bottles must be transported in the plant or laboratory, they should be enclosed in safety bottle carriers that prevent breakage if the bottle is struck or dropped. All containers (especially acid) must be opened slowly and cautiously because of the possible buildup of pressure within the container. Corrosives may be dispensed from drums by means of siphons, drum transfer pumps, or by gravity with the use of a special fitting, such as a self-closing faucet. Under no circumstances should bottles or drums be subjected to air pressure to expel the contents.

One final, and extremely important, consideration is the type of container or receptacle into which corrosives are to be dispensed. The use of an inappropriate or makeshift receptacle can negate the value of all precautionary measures.

These receptacles may be used for temporary storage or merely as a means of transporting from storage area to place of use. In any event, an appropriate receptacle meets several conditions.

1. It is designed for the application.
2. It is used for no other purpose than that for which it is intended.
3. It is maintained in a safe, clean, and dry condition.

Summary

The important information in this chapter is summarized below.

Corrosives Summary

- The hazards of acids:

High concentrations can destroy body tissue, eyes being especially susceptible with permanent damage or loss of sight.

Inhalation of acidic vapors can irritate the respiratory system.

Ingestion can destroy the stomach and throat lining, and if the concentration is strong enough, ingestion can be fatal.

Aqueous solutions can become explosive if combined with other chemicals or combustible materials

If reacting with metal, hydrogen gas may be a byproduct, which is very explosive.

Corrosives Summary (Cont.)

- The hazards of alkalis:

Alkalis are more destructive than the acids.

Alkali dusts, mists, and sprays can cause irritation of nasal passages, eyes, and respiratory tract.

When in contact with the tissue, strong alkalis will cause ulcers, severe burns, and eventual scarring.

Ingestion causes perforations of the mucous membrane and deeper tissues; death may result if penetration is in vital areas.

- Precautions when using corrosives:

An adequate supply of washdown water must be available.

Proper ventilation in corrosive work area must be provided.

Proper drainage must be provided such that exposure is limited.

Face shields and safety glasses that protect the eyes from splashes and extensive vapor should be worn.

Proper personnel safety equipment should be worn when appropriate (chemical gloves, respirators, coveralls, etc.)

- Precautions when storing corrosives:

The building, or area within the building selected, should be of fire-resistant construction.

The floors should be composed of chemical-resistant brick or treated concrete, be washable, and be provided with adequate drainage.

A well-lit and ventilated area in which there are adequate outlets for water should be provided.

A relatively cool and dry environment should be maintained, preventing extremes of temperature and humidity.

Electrical fixtures should be protected against corrosive mists, and wiring should be enclosed and covered with corrosive-resistant material.

TOXIC COMPOUNDS

The various chemicals found in industry as well as the home are useful when properly applied. If the user is uninformed about correct applications, storage, and potential hazards, these chemicals become threats to safety. This chapter gives an overview of handling chemicals and resources of information about these chemicals.

- EO 1.3** **LIST the general safety precautions regarding toxic compounds.**
- EO 1.4** **LIST the criteria used to determine if a compound is a health hazard.**
- EO 1.5** **STATE the methods by which toxic compounds may enter the body.**
- EO 1.6** **SUMMARIZE the purpose and general contents of the following:**
- a.** **Material Safety Data Sheets (MSDS)**
 - b.** **Toxic Substance List**

Toxic Compounds

Because the types of toxic compounds found in industry number in the thousands, and because specific hazards, controls, and corrective measures may vary with the substance, no attempt will be made in this section to address specific compounds. Instead, information of a general nature will be presented on toxic materials. Material Safety Data Sheets (MSDS) are required for all potentially hazardous and toxic materials and should be consulted for specific descriptions and precautions concerning the substance in question.

There are some general precautions that should be universally employed regarding toxic compounds. Many of these precautions are consistent with those already mentioned concerning corrosives. Proper ventilation, appropriate hygienic practices, housekeeping, protective clothing, and training for safe handling and storage will diminish many of the hazards that exist.

The toxicity of a material is not synonymous with its health hazard. *Toxicity* is the capacity of a material to produce injury or harm to a living organism.

Hazard is the possibility that a material will cause injury when a specific quantity is used under specific conditions. Several key elements are considered when evaluating a health hazard.

- Toxicity of the materials used
- Physical properties of these materials
- Absorption probabilities of these materials by individuals
- Extent and intensity of exposure to these materials
- Control measures used

Toxicity is relative. It refers to a harmful effect on some biologic mechanism. The term toxicity is commonly used in comparing one chemical agent with another, but such comparison is meaningless if the biologic mechanism, and the conditions under which the harmful effects occur, are not specified.

Although the toxic effects of many chemical agents used in industry are well known, the toxic effects of many other commonly used chemical agents are not as well defined. The toxicity of a material is not a physical constant (such as boiling point, melting point, or temperature); therefore, only a general statement can be made concerning the harmful nature of a given chemical agent.

Many chemical agents are nonselective in their action on tissue or cells; they may exert a harmful effect on all living matter. Other chemical agents may act only on specific cells. Another agent may be harmful only to certain species; other species may have built-in protective devices.

The degree to which a substance will affect living cells can be measured only after recognizable changes have occurred following absorption. Some changes (impaired judgment, delayed reaction time) may be produced at levels too low to cause actual cell damage. Toxicity is dependent upon the dose, rate, method, and site of absorption, and many other factors including general state of health, individual differences, tolerance, diet, and temperature.

In general, industrial poisonings usually result from inhalation, ingestion, and absorption.

- The inhalation and absorption of toxic agents by the lungs is dependent upon the solubility in body fluids, the diffusion through the lungs, the volume of inhalation, the volume of blood in the lungs, and the concentration gradient of vapors between the inhaled air and the blood.
- Ingestion of the toxic agent can occur to some extent; however, there would generally be considerable inhalation of the material where such conditions exist.

- Absorption through the skin can occur upon exposure to some toxic agents. Some liquids and vapors are known to pass through the skin in concentrations high enough such that respiratory protection is not adequate. For example, hydrogen cyanide (HCN) is known to pass through the unbroken skin. Consideration should be given to the type of work clothes being worn; if they become saturated with solvents, they will act as a reservoir to bathe the body continually with the harmful material.

Most volatile (easily vaporized) organic compounds are eliminated from the body in a matter of hours or, at most, days. Many of the poisonous elements, however, can be stored for long periods of time in various parts of the body. Chronic (long term) toxicity damage is unlikely to have an even distribution throughout the body. In toxicity studies with radioactive isotopes, the organ which suffers the most severe damage and appears to contribute most to the toxic effect on the body as a whole, is called the critical organ. The particular organ that shows the largest amount of damage is the one that is chosen for estimating the effect.

Industrial poisoning may be classified as either acute or chronic. The classification is based on the rate of intake of harmful materials, rate of onset of symptoms, and the duration of symptoms.

Acute poisoning is characterized by rapid absorption of the material and sudden, severe exposure. For example, inhaling high levels of carbon monoxide or swallowing a large quantity of cyanide compound will produce acute poisoning. Generally, acute poisoning results from a single dose which is rapidly absorbed and damages one or more of the vital physiological processes. The development of cancer long after recovery from acute radiation damage is called a delayed acute effect.

Chronic poisoning is characterized by absorption of a harmful material in small doses over a long period of time; each dose, if taken alone, would barely be effective. In chronic poisoning, the harmful materials remain in the tissues, continually injuring a body process. The symptoms in chronic poisoning are usually different from the symptoms seen in acute poisoning by the same toxic agent.

The Occupational Safety and Health Act of 1970 requires that the Health and Human Services publish at least annually, a list of all known toxic substances by generic family, or other useful grouping, and the concentrations at which such toxicity is known to occur. Under the OSHA Act, the Secretary of Labor must issue regulations requiring employers to monitor employee exposure to toxic materials and to keep records of any such exposure.

The purpose of The Toxic Substances List is to identify "all known toxic substances" in accordance with definitions that may be used by all sections of our society to describe toxicity. An excerpt of this list is illustrated in Figure 1. It must be emphatically stated that the presence of a substance on the list does not automatically mean that it is to be avoided. A listing does mean, however, that the substance has the documented potential of being hazardous if misused, and, therefore, care must be exercised to prevent tragic consequences.

