STATES OF MATTER

One reason for focusing on states of matter in this presentation is that it provides a convenient way of presenting problems of containment of chemical substances and of explaining ways in which chemicals can be transported from one place to another. Another reason is that the concept helps draw attention to various routes of exposure.

A consideration of states of matter should help locate the source of a hazard. Solids can be found in containers such as drums or bags but may also sometimes be found on floors or bench tops, even though they shouldn't be there. Liquids are also confined to their containers, which may be cans or bottles; but they also can get loose. Gases are supposed to be in gas cylinders, but when they get out, they diffuse to fill the available space.

The further possibility of a change of state may result in a far wider dispersion of a chemical and a correspondingly greater chance of exposure.

Gases, of course, can be dispersed more easily than chemicals in the other states. They may penetrate ordinary clothing, and they may be adsorbed on various surfaces. It should be noted that the density of gases may cause them to collect in layers and to rise or settle. This may result in an increased fire or explosion hazard or in an increased danger of toxic exposure.

Liquids can evaporate, and the vapors can then pose the same kinds of hazards as gases. Liquids may also act as solvents both for gases and solids, and thus even if they are themselves inert, they may serve as a medium for carrying and dispersing hazardous materials.

Solids can get into the air and be dispersed in the form of dust particles. Some substances can go directly from the solid to the gaseous state (sublime) and so pose the same hazards as gases.

ROUTES OF ENTRY

Industrial hygiene studies have been concentrated on a number of obvious danger points through which chemicals can come in contact with the body. The first point of contact is usually the skin, by direct contact. Because of their particular sensitivity and importance, the eyes are often given special attention. Chemicals can also get into the body by being swallowed. Normally this could only happen by accident in the chemical workplace, and it is something of a strain to imagine how such an accident could happen. It should be fairly obvious that a chemical process area is entirely unsuited for use as a lunch room, but you may feel that it is necessary to point this out. Finally, gases can be particularly dangerous because they will be breathed in.

This consideration of routes of entry leads in turn to a consideration of the kind of protective gear required. The completeness of protection required depends on the severity of the hazard that may be encountered. Protective clothing, goggles, gloves, face masks, and respirators are all possibilities. *The particular hazard in your plant should be evaluated, and the appropriate response made.* The right protective equipment must be picked for the job. Some solvents will go right through shoe leather and on through the skin of the foot.

Obviously, workers must be trained in the location, use, and maintenance of protective equipment. Cleaning and disposal of contaminated equipment should also be provided for; it is not rational or safe to wear a source of contamination.

SIGNS AND SYMPTOMS OF EXPOSURE

The body will probably react to exposure to harmful chemicals. Itching, smarting or stinging sensations, reddening of the skin or a skin rash, eye irritation or reddening, choking or difficulty in breathing may result from exposure to hazardous chemicals. Inhalation of hazardous chemicals can result in nausea or dizziness. Some chemicals will have an anesthetic effect and will cause drowsiness or unconsciousness.

Individuals may vary widely in their sensitivity to chemical exposure so, even if other workers seem to be unaffected, it is no proof that a worker complaining is "goldbricking".

The body's own senses are extremely sensitive detectors. The OSHA standard recognizes this in requiring familiarization with the appearance and odor of chemicals used in a particular work area.

Note that some chemicals can cause harm without being noticed. Hydrofluoric acid, for instance, can penetrate the skin and cause extensive damage without causing pain. Clearly, it is necessary to know about this kind of behavior ahead of time and to take extra precautions in such cases.

MATERIAL SAFETY DATA SHEETS

The OSHA standard requires that chemical manufacturers and importers obtain or develop Material Safety Data Sheets for each hazardous chemical they produce or import. The information contained on the MSDS shall include at least the following:

- The identity used on the label;
- Physical and chemical characteristics, e.g., vapor pressure, flash point;
- Physical hazards, e.g., potential for fire or explosion, reactivity;
- Health hazards, including signs and symptoms of exposure and medical conditions aggravated by exposure to the chemical;
- Primary routes of entry to the body;
- Required or recommended exposure limits or threshold limit values;
- Recognition as a potential carcinogen;
- Required or recommended procedures for handling, use, protective measures during repair, and clean-up procedures;
- Appropriate engineering controls, work practices, or personal protective equipment;
- Emergency and first aid procedures;
- Date of preparation of the MSDS and of changes to it;
- The name, address, and telephone number of a responsible person who can provide further information on the hazardous chemical and emergency procedures, if necessary.

MEASURING AND MONITORING

An essential component of a plant safety program is the monitoring of the plant environment. An explanation of the need for and the importance of the monitoring program will do much to allay the worker's apprehensions. Mysterious black boxes are likely to rouse anyone's suspicions. Process control equipment (temperature and pressure gauges, pH meters, for example) should be easy to explain. Sampling devices, whether batch or continuous, can also be pointed out. If it is appropriate, mention can be made of threshold limit values or peak concentration monitoring.

It is natural enough for a worker to regard a personally worn monitor as a nuisance. Emphasize that personal monitoring equipment has a serious purpose and is used to protect the worker's health.

This is an opportunity for you to provide instruction in the use, proper care, and maintenance of personal monitoring equipment in your plant.

HEALTH HAZARDS

Some of the hazards considered by the OSHA standard can be evaluated in terms of physical measurements. For instance, the Department of Transportation definition of a corrosive substance is based on the rate at which a steel plate is eaten away. However, even though it is less exact, the OSHA standard defines the hazards in terms of health effects. Corrosive hazards are evaluated in terms of results of skin testing on rabbits.

