# CHAPTER 10

# Corrosives

Corrosives are the largest class of chemicals used by industry, so it stands to reason that they would frequently be encountered in transportation and at fixed facilities. DOT Class 8 materials are corrosive liquids and solids. There are no DOT subclasses of corrosives. There are, however, two types of corrosive materials found in Class 8: acids and bases. Acids and bases are actually two different types of chemicals that are sometimes used to neutralize each other in a spill. They are grouped together in Class 8 because the corrosive effects are much the same on tissue and metals, if contacted. It should be noted, however, that the correct terminology for an acid is *corrosive* and for a base is *caustic.* DOT, however, does not differentiate between the two when placarding and labeling. The DOT definition for a corrosive material is "a liquid or solid that causes visible destruction or irreversible alterations in human skin tissue at the site of contact, or a liquid that has a severe corrosion rate on steel or aluminum. This corrosive rate on steel and aluminum is 0.246 inches per year at a test temperature of 131ºF."

A definition for an acid from the *Condensed Chemical Dictionary* is "a large class of chemical substances whose water solutions have one or more of the following properties: sour taste, ability to make litmus dye turn red and to cause other indicator dyes to change to characteristic colors, the ability to react with and dissolve certain metals to form salts, and the ability to react with bases or alkalis to form salts." It is important to note here that tasting any chemical is not an acceptable means of identification for obvious reasons.

In addition to being corrosive, acids and bases can explode or polymerize; they can also be water-reactive, toxic, flammable (applies to organic acids only, because inorganic acids do not burn), reactive, and unstable oxidizers.

There are two basic types of acid: organic and inorganic (see Figure 10.1). Inorganic acids are sometimes referred to as mineral acids. As a group, organic acids are generally not as strong as inorganic acids. The main difference between the two is the presence of carbon in the compound: inorganic acids do not contain carbon. Inorganic acids are corrosive, but they do not burn. They may, however, be oxidizers and support combustion, or may spontaneously combust with organic material.

**Types of Acids**

| Inorganic | Organic |
|---|---|
| Sulfuric $H_2SO_4$ | Formic HCOOH |
| Hydrochloric HCl | Acetic $C_2H_5COOH$ |
| Nitric $HNO_3$ | Propionic $C_2H_5COOH$ |
| Phosphoric $HPO_4$ | Acrylic $C_2H_3COOH$ |
| Perchloric $HClO_4$ | Butyric $C_3H_7COOH$ |

**Figure 10.1**

Inorganic-acid molecular formulas begin with hydrogen (H). For example, $H_2SO_4$ is the molecular formula for sulfuric acid, HCl is hydrochloric acid, and $HNO_3$ is nitric acid. Organic acids are hydrocarbon derivatives, therefore, they have carbon in the compound, and the name begins with the prefix indicating the number of carbons. For example, the prefix for a one-carbon compound with the organic acids is "form," so a one-carbon acid is called formic acid; a two-carbon acid is acetic acid; a three-carbon acid is propionic acid, etc. Organic acids are corrosive, may polymerize, and may burn.

## INORGANIC ACIDS

Acids are materials that release hydrogen ions, $H^+$, when placed in water. Inorganic acids can generally be identified by hydrogen at the beginning of the formula (see Figure 10.2), because few other compounds begin with hydrogen. The hydrogen ion, $H^+$, consists of just a hydrogen nucleus, without electrons, and is composed of just one proton. Acids that supply just one $H^+$ are often referred to as monoprotic acids, e.g., HCl and $HNO_3$. Acids that supply more than one $H^+$ are referred to as polyprotic acids; more specifically, $H_2CO_3$ and $H_2SO_4$ are referred to as diprotic acids and $H_3PO_4$ as triprotic acids.

There are two general types of inorganic acids: binary and oxyacids. Binary acids are composed of just two elements: hydrogen and some other nonmetal, e.g., HCl and $H_2S$. These acids are named by placing the prefix "hydro" before and the suffix "ic" after the nonmetal element; the compound ends with the word "acid." For example, when hydrogen is combined with chlorine, the "ine" is dropped from

**Inorganic Acids Begin with Hydrogen in Formula**

| Binary Acids | Oxy Acids |
|---|---|
| Hydrofluoric HF | Nitric $HNO_3$ |
| Hydrochloric HCl | Perchloric $HClO_4$ |
| Hydrobromic HBr | Sulfuric $H_2SO_4$ |
| Hydrodic HI | Phosphoric $H_3PO_4$ |
| Hydrosulfuric $H_2S$ | Carbonic $H_2CO_3$ |

**Figure 10.2**

chlorine and the prefix “hydro” and suffix “ic” are added: hydrochloric acid; hydrogen combined with sulfur is called hydrosulfuric acid.