TABLE Z-1-CONTINUED			TABLE Z-1-CONTINUED		
SUBSTANCE	p/m ^a	mg./M ^{3b}	SUBSTANCE	p/m ^a	mg./M ^{3b}
RONNEL		15	O-TOLUIDINE-SKIN	5	22
ROTENONE (COMMERCIAL)		5	TOXAPHENE SEE CHLORINATED		
SELENIUM COMPOUNDS (AS Se)		0.2	CAMPHENE		
SELENIUM HEXAFLUORIDE	0.05	0.4	TRIBUTYL PHOSPHATE		5
SILVER, METAL, AND SOLUBLE			1,1,1-TRICHLOROETHANE, SEE		
COMPOUNDS		0.01	METHYL CHLOROFORM		
SODIUM FLUOROACETATE (1080)-			1,1,2-TRICHLOROETHANE-SKIN	10	45
SKIN		0.05	TITANIUMDIOXIDE		15
SODIUM HYDROXIDE		2	TRICHLOROMETHANE, SEE CHLOROFORM		
STIBINE	0.1	0.5	TRICHLORANAPHTHALENE-SKIN		5
STODDARD SOLVENT	500	2,900	1,2,3-TRICHLOROPROPANE	50	300
STRYCHNINE		0.15	1,1,2-TRICHLORO 1,2,2-TRIFLUOROETHANE	1,000	7,600
SULFUR DIOXIDE	5	13	TRIETHYLAMINE	25	100
SULFUR HEXAFLUORIDE	1,000	6,000	TRIFLUOROMONOBROMOMETHANE	1,000	6,100
SULFURIC ACID		1	2,4,6-TRINITROPHENOL SEE PICRIC		
SULFUR MONOCHLORIDE	1	6	ACID		
SULFUR PENTAFLUORIDE	0.025	0.25	2,4,6-TRINITROPHENYLMETHYL-		
SULFURYL FLUORIDE	5	20	NITRAMINE. SEE TETRYL		
SYSTOX, SEE DEMETON®			TRINITROTOLUENE-SKIN		1.5
2,4,5T		10	TRIORTHOCRESYL PHOSPHATE		0.1
TANTALUM		5	TRIPHENYL PHOSPHATE		3
TEBP-SKIN		0.2	TURPENTINE	100	560
TELLURIUM		0.1	URANIUM (SOLUBLE COMPOUNDS)		0.05
TELLURIUM HEXAFLUORIDE	0.02	0.2	URANIUM (INSOLUBLE COMPOUNDS)		0.25
TEPP-SKIN		0.05	C VANADIUM		
C TERPHENYLS	1	9	V ₂ O ₅ DUST		0.5
1,1,1,2-TETRACHLORO-2,2-			V ₂ O ₅ FUME		0.1
DIFLUOROETHANE	500	4,170	VINYL BENZENE SEE STYRENE		
1,1,2,2-TETRACHLORO-2,2-			VINYLCYANIDE SEE ACRYLONITRILE		
DIFLUOROETHANE	500	4,170	VINYL TOLUENE	100	480
1,1,2,2-TETRACHLOROETHANE-			WARFARIN		0.1
SKIN	5	35	XYLENE (XYLOL)	100	435
TETRACHLOROMETHANE, SEE CARBON			XYLIDINE-SKIN	5	25
TETRACHLORIDE			YTRIUM		1
TETRACHLORONAPHTHALENE-SKIN		2	ZINC CHLORIDE FUME		1
TETRAETHYL LEAD (AS Pb)-SKIN		0.075	ZINC OXIDE FUME		5
TETRAHYDROFURAN	200	590	ZIRCONIUM COMPOUNDS (AS Zr)		5
TETRAMETHYL LEAD (AS Pb)-SKIN		0.075			
TETRAMETHYL SUCCINONITRILE-SKIN	0.5	3			
TETRANITROMETHANE	1	8			
TETRYL (2,4,6-TRINITROPHENYL-METHYL-					
NITRAMINE)-SKIN		1.5			
THALLIUM (SOLUBLE COMPOUNDS)-					
SKIN AS Tl		0.1			
THIRAM		5			
TIN (INORGANIC CMPDS, EXCEPT					
OXIDES		2			
TIN (ORGANIC CMPDS)		0.1			
C TOLUENE-2,4-DIISOCYANATE	0.02	0.14			

† THIS STANDARD APPLIES IN COTTON YARN MANUFACTURING UNTIL COMPLIANCE WITH § 1910.1043 (c) AND (e) IS ACHIEVED

a PARTS OF VAPOR OR GAS PER MILLION PARTS OF CONTAMINATED AIR BY VOLUME AT 25° C AND 760mm Hg PRESSURE

b APPROXIMATE MILLIGRAMS OF PARTICULATE PER CUBIC METER OF AIR (NO FOOTNOTE "c" IS USED TO AVOID CONFUSION WITH CEILING VALUE NOTATIONS)

d AN ATMOSPHERIC CONCENTRATION OF NOT MORE THAN 0.02 P.P.M. OR PERSONAL PROTECTION MAY BE NECESSARY TO AVOID HEADACHE

MATERIAL	8-HOUR TIME WEIGHTED AVERAGE	ACCEPTABLE CEILING CONCENTRATION	ACCEPTABLE MAXIMUM PEAK ABOVE THE ACCEPTANCE CEILING CONCENTRATION FOR AN 8-HOUR SHIFT	
			CONCENTRATION	MAXIMUM DURATION
BENZENE (Z37.40-1969)	10 P.P.M.	25 P.P.M.	50 P.P.M.	10 MINUTES
BERYLLIUM AND BERYLLIUM COMPOUNDS (Z37.29-1970)	2µ G./M ³	5µ G./M ³	25µ G./M ³	30 MINUTES
CADMIUM FUME (Z37.5-1970)	0.1 MG/M ³	0.3 MG/M ³		
CADMIUM DUST (Z37.5-1970)	0.2 MG/M ³	0.6 MG/M ³		
CARBON DISULFIDE (Z37.3-1968)	20 P.P.M.	30 P.P.M.	100 P.P.M.	30 MINUTES
CARBON TETRACHLORIDE (Z37.17-1967)	10 P.P.M.	25 P.P.M.	200 P.P.M.	5 MINUTES IN ANY 4 HOURS
CHROMIC ACID AND CHROMATES (Z37.7-1971)		1 MG/10M ³		

Figure 1 Excerpt of Toxic Substance List

The absence of a substance from the list does not necessarily indicate that a substance is not toxic. Some hazardous substances may not qualify for the list because the dose that causes the toxic effect is not known.

Other chemicals associated with skin sensitization and carcinogenicity (ability to cause cancer) may be omitted from the list, because these effects have not been reproduced in experimental animals or because the human data is not definitive.

It is not the purpose of the list to quantify the hazard by way of the toxic concentration or dose that is presented with each of the substances listed. Hazard evaluation involves far more than the recognition of a toxic substance and a knowledge of its relative toxic potency. It involves a measurement of the quantity that is available for absorption by the user, the amount of time that is available for absorption, the frequency with which the exposure occurs, the physical form of the substances, and the presence of other substances, additives, or contaminants (toxic or non-toxic).

The purpose of the Material Safety Data Sheet (MSDS) is to ensure the individuals working with chemicals and in the vicinity of chemicals have specific information on these chemicals. This form identifies the chemical by its technical and common name and lists the physical/chemical characteristics and fire, explosion, and reactivity hazards. The second page specifies health hazards and recommends first aid procedures. The safe handling and control measures are also supplied. The MSDS is a very helpful document, and personnel working around chemicals should make it a practice to review these sheets frequently for their own safety. Figures 2 and 3 are copies of the MSDS.

The Code of Federal Regulations recommends that the hazards of all chemicals produced and imported be evaluated and the information concerning the hazards be transmitted to the employers and employees. The MSDS, labels on containers, and employee training should be part of a comprehensive hazards communication program.

Section V – Reactivity Data			
Stability	Unstable		Conditions to Avoid
	Stable		
Incompatibility (Materials to Avoid)			
Hazardous Decomposition or Byproducts			
Hazardous Polymerization	May Occur		Conditions to Avoid
	Will Not Occur		
Section VI – Health Hazard Data			
Route(s) of Entry:	Inhalation?	Skin?	Ingestion?
Health Hazards (<i>Acute and Chronic</i>)			
Carcinogenicity:	NTP?	IARC Monographs?	OSHA Regulated?
Signs and Symptoms of Exposure			
Medical Conditions Generally Aggravated by Exposure			
Emergency and First Aid Procedures			
Section VII – Precautions for Safe Handling and Use			
Steps to Be Taken in Case Material is Released or Spilled			
Waste Disposal Method			
Precautions to Be Taken in Handling and Storing			
Other Precautions			
Section VIII – Control Measures			
Respiratory Protection (<i>Specify Type</i>)			
Ventilation	Local Exhaust	Special	
	Mechanical (General)	Other	
Protective Gloves		Eye Protection	
Other Protective Clothing or Equipment			
Work/Hygienic Practices			
Page 2		★ USGPO 1986-491-529/45775	

Figure 3 Typical Material Safety Data Sheet (Sections V-VIII)

Summary

The important information in this chapter is summarized below.

Toxic Compounds Summary

- The general safety precautions regarding toxic compounds:
 - Proper ventilation
 - Appropriate hygienic practices
 - Housekeeping
 - Protective clothing
 - Training
- The criteria used to determine if a compound is a health hazard:
 - Toxicity of the materials used
 - The physical properties
 - The absorption probabilities of these materials by individuals
 - The extent and intensity of exposure to these materials
 - The control measures used
- The methods by which toxic compounds may enter the body:
 - Ingestion
 - Inhalation
 - Absorption
- The purpose and general contents of the Material Safety Data Sheets (MSDS) is to ensure the individuals working with and in the vicinity of chemicals have specific information of these chemicals. This form identifies the chemical, by technical and common name, lists the physical/chemical characteristics, any fire or explosion hazard as well as reactivity hazards. The second page will specify health hazards and recommend first aid procedures. The safe handling and control measures are also supplied.
- The purpose and general contents of the Toxic Substance List is to identify "all known toxic substances" in accordance with definitions that may be used by all sections of our society to describe toxicity. This form identifies known toxic chemicals which have been proven in lab tests or have definite human data. It lists the chemical name, level of concentration at which it is hazardous, concentration limits for set time exposures both weighted averages and ceiling limits.

COMPRESSED GASES

Gases are commonly used throughout industry. These gases come in several forms and are often as dangerous as they are useful. This chapter provides background knowledge of these gases.

EO 1.7 **DEFINE** the following terms:

- | | | | |
|-----------|----------------------------|-----------|------------------------|
| a. | Compressed gas | c. | Liquified gases |
| b. | Non-liquified gases | d. | Dissolved gases |

EO 1.8 **STATE** the five major families of gases.

EO 1.9 **STATE** the general safety precautions regarding the use, handling, and storage of gases.

EO 1.10 **STATE** the safety precautions for working with cryogenic liquids.

EO 1.11 **LIST** the physical properties and special precautions for the following gases:

- a.** **Hydrogen**
 - b.** **Oxygen**
 - c.** **Nitrogen**
-

Compressed Gases

Gases in compressed form serve countless indispensable roles in modern technology. Oxygen is used extensively to produce stronger and cheaper steels. Acetylene welding and brazing of certain metals has been common for many years. Other compressed, flammable gases such as hydrogen are equally necessary for the welding of certain metals. Some metals and alloys (such as stainless steel, titanium, and zirconium) can be welded only under an inert gas atmosphere. Carbon dioxide is used extensively in fire extinguishers for chemical and electrical fires. In the nuclear industry, uses of compressed gases range from the addition of nuclear grade hydrogen to reactor plant systems to propane and butane for heating components or spaces.

Gases are compressed for practical reasons of transportation, storage and use. The definition of *compressed gas* by the Interstate Commerce Commission (ICC) reads: "... any material or mixture having in the container an absolute pressure exceeding 40 psi (pounds per square inch) at 70°F, or regardless of the pressure at 70°F, having an absolute pressure exceeding 140 psi at 130°F; or any flammable material having a vapor pressure exceeding 40 psi at 100°F."