The hazards specifically defined by the standard are:

- Carcinogens. These are substances that have been determined to cause cancer or to potentially cause cancer. Carcinogens or potential carcinogens are identified by the United Nations International Agency for Research on Cancer and the U.S. National Toxicology Program and may be already regulated as such by OSHA.
- Corrosives. These substances are defined in terms of a rabbit skin test. Label and MSDS information is important, because the chemical name may mislead an untrained worker. For example, many acids are corrosive, but not *all* acids are corrosive. And not all corrosives are acids.
- Highly toxic. These substances are extremely poisonous in extremely small doses (defined in terms of animal tests). The normal danger is from ingestion, but dermal or inhalation toxicity is also a possibility.
- Irritants. These substances cause inflammation of the skin or eyes. The effects are evaluated in terms of rabbit skin or eye tests;
- Sensitizers. These substances cause a substantial proportion of exposed people to develop an allergic reaction.
- Toxic. These substances are distinguished from the "highly toxic" category because a larger dose is required to cause an effect.
- Target organ effects. The standard gives examples of chemicals that selectively damage the liver (carbon tetrachloride, for example), kidneys (halogenated hydrocarbons), nervous system (carbon disulfide), blood or blood-forming organs (cyanides), lungs (asbestos), reproductive system (dibromochloropropane), skin (ketones), or eyes (acids).

DEFINITION OF CARCINOGENS

Carcinogens are substances that cause cancer. Harmful health effects of chemicals can range from gross destruction of tissue (as with corrosives) to interference with normal body functioning (as with toxic materials) to disruption of processes within body cells that affect their ability to divide. In cancer, modified body cells start reproducing and continue to do so out of control. This leads to tumor formation and is a severe assault on the body s normal functioning.

Cancer is not a single disease. Many types of body cells can show cancerous activity and result in different symptoms. The causes of cancer are not definitely known, although many of them are thought to be dietetic or environmental. Medical research is making continued progress in isolating the causes. Methods of treatment are also improving and showing a higher rate of success.

It has long been known that exposure to some substances is correlated with the development of cancer. With regard to dose levels and the duration of exposure, the range of effects seems to be broad. Some authorities hold that there is no safe exposure level, and this conservative view is certainly the safest one to take. From an occupational safety and health point of view the definition of a carcinogen results from its effects in animal testing. Specific exposure tests have been prescribed to be performed on test animals. The tests take about two years to run and analyze, so they are expensive and the amount of information obtained does not accumulate rapidly. There is an argument about the applicability of test data obtained with animals to humans.

According to the OSHA standard, a chemical is considered to be a carcinogen if it has been:

- Evaluated by the International Agency for Research on Cancer and found to be a carcinogen or potential carcinogen;
- Listed in the *Annual Report on Carcinogens* published by the National Toxicology Program as a carcinogen or potential carcinogen.
- Regulated by OSHA as a carcinogen. OSHA specifically regulates the following 18 substances:

2-Acetylaminofluorene	4-Dimethylaminoazobenzene
Acrylonitrile	Ethyleneimine
4-Aminodiphenyl	Methyl chloromethyl ether
Arsenic, inorganic	alpha-Naphthylamine
Benzidine	beta-Naphthylamine
bis-Chloromethyl ether	4-Nitrobiphenyl
Coke oven emissions	N-Nitrosodimethylamine
1,2-Dibromo-3-chloropropane	beta-Propiolactone
3,3'-Dichlorobenzidine	Vinyl chloride.

It is important to keep the problem of carcinogens in the proper perspective. Millions of chemicals are known. Of these, perhaps 40,000 find some use in the chemical industry and commerce. Any given plant is not likely to use more than 2,000 at the most. Yet OSHA only specifically regulates 18 compounds.

According to the OSHA standard, information on whether a compound is a carcinogen or not must be included on a safety label and a Material Safety Data Sheet for the substance.

HEALTH HAZARDS POSED BY CARCINOGENS

The problem of cancer initiation is extremely complex. Not only are the causes uncertain and possibly a combination of factors, including individual susceptibility; but the effects are not immediate. Some cancers may not become active for twenty years, so it is very difficult to trace back from the effect to the cause.

Further complications arise because of the existence of promoters, substances which are not themselves carcinogenic but which can ultimately allow other substances to have a carcinogenic effect.

DEFINITION OF CORROSIVES

Corrosives are chemical substances that react with sufficient vigor to destroy the structural integrity of other materials. Some of them can eat away metals, and others can cause severe injury to living tissue resulting in the killing of body cells. From an occupational safety and health point of view the definition of a corrosive results from its effects on living tissue rather than on metal plates. Specific tests have been prescribed to be performed on test animals (usually rabbits), and corrosives are compounds that cause, in the words of the OSHA standard, "visible destruction of, or irreversible alterations in, living tissue by chemical action at the site of contact" during a four-hour test period. Corrosives are thus defined in terms of their chemical and physiological action, which does not have any particular relation to the chemical structural class. In other words, the name or structure alone is insufficient to identify a substance as a corrosive. For example, strong acids are corrosives (in its use here, "strong" is a technical term meaning highly ionized), but that is not to say that *all* acids are corrosives. Boric acid, for instance, is used as an eyewash. Information on whether a compound is a corrosive or not must ultimately be based on experimentation and will be recorded on a safety label and a Material Safety Data Sheet for the substance.

HEALTH HAZARDS POSED BY CORROSIVES

The degree of danger posed by a compound depends on its reactivity. The amount of damage that can result depends on this reactivity, the concentration of the chemical, and the duration of exposure.

Some substances are extremely dangerous; they will cause skin destruction in the animal test in less than three minutes exposure. Other substances have a slower corrosive action (resulting in skin destruction in from three to 60 minutes) but are regarded as particularly dangerous because the vapor is toxic. Some chemicals in this worst group are:

Allyl chlorocarbonate
Bromine
Chromium oxychloride
Chromosulfuric acid
Fluorosulfonic acid
Hydrofluoric acid
Hydrofluoric acid
Nitrating acid, mixtures
Nitric acid
Nitrohydrochloric acid
Selenic acid
Selenium oxychloride
Sulfur trioxide
Sulfur chlorides
Sulfuryl chloride
Thionyl chloride
Trifluoroacetic acid
Vanadium tetrachloride.