Acids that contain hydrogen, oxygen, and some other nonmetal element are called oxyacids, e.g., $H_2SO_4$, $HNO_3$, and $HClO_4$ (note the similarities to the oxyradicals). Like the oxysalts, these acids are named according to the number of oxygen atoms in the compound. The acid with the largest number of oxygen atoms in a series ends with the suffix “ic,” and the one with the fewest number of oxygen atoms takes the suffix “ous” (similar to the alternate naming of the transitional metal salts discussed in Chapter 2).

For example, when hydrogen is combined with sulfur, the base state of the compound is $SO_4$ and the acid, $H_2SO_4$, is called sulfur*ic* acid. If there is one less oxygen present in the compound, such as $SO_3$, the ending changes to “ous” and the acid, $H_2SO_3$, is called sulfur*ous* acid. $HNO_3$ is nitric acid, $HNO_2$ is nitrous acid, etc. When halogens are present in the acid, the compound with the most oxygen atoms in the base state ends in “ic,” such as chloric acid, $HClO_3$. If the oxygen is increased by one to $HClO_4$, the prefix “per” is added, yielding the name *per*chlor*ic* acid. The acid compound with the least number of oxygen atoms ends with “ous,” such as chlorous acid, $HClO_2$. If the oxygen is reduced by one, to HClO, the prefix “hypo” is added, yielding the name *hypo*chlor*ous* acid.

## STRENGTH AND CONCENTRATION

Most inorganic acids are produced by dissolving a gas or liquid in water, e.g., hydrochloric acid is derived from dissolving hydrogen chloride gas in water. All acids contain hydrogen. This hydrogen is the form of an ion ($H^+$) and can be measured by using the pH scale (see Figure 10.3). In simple terms, the pH scale measures the hydrogen-ion concentration of a solution. Concentrated acids and bases measure off the pH scale. The pH scale only measures acids and bases in solutions.

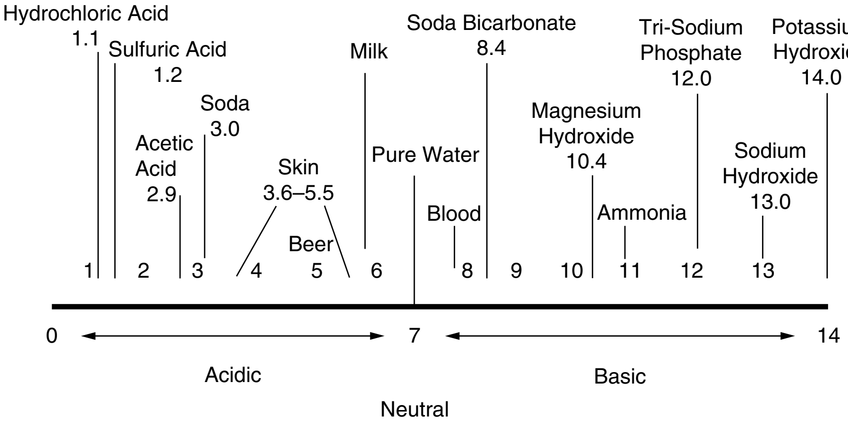


**Figure 10.3**

**Ionization of Common Acids and Bases**

| Completely Ionized | Moderately Ionized | Slightly Ionized |
|---|---|---|
| Nitric | Oxalic | Hydrofluoric |
| Hydrochloric | Phosphoric | Acetic |
| Sulfuric | Sulfurous | Carbonic |
| Hydriodic | | Hydrosulfuric |
| Hydrobromic | | (Most others) |
| Potassium hydroxide | | Ammonium hydroxide |
| Sodium hydroxide | | (All others) |
| Barium hydroxide | | |
| Strontium hydroxide | | |
| Calcium hydroxide | | |

**Figure 10.4**

To determine if a concentrated material is an acid or a base, litmus paper is used; however, this does not yield a numerical value. As a group, acids have high hydrogen-ion concentrations. Bases have low hydrogen ion concentrations and high hydroxyl ($OH^-$) concentrations. The strength or weakness of an acid or base is the amount of hydrogen ions or hydroxyl ions that are produced as the acid or base is created. If the hydrogen ion concentration of an acid is high, the acid is concentrated. If the hydroxyl concentration is high, it is a concentrated base. In both cases, there is almost total ionization of the material dissolved in water to make the strong acid and base (see Figure 10.4). For example, hydrochloric acid is a strong acid because practically all of the hydrogen chloride gas is ionized in the water. Acetic acid is a weak acid because only a few molecules ionize in producing the acid.