Because we often deal in gage pressures, and absolute pressure is equal to atmospheric pressure (14.7 psi at sea level) plus the pressure that would be read on an ordinary gage, we can simplify the above definition. Accordingly, a compressed gas is one that gives a pressure reading of:

1. either 25 psig (pounds per square inch gage) at 70°F; or 125 psig at 130°F; or
2. if the contained substance is flammable, 25 psig at 100°F.

This simplified definition and the range of boiling points among gases classify gases into two major groups that differ in physical state when contained.

1. *Non-liquified gases*, which are gases that do not liquify in containers at ambient temperatures and under pressures attained in commercially used containers that range to 2000 to 2500 psig.
2. *Liquified gases*, which are gases that do become liquids to a very large extent in containers at ordinary ambient temperatures and at pressures from 25 to 2500 psig.

The first group, commonly called non-liquified gases, have relatively low boiling points, approximately -150°F or lower.

Non-liquified gases do, however, become liquids if cooled to temperatures below their boiling points. Those that liquify at "cryogenic" temperatures (from absolute zero [-459.7°F] to around -240°F) are known as cryogenic fluids.

The second group, or liquified gases, have boiling points relatively near atmospheric temperatures (from about -130°F to 30°F). The liquified gases solidify at cryogenic temperatures.

Oxygen, helium and nitrogen are examples of gases in wide use both as non-liquified gases and cryogenic fluids. With respective boiling points of -297°F, -425°F, and -320°F, they are charged into high pressure steel cylinders at more than 2000 psig at 70°F for shipment and use as non-liquified gases. However, when shipped as cryogenic fluids, they are cooled down to liquid form and charged into special insulated containers that keep them below their boiling points and are contained at pressures normally less than 75 psig.

A third physical state in the container is represented by only one widely used gas, acetylene. Acetylene is sometimes referred to as a *dissolved gas*. A dissolved gas is defined as a gas that is dissolved into a solution.

The industry recommends that free acetylene should not ordinarily be handled at pressures greater than 15 psig because, if handled at higher pressures without special equipment, it can decompose with explosive violence. Consequently, acetylene cylinders are packed with an inert porous material that is saturated with acetone. Acetylene charged into the cylinder dissolves in the acetone and in solution will not decompose at or below the maximum authorized shipping pressure of 250 psig at 70°F.

Compressed or liquified gases are also often described according to loosely-knit families to which they belong through common origins, properties, or uses. The major families of gases are atmospheric gases, fuel gases, refrigerant gases, aerosol gases, and poison gases.

Atmospheric gases comprise one family. Its most abundant member is nitrogen, constituting 78 percent of air by volume; oxygen, constituting 21 percent of air by volume, is its second most abundant member. Most of the remaining 1 percent of the atmosphere consists of a sub-family of gases, the inert gases, that share the property of chemical inertness. Inert gases are chiefly argon, with minute quantities of helium, neon, krypton, xenon and radon. The last four are frequently called the rare gases due to their scarcity. Hydrogen also occurs minutely in the atmosphere, as do a large variety of trace constituents, small amounts of carbon dioxide, and large amounts of water vapor.

Another family of gases are the fuel gases. Fuel gases burned in air or with oxygen to produce heat make up a large family related through their major use. Its members are notably the hydrocarbons including liquefied petroleum (LP) gases, propane, butane, methane, and welding gases such as acetylene and hydrogen.

An opposite application relates members of another large family, the refrigerant gases. A refrigerant gas liquifies easily under pressure and works by being compressed to a liquid which then absorbs large amounts of heat as it circulates through coils where it vaporizes back into gaseous form. Examples of refrigerant gases include ammonia and the fluorocarbons (freon).

Aerosol propellant gases make up a family also related by use through the introduction of pressure-packaged products used in the form of a spray or a foam. Propellant gases have moderate vapor pressures at room temperatures (70 psig down to 35 psig, and even lower in some cases). It is usually agreed that a good propellant should also be nontoxic, chemically stable, noncorrosive, and inexpensive. The fluorocarbons (freon) and nitrous oxide are the most commonly used propellant gases.

Gases considered to be members of the poison gas family are generally those that the ICC has classified as poison gases to ensure public safety in interstate shipments. Two examples of these gases are hydrogen cyanide and phosgene.

Basic Safety Precautions Regarding Compressed Gases

Compressed and liquified gases are widely useful due to properties including high heat output in combustion for some gases, high reactivity in chemical processing with other gases, extremely low temperatures available from some gases, and the economy of handling them all in compact form at high pressure or low temperature. These same properties, however, also represent hazards if the gases are not handled with full knowledge and care.

Practically all gases can act as simple asphyxiants by displacing the oxygen in air. The chief precaution taken against this potential hazard is adequate ventilation of all enclosed areas in which unsafe concentrations may build up. A second precaution is to avoid entering unventilated areas that might contain high concentrations of gas without first putting on breathing apparatus with a self-contained or hose-line air supply. A number of gases have characteristic odors which can warn of their presence in air. Others, however, like the atmospheric gases, have no odor or color. Warning labels are required for compressed and liquified gas shipping containers. Similar warning signs are placed at the approaches to areas in which the gases are regularly stored and used.

Some gases can also have a toxic effect on the human system, either inhalation, through high vapor concentrations, or by liquified gas coming in contact with the skin or the eyes. Adequate ventilation of enclosed areas serves as the chief precaution against high concentrations of gas. In addition, for unusually toxic gases, automatic devices can be purchased or built to monitor the gas concentration constantly and set off alarms if the concentration approaches a danger point. Precautions against skin or eye contact with liquified gases that are toxic or very cold, or both, include thorough knowledge and training for all personnel handling such gases, the development of proper procedures and equipment for handling them, and special protective clothing and equipment (for example, protective garments, gloves, and face shields).

With flammable gases, it is necessary to guard against the possibility of fire or explosion. Ventilation, in addition to safe procedures and equipment to detect possible leaks, represents a primary precaution against these hazards. If fire breaks out, suitable fire extinguishing apparatus and preparation will limit damage. Care must also be taken to keep any flammable gas from reaching any source of ignition or heat (such as sparking electrical equipment, sparks struck by ordinary tools, boiler rooms, or open flames).

Oxygen poses a combustible hazard of a special kind. Although oxygen does not ignite, it lowers the ignition point of flammable substances and greatly accelerates combustion. It should not be allowed closer than 10 feet to any flammable substance, including grease and oil, and should be stored no closer than 10 feet to cylinders or tanks containing flammable gases.

Proper storage and handling of containers avoids many possible incidents. Hazards resulting from the rupture of a cylinder or other vessel containing gas at high pressure are protected against by careful and secure handling of containers at all times. For example, cylinders should never be struck nor allowed to fall, because if the cylinder is charged to a high pressure and the cylinder valve is broken off, it could become a projectile. Cylinders should not be dragged or rolled across the floor; they should be moved by a hand truck. Also, when they are upright on a hand truck, floor, or vehicle, they should be chained securely to keep them from falling over. Moreover, cylinders should not be heated to the point at which any part of their outside surface exceeds a temperature of 125°F, and they should never be heated with a torch or other open flame. Similar precautions are taken with larger shipping and storage containers. Initial protection against the possibility of vessel rupture is provided by the demanding requirements and recommendations that compressed gas containers fulfill in their construction, testing and retesting.

Cryogenic Liquids

Most cryogenic liquids are colorless, odorless, and tasteless when vaporized to a gas. As liquids, most have no color (except liquid oxygen which is light blue). However, whenever the cold liquid and vapor are exposed to the atmosphere a warning appears. As the boil-off gases condense moisture in the air, a fog forms that extends over an area larger than the vaporizing gas. Many cryogenic liquids are inert gases, and may inert an enclosed space. Inert gases will not support life.

Both the liquid and its boil-off vapor can rapidly freeze human tissue and can cause many common materials such as carbon steel, plastic, and rubber to become brittle or fracture under stress. Liquids in containers and piping at temperatures at or below the boiling point of liquified air (-318°F) can cause the surrounding air to condense to a liquid.

Extremely cold liquified gases (helium, hydrogen, and neon) can even solidify air or other gases to which they are directly exposed. In some cases, plugs of ice or foreign material will develop in cryogenic container vents and openings and cause the vessel to rupture. If a plug forms, contact the supplier immediately. Do not attempt to remove the plug; move the vessel to a remote location.

All cryogenic liquids produce large volumes of gas when they vaporize. For example, 1 volume of saturated liquid nitrogen at 1 atmosphere vaporizes to 696.5 volumes of nitrogen gas at room temperature at 1 atmosphere.

When vaporized in a sealed container, cryogenic liquids produce enormous pressures. If 1 volume of liquid helium at 1 atmosphere is warmed to room temperature and vaporized in a totally enclosed container, it has the potential to generate a pressure of more than 14,500 psig. Because of this high pressure, cryogenic containers are usually protected with two pressure-relief devices, a pressure-relief valve and a frangible (easily broken) disk.

Many safety precautions that must be taken with compressed gases also apply to liquified gases. However, some additional precautions are necessary because of the special properties exhibited by fluids at cryogenic temperatures.

The properties of cryogenic liquids affect their safe handling and use. Table 1 presents information to help determine safe handling procedures. None of the gases listed are corrosive at ambient temperatures, and only carbon monoxide is toxic.

- Always handle cryogenic liquids carefully. They can cause frostbite on skin and exposed eye tissue. When spilled, they tend to spread, covering a surface completely and cooling a large area. The vapors emitted by these liquids are also extremely cold and can damage tissues. The vapor boil-off may inert the immediate vicinity.
- Stand clear of boiling or splashing liquid and its vapors. Boiling and splashing occurs when a warm container is charged or when warm objects are inserted into a liquid. These operations should always be performed slowly to minimize boiling and splashing. If cold liquid or vapor comes in contact with the skin or eyes, first aid should be given immediately.
- Never allow an unprotected part of the body to touch uninsulated pipes or vessels that contain cryogenic fluids. The extremely cold metal will cause the flesh to stick fast to the surface and tear when withdrawn. Touching even nonmetallic materials at low temperatures is dangerous.

Tongs, or a similar device, should be used to withdraw objects immersed in a cryogenic liquid. Materials that are soft and pliable at room temperature become hard and brittle at extremely low temperatures and will break easily.