Substances are regarded as presenting a medium danger if they can cause skin destruction in from three minutes to 60 minutes under test conditions but have no particular additional hazard. Some of these chemicals are:

Acetic anhydride
Acetic acid (50% to 80% concentration)
Acetic acid, glacial
Acetyl bromide
Acetyl iodide
Acetyl bromide
Acetyl iodide
Acrylic acid
Alkyl, aryl or toluene sulfonic acid
Ethyl chlorthioformate
Ethylphenyldichlorosilane
Ethylsulfuric acid
Fluoroboric acid
Fluorosilicic acid
Formic acid
Fumaryl chloride
Hexafluorophosphoric acid
Hexyl trichlorosilane

Alkylamines

Allyl trichlorosilane

Aluminum chloride

Aluminum bromide

Ammonium hydrogen sulfate

Ammonium hydrogen sulfate

Ammonium polysulfide

Ammonium hydrogen fluoride

Ammonium sulfide

Anisoyl chloride

Antimony pentachloride

Benzotrichloride

Benzoyl chloride

Benzyl bromide

Boron trifluoride diethyl etherate

Boron trifluoride dihydrate

Boron trifluoride propionic acid complex

Boron trifluoride acetic acid complex

Bromoacetyl bromide

Butyl trichlorosilane

Caustic alkali liquids, not otherwise specified

Cesium hydroxide

Chloroacetic acid

Chloroacetyl chloride

Chromic acid

Chromic fluoride

1,5,9-Cyclododecanetriene

Cyclohexenyltrichlorosilane

Di-n-butylamine

Dibenzyldichlorosilane

Dichloroacetic acid

Dichloroacetyl chloride

Dichlorophenyl trichlorosilane

Hydrazine hydrate (not more than 64% by weight)

Hydriodic acid

Hydrobromic acid

Hydrochloric acid

Iodine monochloride

Lithium hydroxide

Nitrosylsulfuric acid

Nonyl trichlorosilane

Octadecyl trichlorosilane

Octyl trichlorosilane

1-Pentol

Phenyacetyl chloride

Phenyl trichlorosilane

Phenyl phosphorus thiodichloride

Phenyl phosphorus dichloride

Phosphorus tribromide

Phosphorus trichloride

Phosphorus oxychloride

Phosphorus pentachloride

Phosphorus pentabromide

Phosphorus oxybromide

Potassium bifluoride

Potassium oxide

Potassium hydrogen sulfate

Potassium hydroxide

Propyl trichlorosilane

Pyrosulfuryl chloride

Rubidium hydroxide

Silicon tetrachloride

Sodium hydroxide

Sodium monoxide

Sodium hydrogen fluoride

Sodium sulfide

Stannic chloride, anhydrous

N,N-Diethyethylene diamine
Diethyldichlorosilane
Diethylenetriamine
Diethylthiophosphoryl chloride
N,N-Dimethylcarbamoyl chloride
N,N-Dimethylcyclohexylamine
Diphenyldichlorosilane
Diphenylmethyl bromide
Dodecyl trichlorosilane
Sulfuric acid
Thiophosphoryl chloride
Titanium trichloride
Trichloroacetic acid
Trichloroacetyl chloride
Triethylenetetramine
Trimethylacetyl chloride
Valeryl chlorides
Vanadium oxytrichloride

Substances regarded as presenting a minor degree of danger (but still meeting the definition of skin destruction in a four-hour test) include:

N-Aminoethylpiperazine
Ammonia solutions (from 10 to 35% ammonia)
Amyl acid phosphate
Benzene sulfonyl chloride
Butyl acid phosphate
Butyric acid
Chloropropionic acid
Crotonic acid
Cyanuric chloride
Dicyclohexylamine
3-(Diethylamino)-propylamine
Dimethylthiophosphoryl chloride
Ethanolamine
2-Ethylhexylamine
Hydroxylamine sulfate
3,3'-Iminobispropylamine
Isophoronediamine
Methacrylic acid
Phosphoric acid
Phosphorous acid
Phosphorus trioxide
Propionic anhydride
Propionic acid
Tetraethylenepentamine
Tributylamine
Triethylenediamine
Trimethylcyclohexylamine
Vanadium trichloride
Zirconium tetrachloride

It should be noted that some materials can pose multiple threats. The possibility of inhalation toxicity has been mentioned, and some substances are not only corrosive but are readily absorbed through the skin and can cause further systemic damage or poisoning. Corrosives are obviously especially reactive chemicals, and sometimes they can react with other chemicals to result in a worsened hazard situation. Some substances can decompose at high temperatures to release toxic gases. Others can react with water or even moisture in the air to release harmful substances. Others can react with organic material to generate heat. Others are not only corrosives but also flammable liquids or oxidizing materials. Information on these added dangers should be obtainable from a Material Safety Data Sheet.

DEFINITION OF GASES

A gas is a material in a state of matter that tends to fill the space available to it. If it is confined in a container it will expand to fill the whole container, and if it is loose in the air it will diffuse to fill a confining space (a room or building). Gases can pose the physical hazards associated with material kept at high pressure or readily flammable. Some gases also pose a health hazard because of their carcinogenic, poisonous, or corrosive characteristics. It is convenient to treat gases as a single class of compounds from the point of view of their handling and use in a chemical plant.

Gases can be liquefied by subjecting them to pressure or by lowering their temperature. The ease with which this can be done depends on the molecular weight and the chemical structure of the substance. Permanent gases are those that cannot be liquefied at ordinary temperatures (hydrogen, oxygen). Liquefied gases can become liquid under pressure at ordinary temperatures (methyl bromide). Some gases will dissolve under pressure in a solvent, usually absorbed on porous material (acetylene). Some gases can be liquified at extremely low temperatures (oxygen is liquid at atmospheric pressure at −183°C or −297°F). The practical consequence of this is that different gases may be stored under a wide range of pressure conditions--from atmospheric pressure to perhaps five times atmospheric. Even higher pressures can occur at higher temperatures or under reaction conditions.