Another term associated with corrosives is *concentration.* Concentration has to do with the amount of acid that is mixed with water and is often expressed in terms of percentages. A 98% concentration of sulfuric acid is 98% sulfuric acid and 2% water; a solution of 50% nitric acid is 50% nitric acid and 50% water. In the 50% concentration, the solution has only half the $H^+$ ions that the 100% concentration would have. A 50% concentration of nitric acid is a solution diluted to 50% of the original acid.

## PH

The pH scale measures the acidity or alkalinity of a *solution*. The pH scale cannot measure some strong acids and bases that are full strength because they have values less than 0 or greater than 14. They would be off the scale. Acid solutions are considered acidic, and base solutions are considered alkaline. Acid solutions have a value on the pH scale from 1 to 6.9. Materials with a pH value of 7 are considered to be neutral, i.e., they are neither acidic nor basic. Base solutions have values on the scale from 7.1 to 14. It is not important for emergency responders to understand or know how the pH scale measures corrosivity or the specific values of any given acid or base. It is, however, important for responders to know that numerical values lower than 7 are acids and values higher than 7 are bases.

**Exponential Logarithm of pH Values**

| pH Value | $H^+$ and $OH^-$ Concentration |
|---|---|
| 1 | 1,000,000 |
| 2 | 100,000 |
| 3 | 10,000 |
| 4 | 1,000 |
| 5 | 100 |
| 6 | 10 |
| 7 | 1 |
| 8 | 10 |
| 9 | 100 |
| 10 | 1,000 |
| 11 | 10,000 |
| 12 | 100,000 |
| 13 | 1,000,000 |

**Figure 10.5**

Usually, when dealing with numerical values, the higher the number, the greater the value that is being measured, and the number 2 is twice the value of 1. When using the pH scale for acids, however, the lower the pH number, the more acidic an acid solution is, and an acid solution with a pH of 1 is 10 times more acidic than an acid solution with a pH of 2, and so on (see Figure 10.5). The ratio and the intervals between the numbers are exponential, e.g., a pH of 5 is 10 times more acidic than a pH of 6, etc. The result of this exponential ratio is that on the full scale, a solution with a pH of 1 is 1,000,000 times more acidic than an acid with a pH of 6.9. So the difference between individual values on the pH scale is great and is one of the reasons why dilution and neutralization are not as simple as they might sound. Those terms will be discussed further under the section Dilution vs. Neutralization.

If the chemical name of a hazardous material is known and it is determined to be a corrosive, looking up the chemical name in reference sources will identify whether the material is an acid or a base. It will not be necessary for responders to get a pH measurement of the material unless it is to verify the reference information. The use of pH measurements can be useful when a material has not been positively identified. The pH measurement can be used to narrow the chemical-family possibilities in the identification process.

There are a number of ways for emergency responders to measure the pH of a corrosive material. First of all, the proper chemical protective clothing must be worn when working around corrosive materials. The simplest and least expensive method of determining pH is the use of pH paper, which changes color based on the type and strength of corrosive material that is present. The colored paper is then compared to a chart on the pH paper container. The chart indicates numerical pH values much the same way as do expensive measuring instruments. Although not as accurate as a pH meter, the numbers will give a "ballpark" measure of the pH of the material.

There are also commercially available pH meters, from handheld to sophisticated laboratory instruments. This equipment can be expensive, and pH paper is accurate enough for emergency response identification purposes. If the only information needed is whether a material is an acid or a base, litmus paper can also be used. Litmus paper turns blue if the corrosive material is a base, red if the corrosive material is an acid. The litmus paper will not give actual pH numerical values.

The definition of a base from the *Condensed Chemical Dictionary* is "a large class of compounds with one or more of the following properties: bitter taste, slippery feeling in solution, ability to turn litmus blue and to cause other indicators to take on characteristic colors, and the ability to react with (neutralize) acids to form salts." It is important to note that while the definition of acid and base mentions the taste and feeling of the materials, these are dangerous chemicals and can cause damage to tissues upon contact. Therefore, it is ***NOT*** recommended that responders come in contact with these materials through taste or touch!

Ionization occurs with the bases, just as with the acids, as they are made. Most bases are produced by dissolving a solid, usually a salt, in water. However, with the bases, the ion produced is the hydroxyl ion ($OH^-$). The base is considered strong or weak depending on the number of hydroxyl ions produced as a corrosive material is dissolved in water. A large $OH^-$ concentration produces a strong base; a small $OH^-$ concentration produces a weak base. Sodium and potassium hydroxide are strong bases; calcium hydroxide (hydrated lime) is a weak base. Bases will have a pH from 7.1 to 14 on the pH scale. The degree of alkalinity increases from 7.1 to 14, with 7.1 being the least basic and 14 the most basic. The amount of alkalinity between the numerical values on the pH scale is exponential, just as with the acids. A base with a pH of 9 is 10 times more basic than one with a pH of 8, and so on.