Workers handling cryogenic liquids should use eye and hand protection to protect against splashing and cold-contact burns. Safety glasses are also recommended. If severe spraying or splashing is likely, a face shield or chemical goggles should be worn. Protective gloves should always be worn when anything that comes in contact with cold liquids and their vapors is being handled. Gloves should be loose fitting so that they can be removed quickly if liquids are spilled into them. Trousers should remain outside of boots or work shoes.

TABLE 1
Safety Properties of Cryogenic Fluids

	Xenon (Xe)	Krypton (Kr)	Methane (CH ₄)	Oxygen (O ₂)	Argon (Ar)	Carbon Monoxide (CO)	Nitrogen (N ₂)	Neon (Ne)	Hydrogen (H ₂)	Helium (He)
Boiling Point, 1 atm °F	-163	-244	-259	-297	-303	-313	-321	-411	-423	-425
°C	-108	-153	-161	-183	-186	-192	-196	-246	-253	-268
Melting Point, 1 atm °F	-169	-251	-296	-362	-309	-341	-346	-416	-435	N/A
°C	-112	-157	-182	-219	-189	-207	-210	-249	-259	
Density, boiling point, 1 atm lb/cu ft	191	151	26	71	87	49	50	75	4.4	7.8
Heat of vaporization boiling point Btu/lb	41	46	219	92	70	98	85	37	193	10
Volume expansion ratio, liquid at 1 atm boiling point to gas at 60° F, 1 atm	559	693	625	881	841	N/A	697	1447	850	754
Flammable	No	No	Yes	N/A	No	Yes	No	No	Yes	No

Treating Cold-Contact Burns

Workers will rarely come in contact with a cryogenic liquid if proper handling procedures are used. In the unlikely event of contact with a liquid or cold gas, a cold-contact "burn" may occur. Actually, the skin or tissue freezes. Medical assistance should be obtained as soon as possible. In the interim, the emergency measures presented in Table 2 are recommended.

TABLE 2
Emergency Measures for Treating Cold-Contact Burns

- Remove any clothing that may restrict circulation to the frozen area. Do not rub frozen parts, as tissue damage may result.
- As soon as practical, immerse the effected part in warm water (not less than 105°F or more than 115°F, or 40°C to 46°C). Never use dry heat. The victim should be in a warm room, if possible.
- If the exposure has been massive and the general body temperature is depressed, the patient should be totally immersed in a warm-water bath. Treatment for shock should be provided.
- Frozen tissues are painless and appear waxy and yellow. They will swell and be painful and prone to infection when thawed. Do not rewarm rapidly. Thawing may require 15 to 60 minutes and should continue until the pale blue tint of the skin turns pink or red. Morphine or tranquilizers may be required to control the pain during thawing and should be administered under professional medical supervision.
- If the frozen part of the body thaws before the doctor arrives, cover the area with dry sterile dressings and a large, bulky protective covering.
- Alcoholic beverages and smoking decrease blood flow to the frozen tissues and should be prohibited. Warm drinks and food may be administered.

Some liquified gases require special precautions. For example, when liquid oxygen is handled, all combustible materials, especially oil or gases, should be kept away. Smoking or open flames should never be permitted where liquid oxygen is stored or handled. NO SMOKING signs should be posted conspicuously in such areas.

Liquid oxygen, or oxygen-rich air atmospheres, should not come in contact with organic materials or flammable substances. Some organic materials (oil, asphalt, kerosene, cloth, or dirt containing oil or grease) react violently with oxygen, and may be ignited by a hot spark. Liquid oxygen may form mixtures that are shock sensitive with fuels, oils, or grease. If liquid oxygen spills on asphalt, or on another surface contaminated with combustibles (for example, oil-soaked concrete or gravel), no one should walk on, and no equipment should pass over, the area for at least 30 minutes after all frost or fog has disappeared.

Any clothing that has been splashed or soaked with liquid oxygen, or exposed to a high gaseous-oxygen atmosphere, should be changed immediately. The contaminated systems should be aired for at least an hour so that they are completely free of excess oxygen. Workers exposed to high-oxygen atmospheres should leave the area and avoid all sources of ignition until the clothing and the exposed area have been completely ventilated. Clothing saturated with oxygen is readily ignitable and will burn vigorously.

Specific Properties of Selected Industrial Gases

Anyone who uses gases must have a thorough knowledge of their chemical properties to maintain a controlled operation. If the gas is flammable, its flammable range and ignition temperature must be known.

The lower flammable limit is the smallest percent of the gas in air which can ignite when exposed to the ignition temperature. The upper flammable limit is the point above which the mixture is too rich in fuel to ignite. The range between these two limits is the flammable, or explosive, range. The most violent explosion will occur at concentrations about the middle of the flammable range. Sources of heat that may cause temperatures that exceed the ignition temperature must be avoided, as well as gas-air mixtures that are within the flammable range.

The physiological effects of the gas must be known, not only types of reactions, but also severity of reactions. All employees who handle gas should be familiar with its effects, and recommended control measures.

The chemical reactivity of the gas must be known. This includes a knowledge of the materials that are resistant to its chemical effects, the materials with which it reacts, and how it reacts with such materials. Some gases become unstable at high pressures, and others become more corrosive at high temperatures.

The term Threshold Limit Value (TLV) is sometimes used and is defined as: The highest time-weighted average concentration of an air contaminant which if breathed for a normal working day is unlikely to result in health injury to the average person, either at the time, or after years of exposure.

The following discussion addresses some of the more commonly used gases, and describes the specific chemical properties and characteristics that are important for accident prevention.

Hydrogen

Hydrogen (H₂) is the lightest of all elements. Its presence cannot be detected by any of the senses. It is flammable in oxygen or air, and has a flammable range of from 4.1 percent to 74.2 percent by volume in air. A mixture of 10 to 65 percent hydrogen by volume in air will explode if ignited. Pure hydrogen burns quietly in air with an almost invisible flame, and when burned with pure oxygen, a very high temperature may be reached. Hydrogen will burn readily in chlorine gas, and under proper conditions, will combine with nitrogen, forming ammonia.

Some chemical reactions produce hydrogen as a byproduct. A lead-acid battery will produce hydrogen when it is being charged. Metallic sodium and potassium are examples of some chemicals that react violently when exposed to water, producing hydrogen, which may flame spontaneously due to the heat of the reaction. Many electroplating processes produce hydrogen. Some chemicals used to remove scale from the water side of boilers give off hydrogen. Whatever the operation, it is important to know whether hydrogen will be produced, and if so, precautions must be taken to prevent its accumulation and ignition. The precautions to take include adequate ventilation to prevent its accumulation and the elimination of possible sources of ignition. Hydrogen is classified as an asphyxiant.

Nitrogen

Nitrogen (N₂) makes up more than 78 percent of the earth's atmosphere. It will not burn or support combustion. It cannot be detected by any of the senses and it is not toxic. Although it is often referred to as an inert gas because it does not oxidize readily, it nevertheless forms many compounds. It is frequently used to inert systems that contain, or have contained, flammable liquids or gases. Inerting a system means replacing the oxygen with an inert gas in order to reduce the possibility of fire or explosion.

Nitrogen is fairly soluble in the blood, and a considerable amount will dissolve in the blood of a person when the air pressure is increased, as in diving, caisson, and some tunnel work. If these employees are not properly decompressed, the dissolved nitrogen escapes from the blood in the form of small bubbles in the bloodstream causing intense pain and is often fatal. This disorder is commonly known as the bends.

If a large amount of nitrogen were released into the air of an enclosed space, it could cause a serious oxygen deficiency. Nitrogen is an asphyxiant.

Oxygen

Oxygen (O₂) supports combustion, but does not burn. Even so, it must be considered a potentially hazardous element from a fire hazard standpoint. The results of an enriched oxygen atmosphere include a lowered ignition temperature, an increased flammable range, and an acceleration of the burning rate. Oxygen readily combines with other elements and compounds, with spontaneous ignition in some cases. When oxygen comes in contact with oil, grease, or fuel oils, it may ignite violently. Every possible precaution must be taken to prevent this combination.

Oxygen sustains life, but if pure oxygen were inhaled continuously for extended periods, the reactions in the body would be too rapid and would cause harmful effects. Oxygen should always be referred to as oxygen, and not air, to prevent confusion. It should never be used to run pneumatic equipment because of the possibility of coming in contact with oil that may be inside the equipment. Finally, oxygen valves should be operated slowly. Abruptly starting and stopping oxygen flow may ignite contaminants in the system.

Sources of Ignition

All known sources of ignition must be eliminated in areas that contain, or may contain, flammable gases. This includes areas where gases are being manufactured or used in some process and in areas where they are stored.

One potential source of ignition is electrical equipment. When used or installed in hazardous locations, this equipment must be explosion-proof and properly installed.

Electrical equipment includes not only the more obvious equipment such as motors, generators, motor controls, switches, and lighting fixtures, but also the not so obvious equipment such as alarm systems, remote controls, telephones and other communication systems.

The use of unapproved portable electric tools and equipment should be strictly prohibited in hazardous locations. When temporary lighting is used, it must be an approved type and in excellent repair.

All possible sources of static electricity should be anticipated to prevent its buildup and discharge. Several methods of control may be used. It is necessary that conductive parts of a system be bonded (described in the following chapter) together to eliminate the difference in potential between the parts, and the whole system grounded to eliminate the difference in potential between the system and ground.

When some gases come in contact with certain other substances, spontaneous ignition may occur. One of the better known of these reactions is that of oxygen with oil. Another reaction is the possible ignition of hydrogen due to the heat of the reaction which liberated it, such as sodium in water. Additional sources of ignition are as follows.

- The spontaneous ignition that may occur in oily rags and other materials.
- Smoking is a principal cause of fire, and calls for strict prohibition in hazardous areas.
- Other sources of ignition include sparks or flame-producing operations such as grinding or welding, and equipment such as heaters or boilers.
- Ferrous handtools can produce a spark when struck against, or by a suitable object, and may cause ignition of some gas-air mixtures.
- Other possible sources of ignition are internal combustion engines and battery-powered electric vehicles.