HEALTH HAZARDS POSED BY GASES

The health hazards identified by the OSHA Hazard Communication Standard are:

- Carcinogens;
- Corrosive materials;
- Toxic materials;
- Irritants;
- Sensitizers;
- Substances affecting target organs.

If a gaseous substance presents one of these health hazards, the OSHA standard requires that information about the hazard should be listed on a hazard label and also be available on a Material Safety Data Sheet (MSDS).

The fact that a substance is in the gaseous state automatically increases the danger of exposure because of the possibility of inhalation and eye and skin exposure.

The OSHA standard requires labeling of "highly toxic" and "toxic" substances as determined from animal testing. Some poisonous gases are:

Ammonia, anhydrous
Arsine
Boron trifluoride
Bromine chloride
Carbon monoxide
Carbonyl fluoride
Carbonyl sulfide
Chlorine
Cyanogen
Diborane
Dichlorosilane
Ethylene oxide
Fluorine
Germane
Hydrogen chloride, anhydrous
Hydrogen fluoride, anhydrous
Hydrogen sulfide
Methyl bromide
Methyl chloride
Nitric oxide
Nitrosyl chloride
Phosgene
Phosphine
Selenium hexafluoride
Sulfur dioxide

Some flammable gases, which may pose a threat of fire or explosion, are:

Acetylene
Butadiene
Butane
Ethylene
Ethyl methyl ether
Hydrogen sulfide

Carbonyl sulfide	Hydrogen
Cyanogen	Methane
Diborane	Phosphine
Dimethyl ether	Propane
Ethane	Silane
Ethylamine	Vinyl chloride
Ethyl chloride	Vinyl bromide

Some corrosive gases are:

Boron trichloride	Hydrogen bromide, anhydrous
Bromine chloride	Hydrogen chloride, anhydrous
Chlorine pentafluoride	Nitrosyl chloride

Many gases are heavier than air and thus tend to form layers at the lowest level they can reach. Concentrations at floor level or in equipment wells may reach unexpectedly high levels. Even inert or nontoxic gases can displace air and collect in concentrations high enough to be suffocating.

DEFINITION OF EXPLOSIVES

An explosive is a chemical substance that in itself can react to produce gas at a temperature and pressure and at such a speed as to damage the surroundings. The explosive reaction can be initiated by ignition or shock. The severity of the reaction depends on the particular material and the conditions present. A whole range of effects is possible, including:

- Mass explosion hazard, in which the whole mass of the explosive substance is affected practically instantaneously;
- Projection hazard, in which a propulsive jet is formed but not a mass explosion hazard;
- Fire hazard or minor blast hazard;
- Relative insensitivity to ignition or shock.

Besides the hazard of explosive substances, there is the hazard of explosive conditions in the workplace. Concentrations of vapor from a flammable substance may build up to form a combustible or explosive atmosphere. There is a characteristic lower concentration limit that must be reached before the mixture becomes explosive. For instance, the following are some lower combustion limits for some substances in air (percent by volume):

Acetone	2.5	Ethyl alcohol	3.2
Benzene	1.4	Hydrogen	4.0
Carbon disulfide	1.2	Octane	0.9
Diethyl ether	1.8	Propane	2.1

Considering the whole air space available, these numbers may seem fairly high. However, an explosive atmosphere need only build up in the immediate vicinity of the source. If an explosion occurs, it will almost certainly start a fire in the main body of material, which will spread and which will also disperse the material.

Characteristically, there is an upper explosive concentration also, where the mixture becomes so fuel-rich that it will not ignite. This is not a significant consideration in a safety program.

Although mixtures of gases and vapors with air are likely to pose the principal explosive hazard, explosive mixtures can also be formed with dust particles in the air. For instance, flour mills have a serious problem controlling airborne particles.

Explosive hazards can also result from the use of chemical equipment. Pressure can build up in pumping operations or in distillation columns.

Chemical processes can also result in explosions. Many reactions result in a release of heat, which in turn will accelerate the reaction, which eventually may proceed with explosive vigor.

HEALTH HAZARDS POSED BY EXPLOSIVES

The principal danger posed by explosives is the physical one of detonation. Some explosive compounds may have a subsidiary health risk. For instance, nitroglycerin and dinitrophenol are toxic. Substances that are toxic, irritants, or sensitizers must be so labeled under the provisions of the Occupational Safety and Health Hazard Communication Standard (effective November 1985). Hazard warning information must be contained on a label and on a Material Safety Data Sheet for the material.

Because considerable physical disruption can be expected from an explosion, the possibility of the release of toxic materials present in the workplace should be considered.

DEFINITION OF OXIDIZERS

The common definition of oxidation is the reaction of a material with oxygen (actually more highly technical definitions are sometimes used, but they need not concern us here). The source of the oxygen can be the atmosphere, which contains about 20% oxygen. Common oxidation reactions using atmospheric oxygen are respiration (breathing), combustion (burning), or slow oxidation processes like rusting. The rate at which these reactions proceed depends on the concentration of oxygen present, among other factors. The oxygen in air is diluted by inert nitrogen in a ratio of four to one, so that the rate of oxidation is much less than it would be with pure oxygen.

Oxidizers are substances that can release oxygen when they react and thus provide a self-contained source of energy to fuel a reaction (again, in a broader technical sense oxidizers may contain no oxygen—chlorine is an example). This property is very important in promoting useful chemical reactions, but it can also be a source of hazard. Oxidizers are very reactive compounds, and the kinds of reactions that can occur depend on the other reactants that they come into contact with and the reaction conditions. When combining with combustible materials, oxidizers will burn fiercely. In contact with other substances spontaneous combustion may occur; that is, a slow oxidation reaction will cause heat to build up and ultimately result in combustion. With other substances, explosive mixtures may form that may be sensitive to friction. And finally, with extremely reactive substances, oxidizers may cause immediate combustion or explosion. All of these reactions are likely to proceed with considerable vigor releasing heat and possibly toxic gases.