Corrosivity is not the only hazard of Class 8 materials. In addition to being corrosive, they may have other hazards, such as toxicity, flammability, or oxidation. Many corrosives, especially acids, can be violently water-reactive. Contact with water may cause splattering of the corrosive, produce toxic vapors, and evolve heat that may ignite nearby combustible materials. Some of the water may be turned to steam by the heat produced in the reaction. This can cause overpressurization of the container. Many corrosives may also be unstable, reactive, may explode, polymerize, or decompose and produce poisons.

**Picric acid**, **$C_6H_2(NO_2)_3OH$**, for example, becomes a high explosive when dried out and is sensitive to shock and heat. The hazard class for picric acid is 4.1 Flammable Solid. It is considered a wetted explosive. The name would indicate acid, however, the corrosivity of picric acid is far outweighed by its explosive dangers. The slightest movement of dry picric acid may cause an explosion. Picric acid, when shipped, is mixed with 12 to 20% water to keep it stable. When this water evaporates in storage over time, the material becomes explosive.

**Perchloric acid**, **$HClO_4$**, is a colorless, volatile, fuming liquid that is unstable in its concentrated form. It is a strong oxidizing agent and will spontaneously ignite upon contact with organic materials. It is corrosive, with the highest concentration of 70%. Contact with water produces heat; when shocked or heated, it may detonate. The boiling point is 66°F, and it is soluble in water, with a specific gravity of 1.77, which is heavier than water. The vapor density is 3.46, which is heavier than air. Perchloric acid is toxic by ingestion and inhalation. It is used in the manufacture of explosives and esters; in electropolishing and analytical chemistry; and as a catalyst.

**Hydrocyanic acid**, **HCN**, is corrosive in addition to toxic. It is also a dangerous fire and explosion risk. It has a wide flammable range of 6 to 41% in air. The boiling point is 79°F, the flash point is 0°F, and the ignition temperature is 1004°F. It is toxic by inhalation, ingestion, and through skin absorption. The TLV of hydrocyanic acid is 10 ppm in air. It is used in the manufacture of acrylonitrile, acrylates, cyanide salts, dyes, rodenticides, and other pesticides.

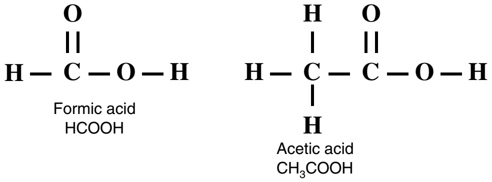
## ORGANIC ACIDS

Organic acids are hydrocarbon derivatives. They are flammable, corrosive, and may polymerize by exposure to heat or sudden shock. Organic acids are "super-duper" polar materials; they are the most polar of the hydrocarbon derivatives. Organic acids have hydrogen bonding and a carbonyl that gives them a double dose of polarity. The functional group is represented by a carbon atom, two oxygen atoms, and a hydrogen atom. The general formula is **R-C-O-O-H**. One radical is attached to the carbon atom of the functional group.

Organic acids use the alternate prefix for one- and two-carbon compounds. When naming them, all of the carbons, including the one in the functional group, are counted to determine the hydrocarbon prefix name. To represent an acid, "ic" is added to the hydrocarbon prefix and the name ends in "acid," e.g., a one-carbon acid uses the alternate prefix name "form"; "ic" is added to "form," making it formic, and "acid" is added to the end: formic acid. A two-carbon acid uses the alternate name for two carbons, which is "acet," plus "ic," and ends with "acid": acetic acid. Naming three- and four-carbon acids reverts back to the normal prefixes for three- and four-carbon radicals, with some minor alterations to make the names flow more smoothly. For example, a three-carbon acid uses the prefix "prop," indicating three carbons; the letters "ion" are then added to make the name flow smoothly. The ending "ic" is added to the radical, and the word "acid" for the compound name: propionic acid. A four-carbon organic acid begins with the radical prefix "but"; the filler letters "yr" are attached; the radical ends with "ic"; acid is added, and the name for a four-carbon organic acid is butyric acid. Structures and molecular formulas for organic acids with one through four carbons are shown in Figure 10.6. Note that the carbon in the functional group is counted when determining which hydrocarbon radical is used in naming it.