The most disastrous accidents involving industrial gases have been caused by ignition of gas-air mixtures. Fires cannot occur without three essential factors being present in the right quantity, at one place, and at the same time. These factors are fuel, heat, and oxygen (which is normally supplied by air). When they are present in the same place, in the right amounts, and at the same time, there will be a fire. To prevent a fire, it is necessary to keep only one of these factors away from the other two. Air is necessary for life and cannot normally be eliminated, but the fuel and heat can be kept separated. Proper operational and maintenance procedures will help prevent a flammable gas from escaping into the air, but because this is always a possibility, it is most important to eliminate the source of ignition.

Summary

The important information in this chapter is summarized below.

Compressed Gases Summary

- The following terms are defined:

Compressed gas is defined as any material or mixture having in the container an absolute pressure exceeding 40 psi (pounds per square inch) at 70°F, or regardless of the pressure at 70°F, having an absolute pressure exceeding 140 psi at 130°F; or any flammable material having a vapor pressure exceeding 40 psi at 100°F.

Compressed Gases Summary (Cont.)

Non-liquified gases are gases that do not liquify in containers at ambient temperatures and under pressures attained in commercially used containers that range to 2000 to 2500 psig.

Liquified gases are gases which do become liquids to a very large extent in containers at ordinary ambient temperatures, and at pressures from 25 to 2500 psig.

Dissolved gases are gases dissolved into a solution.

- The major families of gases are:

atmospheric gases	aerosol gases
fuel gases	poison gases
refrigerant gases	

- The general safety precautions for gases:

Ensure there is adequate ventilation of enclosed areas.

Avoid entering unventilated areas that might contain high concentrations of gas without first putting on breathing apparatus with a self-contained or hose-line air supply.

Take precautions against skin or eye contact with liquified gases that are toxic or very cold, or both.

The proper storage and handling of containers avoids many possible incidents.

- The safety precautions for working with cryogenic liquids are:

Stand clear of boiling or splashing liquid and its vapors.

Never allow an unprotected part of the body to touch uninsulated pipes or vessels that contain cryogenic fluids.

Use tongs, or a similar device, to withdraw objects immersed in a cryogenic liquid.

Use appropriate eye and hand protection.

Compressed Gases Summary (Cont.)

- The physical properties and special precautions for hydrogen include the following:

It is the lightest of all elements

It cannot be detected by any of the senses

It has a flammable range of from 4.1 percent to 74.2 percent by volume in air

It burns with an almost invisible flame

- Hydrogen is classified as an asphyxiant, and special precautions, such as adequate ventilation and the elimination of possible sources of ignition, should be taken to prevent hydrogen accumulation.

- The physical properties and special precautions for nitrogen include the following:

It makes up more than 78 percent of the earth's atmosphere

It will not burn or support combustion

It cannot be detected by any of the senses

It is used to inert systems that contain, or have contained, flammable liquids or gases

It is fairly soluble in the blood and if the dissolved nitrogen escapes from the blood in the form of small bubbles in the bloodstream, intense pain occurs and effects are often fatal

- Nitrogen is an asphyxiant and it could cause a serious oxygen deficiency. Special precautions, such as adequate ventilation, should be taken to prevent nitrogen accumulation.

- The physical properties and special precautions for oxygen include the following:

It supports combustion, but does not burn

Ignition temperature of a combustible material is lower in enriched oxygen

It readily combines with other elements and compounds, with spontaneous ignition in some cases

- When oxygen comes in contact with oil, grease, or fuel oils, it may ignite violently. Every possible precaution must be taken to prevent this combination. If pure oxygen were inhaled continuously for extended periods the reactions in the body would be too rapid and cause harmful effects. Finally, oxygen valves should be operated slowly. Abruptly starting and stopping oxygen flow may ignite contaminants in the system.

FLAMMABLE AND COMBUSTIBLE LIQUIDS

One of the most devastating industrial accidents is an explosion resulting in fire. Carelessness is often the root cause. Improper handling and storage can also lead to disastrous results. This chapter introduces precautions taken to avoid accidents with flammable and combustible liquids.

EO 1.12 DEFINE the following terms:

- a. Flammable liquid**
- b. Combustible liquid**

EO 1.13 STATE general safety precautions regarding the use, handling, and storage of flammable and combustible liquids.

EO 1.14 STATE the reasons for and techniques used in bonding and grounding of flammable liquid containers.

EO 1.15 LIST four sources of ignition of flammable liquids.

EO 1.16 STATE the health hazards associated with flammable and/or combustible liquids.

Flammable And Combustible Liquids Definitions

As defined by OSHA, DOT, and the National Fire Protection Association Standard, Flammable and Combustible Liquids Code, NFPA 30, a *flammable liquid* is one having a flash point below 100°F, and having a vapor pressure not exceeding 40 psia at 100°F. *Combustible liquids* are those with flash points at or above 100°F, but below 200°F. Although combustible liquids do not ignite as easily as flammable liquids, they must be handled with caution because of their ability to ignite under certain conditions. Flammable and combustible liquids are further subdivided by NFPA 30 into classes as follows.

- Class I - Those liquids having flash points below 100°F.
 - IA - Those liquids having flash points below 73°F and having a boiling point below 100°F.
 - IB - Those liquids having flash points below 73°F and having a boiling point at or above 100°F.

- IC - Those liquids having flash points at or above 73°F and below 100°F.
- Class II - Those liquids having flash points at or above 100°F and below 140°F.
- Class III - Those liquids having flash points above 140°F.
- IIIA - Those liquids having flash points at or above 140°F and below 200°F.
- IIIB - Those liquids having flash points above 200°F.

Flammable and combustible liquids vaporize to form flammable mixtures when they are stored in open containers, when they leak or are spilled, or when heated. The hazard that exists from these mixtures is largely dependent upon the flash point of the liquid, the concentration of the mixture, and the potential of a source of ignition at a temperature sufficient to cause the mixture to burst into flame.

Since it is the vapor-air mixture formed from the evaporation of the liquid that poses the hazard, exposures of large liquid surface areas and sources of heat should be avoided or prevented during handling or storage of these liquids.

Some of the commonly used terms associated with flammable and combustible liquids are provided below.

- Auto-Ignition Temperature -
The minimum temperature at which a flammable mixture will ignite from its own heat source or contact with a heated surface without necessity of a spark or flame.
- Flash Point -
The minimum temperature at which a liquid gives off vapor in sufficient concentration to form an ignitable mixture with air near the surface of the liquid (under controlled test conditions).
- Flammable Limits -
The minimum concentration of vapor in air below which propagation of flame does not occur on contact with a source of ignition. This is known as the lower flammable limit (LFL). There is also a maximum concentration of vapor or gas in air above which propagation of flame will not occur. This is called the upper flammable limit (UFL).
- Flammable Range -
The difference between the lower and upper flammable limits, expressed in percentage of vapor or gas in air by volume. Also known as the explosive range.
- Propagation of Flame -
The spread of flame through the entire volume of the flammable mixture from a single source of ignition.

- Volatility -
The tendency or ability of a liquid to vaporize.
- Oxygen Limits -
The concentration of oxygen below which a normally flammable vapor mixture will not ignite (normally 12 to 14 percent oxygen). An increase of pressure or temperature will reduce the required lower oxygen limit, however.
- Rate of Diffusion -
The tendency of one gas or vapor to disperse into or mix with another gas or vapor. Dependent upon the density of the vapor or gas as compared to air.
- Vapor Pressure -
The pressure exerted by a volatile liquid under any of the conditions of equilibrium that may exist between the vapors and the liquid.
- Oxygen Deficiency -
The designation given to an atmosphere containing less than the percentage of oxygen normally found in air (<21%).

The volatility of liquids will increase as heat is applied to them. Accordingly, combustible liquids should be treated as flammable when they are heated even though the liquid, when not heated, is outside the flammable range.

The Department of Transportation (DOT) has modified the definition of flammable liquids in its Hazardous Materials Regulation, 49 CFR parts 170 to 179. They are defined as any liquid that gives off flammable vapors at or below a temperature of 80°F. This definition is important because the DOT Flammable Liquid Label, illustrated in Figure 4, is one means by which containers of flammable liquids can be identified for shipping, receiving, and transportation.

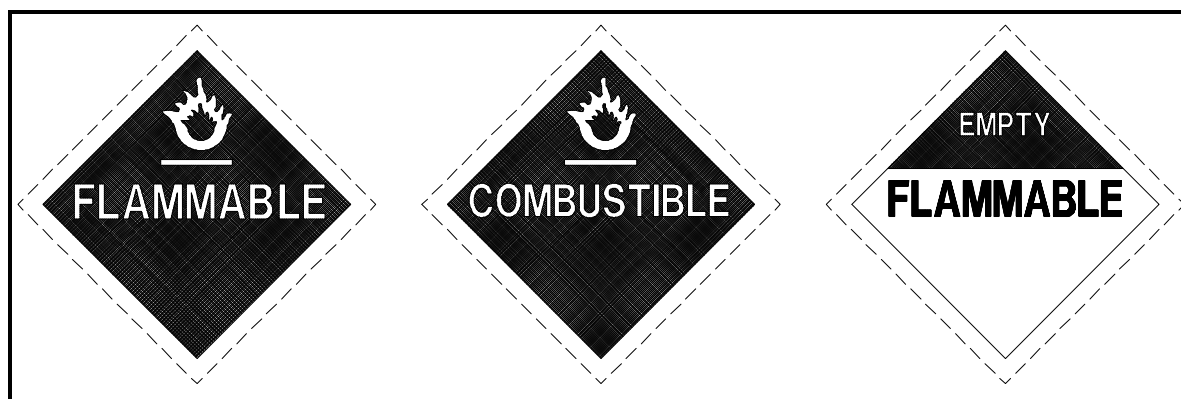


Figure 4 DOT Flammable Liquid Labels

Safety Precautions

Avoid accidental mixture of flammable and combustible liquids. A small amount of a highly volatile substance may lower the flash point of a less volatile substance and form a more flammable mixture. In addition, the lower flash point liquid can act as a fuse to ignite the higher flash point material in the same manner as if it were a flammable mixture.

Fill and discharge lines and openings, as well as control valves associated with flammable and combustible systems, shall be identified by labels, color coding, or both, to prevent mixing different substances. All storage tanks shall be clearly labeled with the name of its contents, and products stored within shall not be intermixed. Transfer lines from different types and classes of flammable products should be kept separate, and preferably, different pumps should be provided for individual products.