Some common oxidizers are:

Aluminum nitrate	Chlorates	Potassium nitrate
Ammonium dichromate	Hydrogen peroxide	Potassium peroxide
Ammonium nitrate	Magnesium nitrate	Potassium persulfate
Bromine pentafluoride	Perchlorates	Sodium nitrate
Calcium chlorate	Permanganates	Sodium permanganate
Calcium perchlorate	Potassium nitrate	Sodium peroxide

ORGANIC PEROXIDES

A special class of oxidizers very useful for their chemical properties is organic peroxides. They, too, can react explosively when involved in a fire. The transportation hazard label will normally say "Organic Peroxide." A few examples of organic peroxides are:

Acetyl peroxide

Benzoyl peroxide

Bis-(1-hydroxycyclohexyl) peroxide

iso-Butyl methyl ketone peroxide

tert-Butyl peroxyacetate

Di-(tert-butyl peroxy) phthalate

Peracetic acid

Tetralin hydroperoxide.

HEALTH HAZARDS POSED BY OXIDIZERS

Oxidizers as a class are not defined as a health hazard. They are more of a safety hazard, and the dangers of fire and explosion either from the compound itself or on reaction with another material have been pointed out. The health hazards identified by the OSHA Hazard Communication Standard are:

- Carcinogens;
- Corrosive materials;
- Toxic materials;
- Irritants;
- Sensitizers;
- Substances affecting target organs.

If a substance presents one of these health hazards, and many oxidizers do, information about the hazard should be contained on a health-hazard label and also be available on a Material Safety Data Sheet, according to the requirements of the OSHA standard.

Apart from these possible dangers, unnecessary exposure to any chemical should be avoided. Oxidizers are highly reactive, sometimes react with moisture to release toxic materials, and can cause burns.

DEFINITION OF POISONS

Poisons are substances that are liable to cause death or serious injury if they are swallowed, inhaled, or come in contact with the skin. Mechanisms by which poisons act may differ widely, but the level of action is usually physiological. The poison interferes with the proper functioning of the body, for instance by affecting oxygen distribution in the bloodstream or by blocking nerve impulses. From an occupational safety and health point of view the definition of a toxic substance results from its effects on test animals. The OSHA standard defines two categories of health hazard. These are:

- Highly toxic materials. A chemical falling within any of the following categories:
  a. A chemical that has a median lethal dose of 50 milligrams or less per kilogram of body weight when administered orally to albino rats weighing between 200 and 300 grams each.
  b. A chemical that has a median lethal dose of 200 milligrams or less per kilogram of body weight when administered by continuous contact for 24 hours (or less if death occurs within 24 hours) with the bare skin of albino rabbits weighing between two and three kilograms each.
  c. A chemical that has a median lethal concentration in air of 200 parts per million by volume or less of gas or vapor, or 2 milligrams per liter or less of mist, fume, or dust, when administered by continuous inhalation for one hour (or less if death occurs within one hour) to albino rats weighing between 200 and 300 grams each.

- Toxic materials. A chemical falling within any of the following categories:

  a. A chemical that has a median lethal dose of more than 50 milligrams per kilogram but not more than 500 milligrams per kilogram of body weight when administered orally to albino rats weighing between 200 and 300 grams each.

  b. A chemical that has a median lethal dose of more than 200 milligrams per kilogram but not more than 1,000 milligrams per kilogram of body weight when administered by continuous contact for 24 hours (or less if death occurs within 24 hours) with the bare skin of albino rabbits weighing between two and three kilograms each.

  c. A chemical that has a median lethal concentration in air of more than 200 parts per million but not more than 2,000 parts per million by volume of gas or vapor, or more than 2 milligrams per liter but not more than 20 milligrams per liter of mist, fume, or dust, when administered by continuous inhalation for one hour (or less if death occurs within one hour) to albino rats weighing between 200 and 300 grams each.

Other classes of substances that have a physiological action and are defined as health hazards by the OSHA standard are:

- Irritants. Chemicals that are not corrosive but cause a reversible inflammatory effect on living tissue by chemical action at the site of contact. Conditions for a rabbit skin test are specified in federal regulations. Eye irritants are also defined in terms of animal tests in federal regulations. Note that the definition of an irritant is different in the shipping regulations of the Department of Transportation; an irritant is defined as a substance that in contact with fire or air gives off dangerous or intensely irritating fumes. Because this is a more severe hazard, care should be taken to distinguish between shipping labels and health-effects labels.
- Sensitizers. Chemicals that cause a substantial proportion of exposed people or animals to develop an allergic reaction in normal tissue after repeated exposure to the chemical.

HEALTH HAZARDS POSED BY POISONS

The degree of danger posed by a poison depends on its physiological action, its route of attack, and its reactivity. The amount of damage that can result depends on these factors, the concentration of the chemical, and the duration of exposure.

A whole range of physiological effects is possible. Poisons can interfere with the oxygen-distribution system of the body, paralyze muscles, and affect nervous-system activity. It is more difficult to guard against poisons that can be inhaled in the vapor phase or be absorbed through the skin. If the main hazard is ingestion of the poison, it should be relatively easy to guard against.

Poisons can act almost instantaneously; cyanides are an example. Other materials may take a period of hours or a day: acute arsenic poisoning is an example. In cases of chronic poisoning, repeated small doses over a long period of time can impair health and even be life-threatening; chronic lead poisoning is an example of this.

The symptoms of poisoning also have a wide range--from convulsions or cessation of breathing to no noticeable symptoms. It is possible for a poison to enter the system with no noticeable effect and then to result in delayed symptoms some time later.