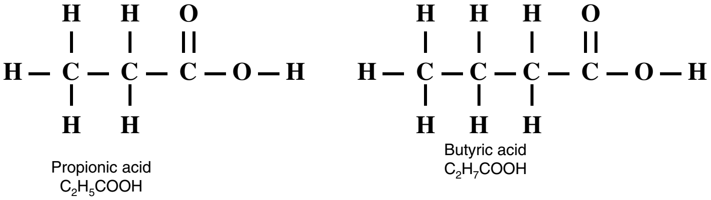
It is also possible to add double-bonded radicals to the organic-acid functional group. For example, when the vinyl radical is attached to the carbon atom in the functional group, a three-carbon, double-bonded radical is created. The acryl radical is used for three carbons with a double bond; the ending "ic" is added to the radical, and the word "acid" is added to the end. The compound formed is acrylic acid. The double bond between the carbons can come apart in a polymerization reaction. Generally, materials that have double bonds are reactive in some manner. If polymerization occurs inside a container, an explosion may occur that can produce heat, light, fragments, and a shock wave.

**Formic acid**, **HCOOH**, is a colorless, fuming liquid with a penetrating odor. The highest commercial concentration is 90%. Formic acid, as well as all organic



Formic acid
$HCOOH$

Acetic acid
$CH_3COOH$



Propionic acid
$C_2H_5COOH$

Butyric acid
$C_2H_7COOH$

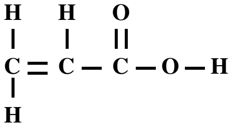
Figure 10.6

acids, are polar materials that are soluble in water, and it has a specific gravity of 1.2, which is heavier than water. As with many of the organic acids, formic acid is flammable. The boiling point is 213°F, the flash point is 156°F, and the flammable range is 18 to 57%. The ignition temperature is 1004°F, and the vapor density is 1.6, which is heavier than air. Formic acid is toxic, with a TLV of 5 ppm in air. The four-digit UN identification number is 1779. The NFPA 704 designation is health 3, flammability 2, and reactivity 0. It is used in the dyeing and finishing of textiles, the treatment of leather, and the manufacture of esters, fumigants, insecticides, refrigerants, etc.

**Propionic acid**, **$C_2H_5COOH$**, is a colorless, oily liquid with a rancid odor. It is a polar compound and soluble in water. Propionic acid is flammable, with a flammable range of 2.9 to 12% in air, a boiling point of 286°F, a flash point of 126°F, and an ignition temperature of 955°F. Polar-solvent foam will have to be used to extinguish fires. It is toxic, with a TLV of 10 ppm in air. The four-digit UN identification number for propionic acid is 1848. The NFPA 704 designation is health 3, flammability 2, and reactivity 0. It is used as a mold inhibitor in bread and as a fungicide, an herbicide, a preservative for grains, in artificial fruit flavors, pharmaceuticals, and others.

**Butyric acid,** also known as butanoic acid, is a colorless liquid with a penetrating, obnoxious odor. It is miscible in water, with a specific gravity of 0.96, which makes it slightly lighter than water. Butyric acid is flammable, with a boiling point of 326°F and a flash point of 161°F. The flammable range is 2 to 10% in air, and the ignition temperature is 846°F. Butyric acid is a strong irritant to skin and eyes. The four-digit UN identification number is 2820. The NFPA 704 designation is health 3, flammability 2, and reactivity 0. The primary uses of butyric acid are in the manufacture of perfume, flavorings, pharmaceuticals, and disinfectants.

**Acrylic acid**, **$C_2H_3COOH$**, is a colorless liquid with an acrid odor. It polymerizes readily and may undergo explosive polymerization. The boiling point is 509°F, the flash point is 122°F, and the ignition temperature is 820°F. The flammable range is



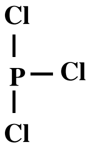
Acrylic acid
$C_2H_3COOH$

**Figure 10.7**

2.4 to 8% in air. Acrylic acid is miscible with water and has a specific gravity of 1.1, which is slightly heavier than water. The vapor density is 2.5, which is heavier than air. It is an irritant and corrosive to the skin, with a TLV of 2 ppm in air. The four-digit UN identification number is 2218. Acrylic acid must be inhibited when transported. The NFPA 704 designation is health 3, flammability 2, and reactivity 2. The primary uses are as a monomer for polyacrylic and polymethacrylic acids and other acrylic polymers. The structure and molecular formula for acrylic acid are shown in Figure 10.7.

**Phosphorus trichloride**, **$PCl_3$**, is a clear, colorless, fuming, corrosive liquid. It decomposes rapidly in moist air and has a boiling point of about 168°F. $PCl_3$ is corrosive to skin and tissue and reacts with water to form hydrochloric acid. The TLV is 0.2 ppm, and the IDLH is 50 ppm in air. The four-digit UN identification number is 1809. The NFPA 704 designation is health 4, flammability 0, and reactivity 2. The white section at the bottom of the diamond contains a W with a slash through it, indicating water reactivity. The primary uses are in the manufacture of organophosphate pesticides, gasoline additives, and dyestuffs; as a chlorinating agent; as a catalyst; and in textile finishing.