For handling quantities of flammable liquids up to five gallons, a portable FM (Factory Mutual Engineering Corp.) or UL (Underwriters Laboratory) approved container should be used. The container should be clearly identified by lettering or color code.

Smoking, the carrying of strike-anywhere matches, lighters, and other spark-producing devices should not be permitted in a building or area where flammable liquids are stored, handled, or used. The extent of the restricted area will depend on the type of products handled, the design of the building, local codes, and local conditions.

Suitable NO SMOKING signs should be posted conspicuously in those buildings and areas where smoking is prohibited.

Static electricity is generated by the contact and separation of dissimilar material. For example, static electricity is generated when a fluid flows through a pipe or from an orifice into a tank. Examples of several methods of generating static electricity are shown in Figure 5. The principal hazards created by static electricity are fire and explosion, which are caused by spark discharges.

A point of great danger from a static spark is where a flammable vapor is present in the air, such as the outlet of a flammable liquid fill pipe, at a delivery hose nozzle, near an open flammable liquid container, and around a tank truck fill opening. In the presence of a mechanism for generating a static charge, a spark between two bodies occurs when there is a poor electrical conductive path between them. Hence, grounding or bonding of flammable liquid containers is necessary to prevent static electricity from causing a spark.

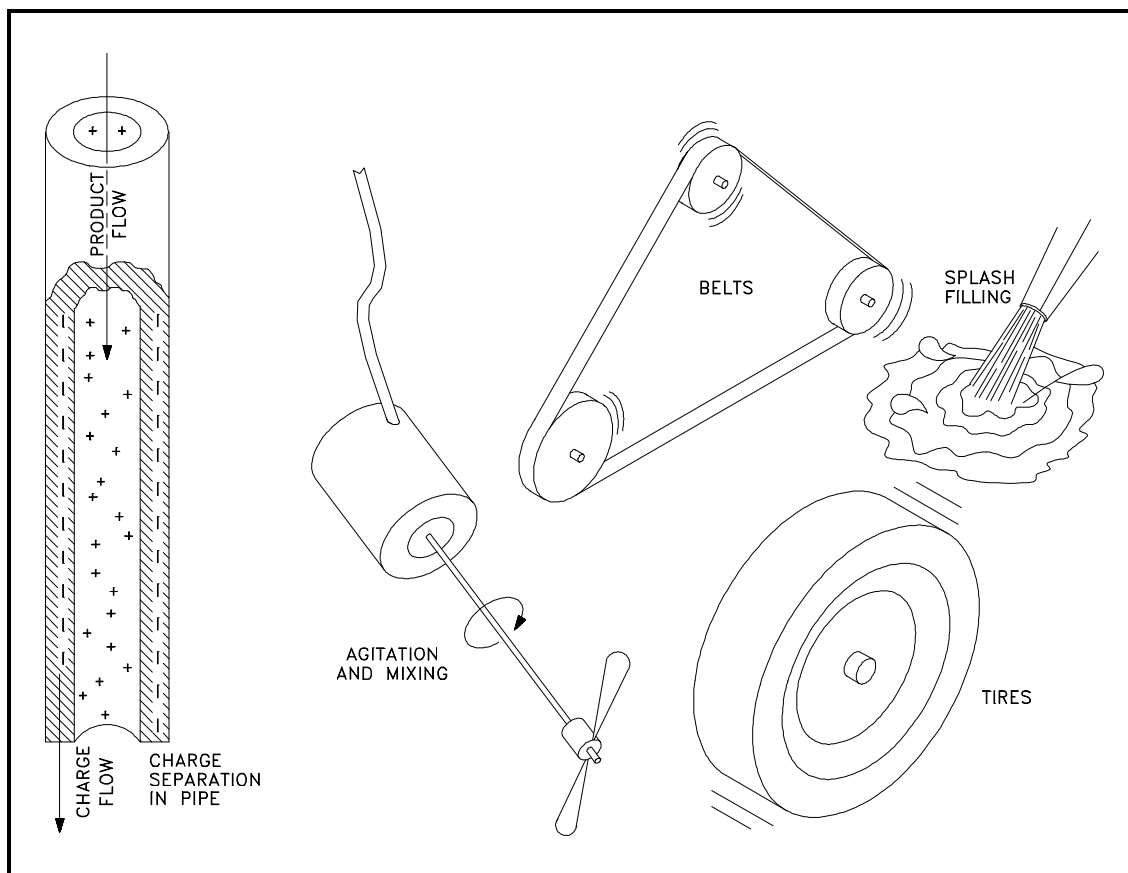


Figure 5 Typical Static-producing Situations, Including Charge Separation in Pipe

The terms bonding and grounding have sometimes been used interchangeably because of a poor understanding of the terms. As illustrated in Figure 6, bonding eliminates a difference in potential between objects. Grounding eliminates a difference in potential between an object and ground. Bonding and grounding are effective only when the bonded objects are conductive.

When two objects are bonded, the charges flow freely between the bodies, and there is no difference in their charge. Therefore, the likelihood of sparking between them is eliminated.

Although bonding eliminates a difference in potential between the objects that are bonded, it does not eliminate a difference in potential between these objects and the earth unless one of the objects possesses an adequate conductive path to earth. Therefore, bonding will not eliminate the static charge, but will equalize the potential between the objects bonded so that a spark will not occur between them.

An adequate ground will discharge a charged conductive body continuously and is recommended as a safety measure whenever any doubt exists concerning a situation.

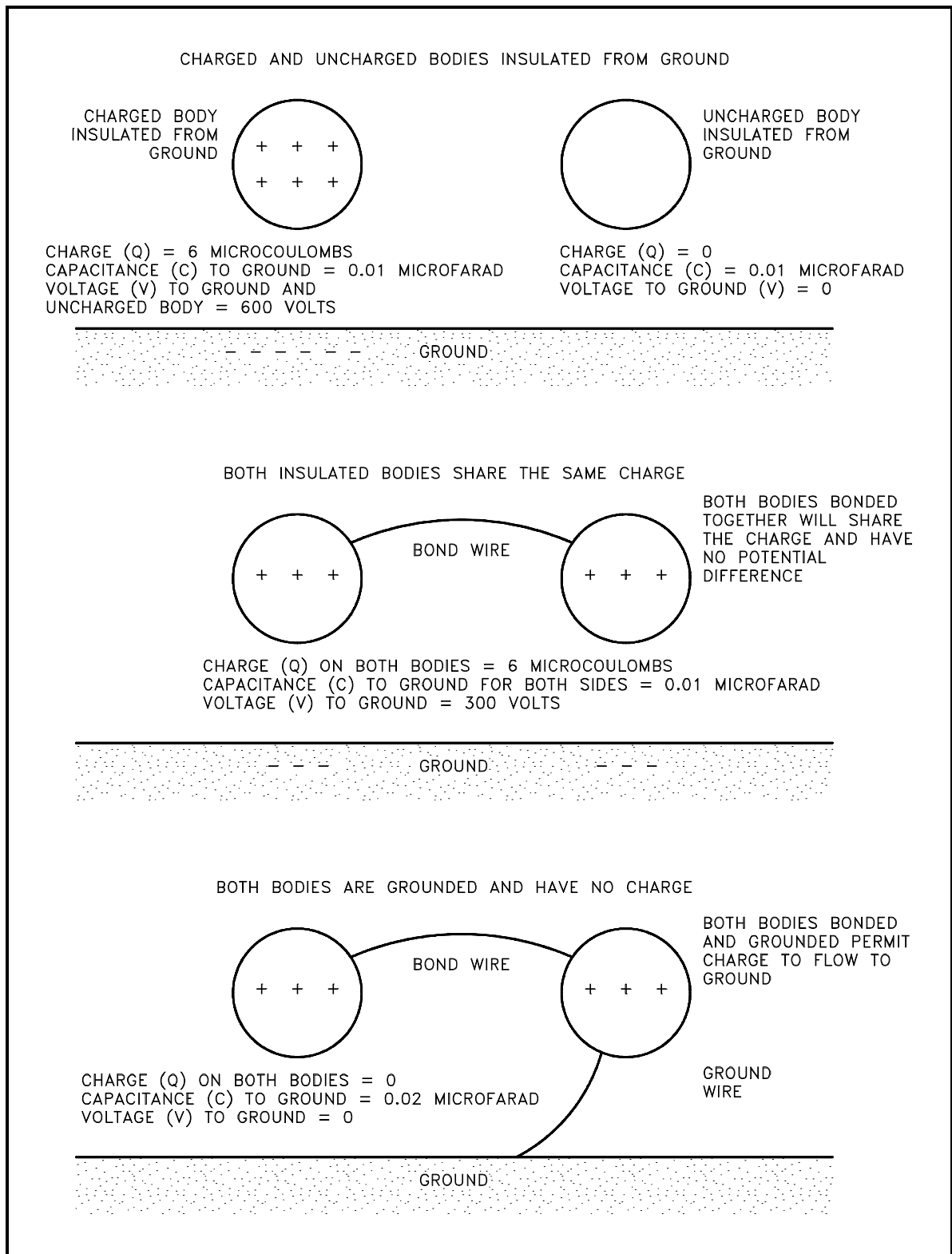


Figure 6 Bonding and Grounding

To avoid a spark from discharge of static electricity during flammable liquid filling operations, a wire bond should be provided between the storage container and the container being filled, unless a metallic path between the container is otherwise present.

Above-ground tanks used for storage of flammable liquids do not have to be grounded unless they are on concrete or on nonconductive supports. Ground wires should be uninsulated so they may be easily inspected for mechanical damage and should never be painted. Figure 7 illustrates grounding above-ground storage tanks.