Some toxic substances that are regarded as particularly dangerous because of their high toxicity or threat of exposure are:

Acetone cyanohydrin
Arsenic acid, liquid
Barium cyanide
Bromobenzyl cyanide
Calcium cyanide
Chloropicrin
Cyanogen bromide
sym-Dichlorodimethyl ether
Dimethyl sulfate
Epibromohydrin
Fluoroacetic acid
Hydrocyanic acid
Iron pentacarbonyl
Lead tetraethyl
Mercuric potassium cyanide
Nickel carbonyl
Osmium tetroxide
Phenyl mercaptan
Potassium fluoroacetate
Potassium cyanide
Sodium cyanide
Sodium fluoroacetate

Other toxic substances posing an intermediate level of hazard are:

Aldol
Allyl isothiocyanate
Aniline
Benzidine
Benzonitrile
Bromoacetone
Cacodylic acid
Carbontetrachloride
Chloral
Chloroform
Diethylsulfate
Dinitrobenzenes
Dinitrotoluenes
Epichlorohydrin
Ethyl bromide
Ethylene dibromide
Lead arsenates
Mercuric chloride
Nitroanilines
Nitrobenzene
Nitrotoluenes
Phenol
Potassium arsenate
Toluidines

Substances posing a relatively small hazard are:

Acrylamide	Furfuryl alcohol
Ammonium fluoride	Hexachlorobenzene
Bromoform	Hexachlorophene
Dichlorobenzenes	Resorcinol
Dichloromethane	

Some toxic gases, which pose an inhalation hazard, are:

Ammonia, anhydrous	Germane
Arsine	Hydrogen chloride, anhydrous
Boron trifluoride	Hydrogen fluoride, anhydrous
Bromine chloride	Hydrogen sulfide
Carbon monoxide	Methyl bromide
Carbonyl fluoride	Methyl chloride
Carbonyl sulfide	Nitric oxide
Chlorine	Nitrosyl chloride
Cyanogen	Phosgene
Diborane	Phosphine
Dichlorosilane	Selenium hexafluoride
Ethylene oxide	Sulfur dioxide
Fluorine	

Note that the OSHA standard is based only on toxicity data without regard to subsidiary factors such as volatility. Whether or not the compounds listed above would be classed as "highly toxic" or "toxic" would depend on the results of toxicity testing. The information should be given on a warning label and on a Material Safety Data Sheet (MSDS) for the substance.

DEFINITION OF SOLVENTS

No single chemical class can be defined as a solvent, but in looking at plant operations in the chemical industry it is natural to consider solvents as a group because of their common characteristics in handling, use, and storage.

Solvents are used to dissolve other materials. Some of them are thus used as cleaning fluids or for degreasing and others are used for extracting soluble materials from raw materials. Solvents are also used in chemical processing, because more uniform and controlled behavior can be obtained with chemicals uniformly present in solution. A wide variety of solvents is used because favorable reaction conditions have to be tailored to the kind of dissolved substances and reaction conditions required. Water is a very common solvent and dissolves a wide range of substances, particularly inorganic salts. However, many specialized organic liquids are also used because they meet particular requirements better.

Many solvents are flammable liquids, and they thus present more of a safety hazard than a health hazard. However, there can also be health effects of all kinds--solvents may be toxic, corrosive, or irritant. Information on these hazards should be available on a safety label and a Material Safety Data Sheet for the substance.

FLAMMABLE LIQUIDS

The flammability of materials is measured by a flashpoint test. The flashpoint is the lowest temperature at which the vapor of a combustible liquid can be made to ignite. Therefore, the lower the flashpoint, the greater is the danger of combustion. The flashpoint measured depends on the configuration of the test apparatus. The most consistent results are obtained in a closed-cup method. The Department of Transportation classifies "flammable liquids" as those having a flashpoint below 100°F (37.8°C) and "combustible liquids" as those having a flashpoint between 100°F and 200°F (93.3°C). A classification more closely reflecting the degree of personal hazard has been developed by a United Nations committee of experts. This classification divides substances into three flashpoint ranges.

The low flashpoint group consists of substances having a flashpoint below −18°C (0°F) (closed cup method), which are regarded as presenting great danger. Following are some of these substances:

Acetal
Acetaldehyde
Acetone
Acrolein
Allyl amine
Allyl chloride
Amyl nitrite
isoButyraldehyde
Carbon disulfide
2-Chloropropane
2-Chloropropene
Cyclohexane
Cyclohexene
Cyclopentane
Cyclopentene
Diethoxymethane
Diethyl ether
Diethylamine
Diisopropyl ether
1,1-Dimethoxyethane
Dimethyl sulfide
2,3-Dimethylbutane
Dipropyl ether
Ethyl propyl ether
Ethyl mercaptan
Ethylamine
Furan
isoHeptene
Hex-1-ene
Hexadiene
Hexane
Isoprene
Methyl formate
Methyl propyl ether
Methylal
2-Methylfuran
Methylpentanes
Monopropylamine
Pentenes iso
Petroleum spirit
Propionaldehyde
Propylene oxide
Tetrahydrofuran
Vinylidene chloride

The intermediate flashpoint group consists of materials having a flashpoint from −18°C (0°F) to 23°C (73°F),which are regarded as presenting medium danger. Following are some substances in this group:

Acrylonitrile
Alkylamines
Allyl alcohol
Allyl formate
Allyl ethyl ether
Allyl bromide
Amyl acetates
Amyl amine
Benzene
Benzotrifluoride
2-Bromobutane
Bromopropanes
Butanedione
Butyl methyl ether
Butyl isocyanate
Butyl acetates
Butyraldehyde
Chloromethyl ethyl ether
Chloroprene
Cycloheptane
Cyclohexene
Diallylether
Diethyl ketone
Diethyl sulfide
Dioxane
Dipropylamine
Ethanol
Ethyl methyl ketone
Ethyl butyl ether
Ethyl acetate
Ethylbenzene
Heptanes
Methanol
Methyl propyl ketone
1-Methylpiperidine
Naphtha, petroleum
Propanol
Pyrrolidine
Toluene
Xylenes

The high flashpoint group consists of substances having a flashpoint from 23°C (73°F) to 61°C (141°F), which are regarded as presenting minor danger. Following are some substances in this group:

Amyl acetates
Amyl nitrate
Amyl butyrates
Anisole
Bromobenzene
Bromopropanes
Butanol
isoButyric acid
Chlorobenzene
Dibromobenzene
Diethylbenzene
Ethyl butyrate
Ethyl amyl ketone
Formalin
Furfural
Hydrazine
Nitroethane
2,4-Pentanedione
Turpentine

Substances having a flashpoint above 61°C (141°F) are not considered to present a fire hazard, according to this classification scheme.