Corrosives in contact with a poison may produce poison gases as the poison decomposes. In responding to an incident involving corrosives, the toxicity of the vapors could be much more of a concern for personnel than the corrosivity. When acids come in contact with cyanide, hydrogen cyanide gas, which is highly toxic, with a TLV of 10 ppm in air, is produced. The structure and molecular formula of phosphorous trichloride are shown in Figure 10.8.



Phosphorus trichloride
$PCl_3$

**Figure 10.8**

When strong corrosives contact flammable liquids, the chemical reaction that occurs may produce heat. The heat produced will cause more vapor to be produced and, if an ignition source is present, combustion may occur. Corrosives may also be strong oxidizers. If they come in contact with particulate combustible solids, spontaneous combustion may occur. Once ignition has occurred, the corrosive will act as an oxidizer and accelerate the rate of combustion. Nitric acid in contact with combustible organic materials containing cellulose will produce a chemical reaction. This reaction will produce nitrocellulose, which is a dangerous fire and explosion risk. Toxic vapors may also be produced when the cellulose burns. After flammable liquids and gases, corrosives are the next most-common hazardous material encountered by emergency responders.

**Sulfuric acid**, **$H_2SO_4$**, is a strong corrosive, with a solution pH of 1.2. It is a dense, oily liquid, colorless to dark brown, depending on purity. Sulfuric acid is miscible in water, but violently water-reactive, producing heat and explosive splattering if water is added to the acid. The boiling point is 626ºF, and the specific gravity is 1.84, which is heavier than water. Sulfuric acid is highly reactive and dissolves most metals. When in contact with metals, hydrogen gas is released. The vapors are toxic by inhalation, and the TLV is 1 ppm in air. Sulfuric acid is incompatible with potassium chlorate, potassium perchlorate, potassium permanganate, and similar compounds of other light metals. Sulfuric acid has a four-digit UN identification number of 1830. The NFPA 704 designation is health 3, flammability 0, and reactivity 2. The white section contains a W with a slash through it, indicating water reactivity. Sulfuric acid is used in batteries for cars and other vehicles. It is also used in the manufacture of fertilizers, chemicals, and dyes; as an etchant and a catalyst; in electroplating baths and explosives; in or for pigments; and many other uses.

Bulk container of sulfuric acid.

Railcar with liquid sulfuric acid.

**Fuming sulfuric acid** is also called oleum, which is a trade name. Fuming sulfuric acid is a solution of sulfur trioxide in sulfuric acid. Sulfur trioxide is forced into solution with sulfuric acid to the point that the solution cannot hold any more. As soon as the solution is exposed to air, the fuming begins, forming dense vapor clouds. It is violently water-reactive, as are most acids. The four-digit UN identification number is 1831.

**Lime**, **CaO** (also known as calcium oxide, quicklime, hydrated lime, and hydraulic lime), a binary oxide salt, is a white or grayish-white material in the form of hard clumps. It may have a yellowish or brownish tint due to the presence of iron. Lime is odorless and crumbles upon exposure to moist air. It is a corrosive caustic that yields heat and calcium hydroxide when mixed with water, and is a strong irritant, with a TLV of 2 mg/m$^3$ of air. The four-digit UN identification number for calcium oxide is 1910. The primary uses are in the manufacture of other chemicals, like calcium carbide; pH control; and in the neutralization of acid waste, insecticides, and fungicides.

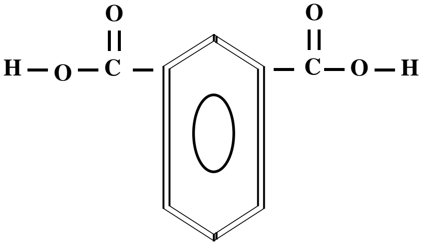
**Sodium hydroxide**, **NaOH**, also known as caustic soda, is a hydroxide salt. Sodium hydroxide is a strong base and is severely corrosive, with a solution pH of 13. It is the most important industrial caustic material. Sodium hydroxide is a white, deliquescent solid found in the form of beads or pellets. It is also found in solutions with water of 50 and 73%. Sodium hydroxide is water-soluble, water-reactive, and absorbs water and carbon dioxide from the air. The specific gravity is 2.8, which is heavier than water. It is corrosive to tissues in the presence of moisture and is a strong irritant to eyes, skin, mucous membranes, and is toxic by ingestion. The TLV ceiling is 2 mg/m$^3$ of air. The four-digit UN identification number is 1823 for dry materials and 1824 for solutions. The NFPA 704 designation is health 3, flammability 0, and reactivity 1. It is used in the manufacture of chemicals, as a neutralizer in petroleum refining, in metal etching, electroplating, and as a food additive.