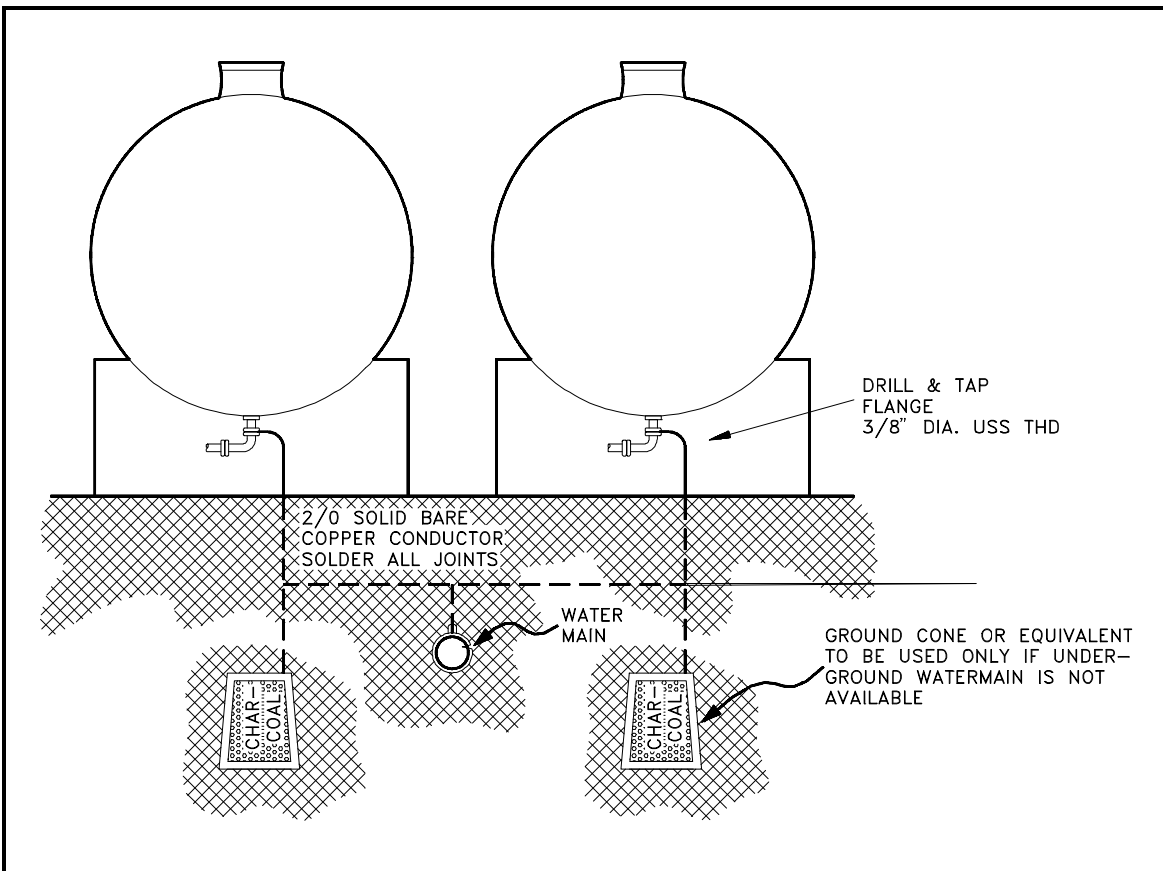


Figure 7 Grounding Above-Ground Storage Tanks

Petroleum liquids are capable of building up electrical charges when they (a) flow through piping, (b) are agitated in a tank or a container, or (c) are subjected to vigorous mechanical movement such as spraying or splashing. Proper bonding or grounding of the transfer system usually dissipates this static charge to ground as it is generated. However, rapid flow rates in transfer lines can cause very high electrical potentials on the surface of liquids regardless of vessel grounding. Also, some petroleum liquids are poor conductors of electricity, particularly the pure, refined products, and even though the transfer system is properly grounded, a static charge may build up on the surface of the liquid in the receiving container. The charge accumulates because static electricity cannot flow through the liquid to the grounded metal container as fast as it is being generated. If this accumulated charge builds up high enough, a static spark with sufficient energy to ignite a flammable air-vapor mixture can occur when the liquid level approaches a grounded probe or when a probe is lowered into a tank for sampling or gaging.

This high static charge is usually controlled by reducing the flow rates, avoiding violent splashing with side-flow fill lines, and using relaxation time, which allows time for the static charge to discharge.

When flammable liquids are transferred from one container to another, a means of bonding should be provided between the two conductive containers prior to pouring, as shown in Figure 8.

In areas where flammable liquids are stored or used, hose nozzles on steam lines used for cleaning should be bonded to the surface of the vessel or object being cleaned. Also, there should be no insulated conductive objects on which the steam could impinge and induce a static charge accumulation.

Nonconductive materials, such as fabric, rubber, or plastic sheeting, passing through or over rolls will also create charges of static electricity. Static from these materials, as well as static from the belts, can be discharged with grounded metal combs or tinsel collectors. Radioactive substances and static neutralizers using electrical discharges are also employed for this purpose.

Bonding and grounding systems should be checked regularly for electrical continuity. Preferably before each fill, the exposed part of the bonding and ground system should be inspected for parts that have deteriorated because of corrosion or that have otherwise been damaged. Many companies specify that bonds and grounds be constructed of bare-braided flexible wire because it facilitates inspection and prevents broken wires from being concealed.

Electricity becomes a source of ignition where flammable vapors exist if the proper type of electrical equipment for these atmospheres either has not been installed or has not been maintained.

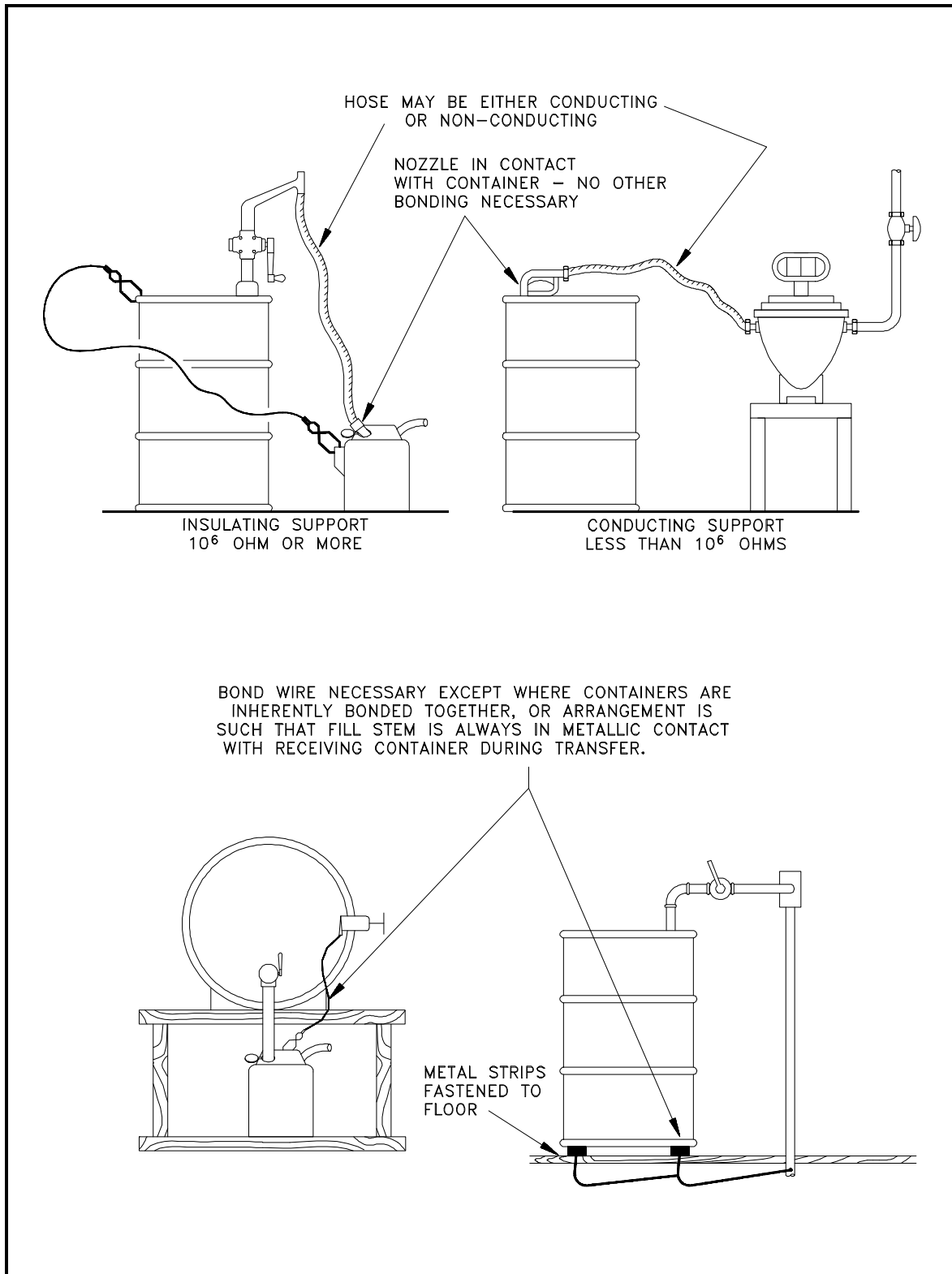


Figure 8 Bonding During Container Filling

A summary of reports of experimental evidence and practical experience in the petroleum industry shows that no significant increase in fire safety is gained by the use of spark-resistant hand tools in the presence of gasoline and similar hydrocarbon vapors. However, some materials such as carbon disulfide, acetylene, and ethyl ether have very low ignition energy requirements. For these and similar materials, the use of special tools designed to minimize the danger of sparks in hazardous locations can be recognized as a conservative safety measure. Leather-faced, plastic, and wood tools are free from the friction-spark hazard, although metallic particles may possibly become embedded in them.

Flammable and combustible liquids and their vapors may create health hazards from both skin contact and inhalation of toxic vapors. Irritation results from the solvent action of many flammable liquids on the natural skin oils and tissue. A toxic hazard of varying degree exists in practically all cases, depending on the concentration of the vapor.

Most vapors from flammable and combustible liquids are heavier than air and will flow into pits, tank openings, confined areas, and low places in which they contaminate the normal air, and cause a toxic as well as explosive atmosphere. Oxygen deficiency occurs in closed containers, such as a tank which has been closed for a long time, and in which rusting has consumed the oxygen. All containers should be aired and tested for toxic and flammable atmosphere as well as the oxygen level before entry.