The flashpoint is not the sole measure of the degree of hazard. Substances with low boiling points will evaporate to form combustible atmospheres so that the hazard is enhanced. Substances with high viscosity do not flow easily, so the hazard is less.

TOXIC AND CORROSIVE HAZARDS

Some common toxic solvents or reactants are:

Aniline
Benzonitrile
Carbon tetrachloride
Chloroform
Chloropicrin
Dichlorobenzenes
Dinitrobenzenes
Dinitrotoluenes
Epichlorohydrin
Ethylene dibromide
Hexachlorobenzene
Nitroanilines
Nitrobenzene
Nitrotoluenes
Tetrachloroethylene
Toluidines
Xylidines

Some corrosive solvents or reagents are:

Acetic anhydride
Acetic acid (50% to 80% concentration)
Acetic acid, glacial
Acrylic acid
Alkylamines
Benzoyl chloride
Benzyl bromide
Di-n-butylamine
Diethylenetriamine
Ethanolamine
2-Ethylhexylamine
1-Pentol
Tributylamine

Again, warnings of these hazards should be available on safety labels and Material Safety Data Sheets.

HEALTH HAZARDS POSED BY SOLVENTS

Various solvents can present any of the heath hazards specifically identified in the OSHA standard—carcinogens, corrosives, highly toxic substances, irritants, sensitizers, toxic substances, and substances having target-organ effects. A substance posing one of these health hazards should have a health-hazard warning label, and information should also be available on a Material Safety Data Sheet.

Solvents should be used with adequate ventilation, because almost all organic solvents if inhaled will have an anesthetic effect, leading to wooziness and sleepiness or unconsciousness. Prolonged exposure, which could occur if an unconscious person remained in an atmosphere polluted by solvent fumes, could lead to death.

Skin exposure to solvents should be avoided as a matter of common sense. Solvents can remove protective oils in the skin, and some of them can even penetrate the skin. Many solvents can cause systemic or target-organ damage (particularly to the liver and blood-forming organs). Even if the substance is not corrosive or toxic, chemical exposure is to be avoided.

Chemical

Toxicity

&

First Aid

HASKELL LABORATORY TOXICITY CLASSIFICATIONS

	Acute Oral LD 50 (rats) (mg/kg)	Examples	Probable Lethal Dose For 70 kg Man (150 lb)
Extremely Toxic	< 5	Sodium cyanide, parathion	A taste (less than 7 drops)
Highly Toxic	5-50	Acrolein, propionitrile and Class B Poisons	Between 7 drops and 1 teaspoonful
Moderately Toxic	50-500	DDT	Between 1 teaspoon and 1 ounce
Slightly Toxic	500-5000	Aspirin, sodium chloride	Between 1 ounce and 1 pint (or 1 lb)
Very Low Toxicity	> 5000	Sugar	More than 1 pint (1 lb)

	Acute Vapor Inhalation, Not for Dusts or Aerosols 4-hour LC50 (rats) Atmospheric Concentration*		
	ppm	mg/l	
Extremely Toxic	<10	< 0.08	Perfluoroisobutylene (PFIB), acrolein
Highly Toxic	10-100	0.08-0.8	Nitrogen dioxide
Moderately Toxic	100-1000	0.8-8.0	HF, chlorine, sulfur dioxide
Slightly Toxic	1000-5000	8.0-40	CO
Very Low Toxicity	>5000	>40	Freon® 12 (Dichlorodifluoromethane)

	Acute Skin Absorption LD50 (rabbits) (mg/kg)		
Extremely Toxic	< 10	Tetraethylpyrophosphate	A few drops
Highly Toxic	10-200	Acrylonitrile, Class B Poisons	Between a few drops and 1 ounce
Moderately Toxic	200-5000	Sodium laurylsulfate	Between 1 ounce and 1 pint (or 1 lb)
Slightly Toxic	5000-10,000	Dimethyl formamide	Between 1 pint and 1 quart (or 2 lb)
Very Low Toxicity	>10,000	Isopropyl alcohol, ethylene glycol, trichlorethylene, acetone	More than 1 quart (2 lb)

	Aquatic Toxicity 96-hour LC50 (mg/l)	
Extremely Toxic	< 0.5	Pentachlorophenol, DDT
Highly Toxic	0.5-1	Chlordane
Moderately Toxic	1-50	Phenol, formaldehyde, benzene
Slightly Toxic	50-500	Sodium hydroxide, acetic acid
Low Toxicity	500-5000	Adiponitrile
Very Low Toxicity	> 5000	Ethyl alcohol

*Based on a chemical with molecular weight of 200.

CHAPTER XIII

MODIFICATION OF PELs FOR PROLONGED EXPOSURE PERIODS

A. Purpose and Scope. The 1968 ACGIH Threshold Limit Values (TLVs) adopted by OSHA as permissible exposure limits (PELs) are directly related to assumed conventional exposure periods of no more than 8 hours/day, 40 hours/week.

1. The 8-hour exposure limits for some substances may not provide appropriate protection from health hazards when novel work schedules are utilized; e.g., exposures longer than 8 hours/day, four 10-hour days/week, six 7-hour days/week, etc. This chapter identifies those PELs which may inadequately protect workers for prolonged exposure periods and describes how an "adjusted PEL" may be calculated.