Tank car of sodium hydroxide solution, a corrosive material.

**Phosphoric acid**, $\mathbf{H_3PO_4}$, is a colorless, odorless, sparkling liquid or crystalline solid, depending on concentration and temperature. Phosphoric acid has a boiling point of 410ºF; at 20ºC, the 50 and 75% concentrations are mobile liquids. The 85% concentration has a syrupy consistency, and the 100% acid is in the form of crystals. Phosphoric acid is water-soluble and absorbs oxygen readily, and the specific gravity is 1.89, which is heavier than water. It is toxic by ingestion and inhalation, and an irritant to the skin and eyes, with a TLV of 1 $mg/m^3$ of air. The four-digit UN identification number is 1805. The NFPA 704 designation is health 3, flammability 0, and reactivity 0. The primary use of phosphoric acid is in chemical analysis and as a reducing agent.

**Sodium carbonate**, $\mathbf{Na_2CO_3}$, also known as soda ash and sodium bicarbonate, is an oxysalt and is a base with a pH of 11.6. It is not particularly hazardous and is used to neutralize acid spills.

**Nitric acid**, $\mathbf{HNO_3}$, an inorganic acid, is a colorless, transparent, or yellowish, fuming, suffocating, corrosive liquid. Nitric acid will attack almost all metals. The yellow color results from the exposure of the nitric acid to light. Nitric acid is a strong oxidizer, is miscible in water, and has a specific gravity of 1.5, which is heavier than water. It may be found in solutions of 36, 38, 40, and 42, degrees B′e (specific gravity) and concentrations of 58, 63, and 95%. Nitric acid is a dangerous fire risk when in contact with organic materials. It is toxic by inhalation and is corrosive to tissue and mucous membranes. The TLV is 2 ppm in air. Nitric acid is incompatible with acetic acid, hydrogen sulfide, flammable liquids and gases, chromic acid, and aniline. The four-digit UN identification number for nitric acid at <40% concentration is 1760. The NFPA 704 designation for nitric acid at <40% concentration is health 3, flammability 0, and reactivity 0. There is not any information in the white area of the diamond for <40% concentrations. Below 40% concentration, nitric acid is not considered an oxidizer.



Terephthalic acid
TPA
$C_6H_4(COOH)_2$

**Figure 10.9**

The four-digit UN identification number for nitric acid at >40% is 2031. It is placarded as a Class 8 Corrosive; however, individual containers are labeled corrosive, oxidizer, and poison. The NFPA 704 designation for nitric acid at >40% concentration is health 4, flammability 0, and reactivity 0. The prefix "oxy" appears in the white section of the diamond. Nitric acid >40% concentration is an oxidizer.

Nitric acid is used in the manufacture of ammonium nitrate fertilizer and explosives, in steel etching, and in reprocessing spent nuclear fuel. There are two types of fuming nitric acid. **White fuming nitric acid** is concentrated with 97.5% nitric acid and less than 2% water. It is a colorless to pale-yellow liquid that fumes strongly. It is decomposed by heat and exposure to light and becomes red in color from nitrogen dioxide. **Red fuming nitric acid** contains more than 85% nitric acid, 6 to 15% nitrogen dioxide, and 5% water. The four-digit UN identification number for red fuming nitric acid is 2032. The NFPA 704 designation is health 4, flammability 0, and reactivity 1. The prefix "oxy" appears in the white section of the diamond. Red fuming nitric acid is considered an oxidizer. Both white and red fuming acids are toxic by inhalation, strong corrosives, and dangerous fire risks that may explode upon contact with reducing agents. They are used in the production of nitro compounds, rocket fuels, and as laboratory reagents.

**Terephthalic acid (TPA)**, **$C_6H_4(COOH)_2$**, is an organic acid. It is a white crystalline or powdered material that is insoluble in water. It undergoes sublimation above 572ºF. In addition to being corrosive, it is also combustible. The primary uses are in the production of polyester resins, fibers, and films; it is also an additive to poultry feeds. The structure and molecular formula for terephthalic acid are shown in Figure 10.9.

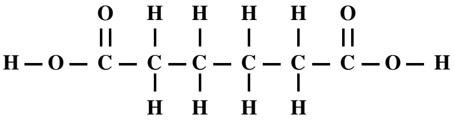
The naming of terephthalic acid does not follow any of the rules of naming organic acids under the trivial naming system. However, the formula and the structure indicate an organic compound and the name indicates acid. The hazards of the acids, except for flammability, are similar. The fact that the name indicates acid should lead you to assume flammability and toxicity, in addition to corrosiveness, until other information is known.