Storage

Class I and Class II liquids should not be kept or stored in a building except in approved containers, as illustrated in Figure 9, within either a storage cabinet or a storage room that does not have an opening that communicates with the public portion of the building. The spring-loaded cover is designed to open in order to relieve internal vapor pressure. Quantities stored in such locations should be limited. They should not be stored so as to limit use of exits, stairways, or areas normally used for the safe egress of people. Neither should they be stored close to stoves or heated pipes, nor exposed to the rays of the sun or other sources of heat.

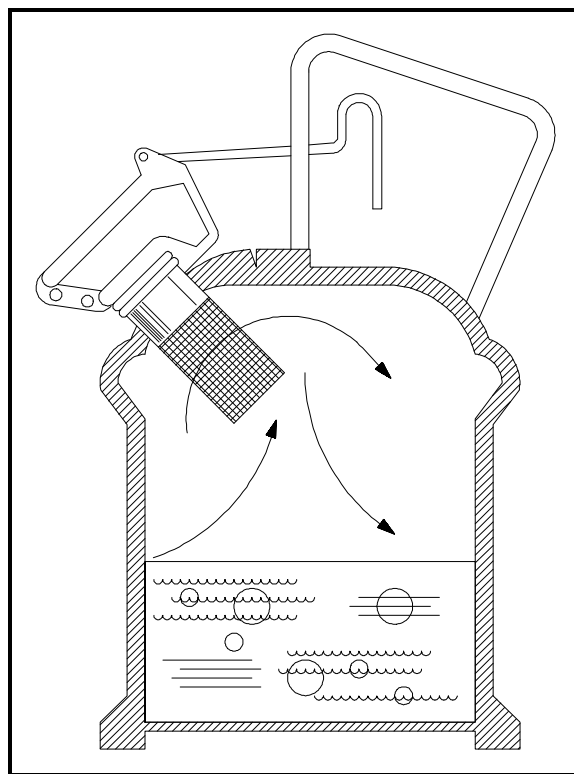


Figure 9 Storage Container With Spring-loaded Cover

Losses by evaporation of liquid stored in safety cans at ordinary temperatures are negligible. Storage of flammable and combustible liquids in open containers should not be permitted. Approved containers for flammable liquids should be closed after each use and when empty. Warning labels should be removed from flammable liquid containers when empty (vapor free). Bulk Class I liquids should be stored in an underground (buried) tank or outside a building. No outlet from the tank should be inside a building unless it terminates in a special room, as illustrated in Figure 10.

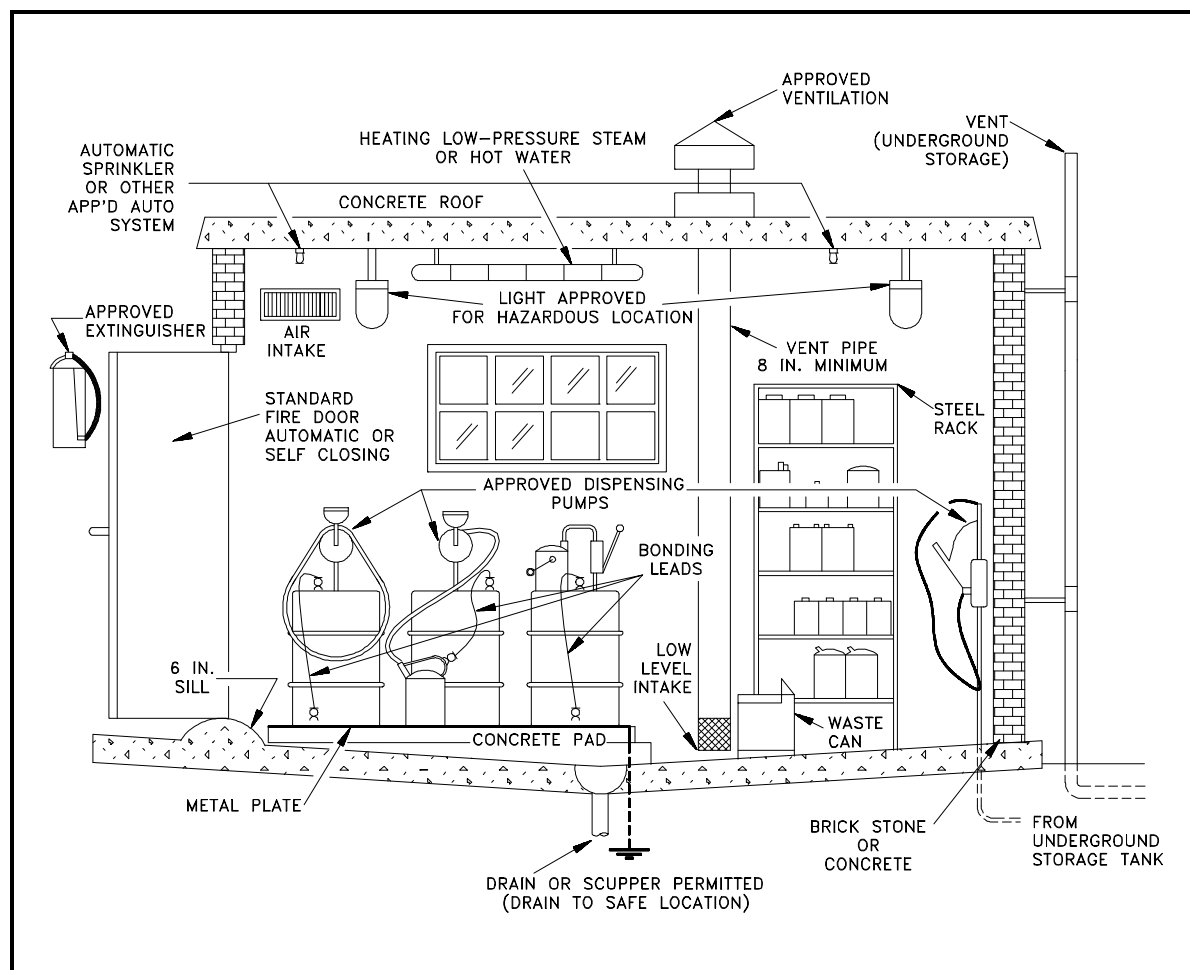


Figure 10 A Flammable Liquids Mixing and Storage Room

Vehicles used on plant property to transport flammable and combustible liquids in sealed containers should be designed to minimize damage to the containers.

When employees are filling tanks and other containers, they should be sure to allow sufficient vapor space (ouage) above the liquid level in order to permit expansion of the liquid with changing temperatures. For example, gasoline expands at the rate of about one percent for each

14°F rise in temperature. Outage space for gasoline of two percent of the capacity of the tank or compartment is recommended, and permanent high-level markings should be installed.

Storage tanks should be provided with vents. Vent pipes of underground tanks storing Class I flammable liquids should terminate outside buildings, higher than the fill pipe opening, and not less than 12 feet above the adjacent ground level. They should discharge vertically upward, and be located so that flammable vapors cannot enter building openings or be trapped under eaves or other obstructions. Vent pipes from underground tanks storing Class II or Class III liquids should terminate outside buildings and higher than the fill pipe opening. Vent outlets should be above normal snow level.

Additional information concerning installation, protection, and spacing of storage tanks located above ground, underground, or in areas subject to flooding is beyond the scope of this course. If this information is desired, it may be found in the National Fire Protection Association Standards.

Flammable or combustible liquids in sealed containers represent a potential hazard rather than an active hazard -- the possibility of fire from without. By the same reasoning, inside storage rooms are undesirable. If they must be used, they should be isolated as much as possible, and located at or above ground level. They should not be located over basements and should preferably be along an exterior wall.

Every inside storage room shall be provided with either a gravity (low level intake) or a continuous mechanical exhaust ventilation system. Mechanical ventilation must be used if Class I liquids are contained or dispensed inside the room.

Storage cabinets have specific limits on the amount and class of flammable or combustible liquids that may be stored in them. They must be constructed and sealed so as to be fire resistant. Cabinets shall be labeled conspicuously -- FLAMMABLE-KEEP FIRE AWAY.

The most advisable storage facility is a separate building set some distance from normally occupied plant areas. The construction can be similar to that specified for inside storage rooms. The types and classes of flammable and combustible liquids stored will determine the best design to be used.

Summary

The important information from this chapter is summarized below.

Flammable and Combustible Liquids Summary

- The following terms are defined:

Flammable liquid is one having a flash point below 100°F, and having a vapor pressure not exceeding 40 psia at 100°F.

Combustible liquids are liquids with flash points at or above 100°F, but below 200°F.

- General safety precautions regarding the use, handling, and storage of flammable and combustible liquids include the following:

The vapor-air mixture formed from the evaporation of the liquid poses a hazard; therefore, exposures of large liquid surface areas and sources of heat shall be avoided or prevented during handling or storage of these liquids.

Accidental mixture of flammable and combustible liquids shall be avoided.

Fill and discharge lines and openings, as well as control valves associated with flammable and combustible systems, shall be identified by labels, color coding, or both to prevent mixing different substances.

All storage tanks shall be clearly labeled with the name of contents.

Transfer lines from different types and classes of flammable products should be kept separate, and preferably, different pumps should be provided for individual products.

When handling quantities of flammable liquids up to five gallons, a portable FM (Factory Mutual Engineering Corp.) or UL (Underwriters Laboratory) approved container should be used. The container should be clearly labeled.

Smoking, the carrying of strike-anywhere matches, lighters, and other spark-producing devices should not be permitted in a building or area where flammable liquids are stored, handled, or used.

Flammable and Combustible Liquids Summary (Cont.)

- The reasons for and techniques used in bonding and grounding of flammable liquid containers are:

Static electricity is generated by the contact and separation of dissimilar material. The principal hazards created by static electricity are those of fire and explosion, which are caused by spark discharges. A spark between two bodies occurs when there is a poor electrical conductive path between them. Bonding is done to eliminate a difference in potential between objects. Grounding is done to eliminate a difference in potential between an object and ground.

- Four sources of ignition concerning flammable liquids include the following:

All sources of static electricity (induce sparks)

Improper type of electrical equipment for these atmospheres or poorly maintained electrical equipment

Flame-producing operations (smoking, grinding or welding)

Improper hand tools that cause sparks

- The health hazards associated with flammable and/or combustible liquids are:

Fire and explosions

Skin irritation from the solvent action of many flammable liquids

Vapors gather in low points or enclosed areas and cause a toxic environment