2. Instructions on sampling and citation procedures shall be sought from the Assistant Regional Administrator (ARA) for Technical Support who shall in turn contact the Directorate of Technical Support.

B. Procedure.

1. Each substance listed in the Substance Toxicity Table in Chapter II has been assigned to one of the six "Work Schedule" categories described in Figure XIII-1 on the basis of the 1968 Documentation of TLVs published by ACGIH.

2. During a health inspection, the Industrial Hygienist has the responsibility of documenting any work schedules resulting in excessive exposures to a hazardous substance caused by exposure periods longer than 8 hours/day or 40 hours/week. This would include routine overtime shifts.

3. The Industrial Hygienist should determine an "adjusted PEL" as necessary for each hazardous substance sampled, according to the specifications given for the category to which it is assigned.

4. No adjustment should be made to the PELs of substances in category 1. For all other categories, the equivalent PELs should be calculated according to the methods described in paragraphs C.1 through 6 and used as a professional guide or in the evaluation of actual employee risk.

5. In all situations, the equivalent PEL will be equal to or lower (i.e. more restrictive) than the PEL values listed in 29 CFR 1910.1000.

6. The Industrial Hygienist should also elicit from the employees and document any symptomatology that may be related to the exposure.

C. Work Schedule Categories.

1. Category 1A. Ceiling Limit Standards. Substances in this category (e.g., butylamine) have ceiling limit standards which were intended never to be exceeded at any time, and so, are independent of the length or frequency of work shifts. The ceiling PELs for substances in this category should not be adjusted.

2. Category 1B. Standards Preventing Mild Irritation. Substances in this category have a PEL designed primarily to prevent acute irritation or discomfort (e.g., cyclopentadiene). There are essentially no known cumulative effects resulting from exposures for extended periods of time at concentration levels near the PEL. The PELs for substances in this category should not be adjusted.

3. Category 1C. Standards Limited by Technologic Feasibility. The PELs of substances assigned to this category have been set either by technologic feasibility (e.g., vinyl chloride) or good hygiene practices (e.g., methyl acetylene). These factors are independent of the length or frequency of work shifts. The PELs for substances in this category should not be adjusted.

4. Category 2. Acute Toxicity Standards.

a. The substances in this category have PELs which prevent excessive accumulation of the substance in the body during 8 hours of exposure in any given day (e.g., carbon monoxide).

b. The following equation determines a level which ensures that employees exposed more than 8 hours/day will not receive a dosage (i.e. length of exposure X concentration) in excess of that intended by the standard.

$$\text{Equivalent PEL} = \text{8-hour PEL} \times \frac{8 \text{ hours}}{\text{hours of exposure in one day}} \qquad \text{(Equation XIII-1)}$$

c. The Industrial Hygienist should normally conduct sampling for the entire shift minus no more than one hour for equipment set-up and retrieval (e.g., at least 9 hours of a 10-hour shift). In situations where an employee works multiple shifts in a day (e.g., two 7-hour shifts), and the Industrial Hygienist can document sufficient cause to expect exposure concentrations to be similar during the other shifts, the sampling should be done during only one shift.

5. Category 3. Cumulative Toxicity Standards

a. Substances assigned to this category present cumulative hazards (e.g., lead, mercury, etc.). The PELs for these substances are designed to prevent excessive accumulation in the body resulting from many days or even years of exposure.

b. The following equation ensures that workers exposed more than 40 hours/week will not receive a dosage in excess of that intended by the standard.

$$\text{Equivalent PEL} = \text{8-hour PEL} \times \frac{40 \text{ hours}}{\text{hours of exposure in one week}} \qquad \text{(Equation XIII-2)}$$

c. It is the responsibility of the Industrial Hygienist to conduct sufficient sampling to document exposure levels for the entire week when evaluating conditions on the basis of this equivalent PEL. For most operations the Industrial Hygienist will be able to sample during one shift only and then document sufficient cause to predict exposure concentrations during the other shifts.

6. Category 4. Acute and Cumulative Toxicity Standards. Substances in this category may present both an acute and a cumulative hazard. For this reason, the PELs of these substances should be adjusted by either equation XIII-1 or XIII-2; i.e. whichever provides the greatest protection.

7. Refined Adjustment Equations for Specific Standards. The adjustment equation presented for categories 2 and 3 reflect an oversimplification of the actual accumulation and removal of a toxic agent from the body. Additional research, however, is needed in order to apply more complex equations to estimate resulting body burden and health risk due to prolonged exposure periods. This chapter will be updated when the necessary data become available. Industrial Hygienists having sufficient data to validate adjusting PELs by a more rigorous method such as those proposed in the following articles are encouraged to do so following approval from the ARA for Technical Support:

Brief, R.S. and R.A. Scala, "Occupational Exposure Limits for Novel Schedules," Amer. Ind. Hyg. Assn. Jour. 36:467, 1975.

Roach, S.A., "A More Rational Basis for Air Sampling Programmes," Ann. Occup. Hyg. 20:65, 1977.

Hickey, J.L.S. and P.C. Reist, "Application of Occupational Exposure Limits to Unusual Work Schedules," Amer. Ind. Hyg. Assn. Jour. 38:613, 1977.

FIGURE XIII-1

Summary of Work Schedule Categories

Work Schedule Category	Principle Group Characteristic	Conditions Resulting In Adjustment	Adjustment Formula
1A	Ceiling limit standards	None	None
1B	Irritants	None	None
1C	Technologic limitations	None	None
2	Acute toxicity only	Exposed greater than 8 hours/day	Adj. PEL = PEL X 8 hours/ hours exposed/day
3	Cumulative toxicity only	Exposed greater than 40 hours/week	Adj. PEL = PEL X 40 hours/ hours exposed/week
4	Both acute and cumulative toxicity	Exposed greater than 8 hours/day and/or exposed greater than 40 hours/week	The equation for category 2 or 3, whichever results in the greatest protection