**Hydrochloric acid**, **HCl**, an inorganic acid, is a colorless or slightly yellow, fuming, pungent liquid produced by dissolving hydrogen chloride gas in water. Hydrochloric acid in solution has a pH of 1.1. The specific gravity is 1.19, which is heavier than water. It is water-soluble, a strong corrosive, and toxic by ingestion and inhalation. It is an irritant to the skin and eyes. The four-digit UN identification number is 1050 for anhydrous and 1789 for solution. Hydrochloric acid is used in food processing, pickling, and metal cleaning, as an alcohol denaturant, and as a laboratory reagent.

**Acetic acid**, **$CH_3COOH$**, an organic acid, also known as ethanoic acid and vinegar acid. Acetic acid is a clear, colorless, corrosive liquid with a pungent odor. In solution, acetic acid has a pH of 2.9. The glacial form is the pure form without water; it is 99.8% pure. Glacial acetic acid is a solid at normal temperatures. It is flammable, with a flash point of 110ºF and a flammable range of 4 to 19.9%. The ignition temperature is 800ºF. Acetic acid is "super-duper" polar and water-soluble. It will require polar-solvent type foam to extinguish fires. The specific gravity is 1.05, which is slightly heavier than water, but being miscible, it will mix rather than form layers. It is toxic by inhalation and ingestion, with a TLV of 10 ppm in air. Acetic acid is a strong irritant to skin and eyes. It is incompatible with nitric acid, peroxides, permanganates, ethylene glycol, hydroxyl compounds, perchloric acid, and chromic acid. The four-digit UN identification number is 2789. The NFPA 704 designation is health 3, flammability 2, and reactivity 0. It is a food additive at lower concentrations; it is used in the production of plastics, pharmaceuticals, dyes, insecticides, and photographic chemicals. The structure for acetic acid is shown in the Organic Acids section of this chapter.

**Caustic potash**, **KOH**, also known as potassium hydroxide and lye, is a hydroxide salt. It is found as a white solid in the form of pieces, lumps, sticks, pellets, or flakes. Potassium hydroxide may also be found as a liquid. It is water-soluble and may absorb water and carbon dioxide from the air. The specific gravity is 2.04,

Hydrofluoric acid in 55-gal drums.



Adipic acid
(Hexanedioic acid)
$COOH(CH_2)_4COOH$

**Figure 10.10**

which is heavier than water; however, it is miscible in water, so it will mix rather than form layers. It is a strong base and is toxic by ingestion and inhalation. The TLV ceiling is 2 mg/m$^3$ of air. The four-digit UN identification number is 1813 for the solid and 1814 for the solution. The NFPA 704 designation is health 3, flammability 0, and reactivity 1. It is used in soap manufacture, bleaching, as an electrolyte in alkaline storage batteries and some fuel cells, as an absorbent for carbon dioxide and hydrogen sulfide, and in fertilizers and herbicides.

**Adipic acid**, also known as hexanedioic acid, is an organic acid. It is a white, crystalline solid that is slightly soluble in water. In addition to being a corrosive, it is also flammable; however, it is a relatively stable compound. Adipic acid is used in the manufacture of nylon and polyurethane foams. It is also a food additive and adhesive. The structure and molecular formula are shown in Figure 10.10; notice that the structure has two organic-acid functional groups attached.

The naming of adipic acid does not follow any of the rules of naming organic acids under the trivial naming system. However, the formula and the structure indicate an organic acid, and the name indicates acid. The hazards of the acids, except for flammability, are similar. The fact that the name indicates acid should lead you to assume flammability and toxicity, in addition to corrosiveness, until other information is known.

## DILUTION VS. NEUTRALIZATION

Dilution and neutralization are often tactics considered when dealing with spills of corrosive materials. **Dilution** involves placing water into the acid to reduce the pH level. The addition of water to a corrosive can create a dangerous chemical reaction. Acids are highly water-reactive, creating vapors, heat, and splattering. With dilution, you must consider the exponential values of the numbers on the pH scale. Just moving the pH from 1 to 2 on the scale will take an enormous amount of water. Dilution may not be a practical approach for large spills. For example, if a 2000-gal spill of concentrated hydrochloric acid occurs, enough water to dilute the material to a pH of 6 would require the following efforts: one 1000-gpm pumper, pumping 24 hours a day, 7 days a week, 365 days a year, for 64 years. This would produce 1,440,000 gal of water per day! A large reservoir would be required to hold the water. As the process proceeds, it would become necessary to stir the mixture of water and acid to ensure uniformity in the dilution process. Dilution may work on small spills, but it will not work well on large spills.

**Neutralization** involves a chemical reaction that works well under laboratory conditions, using small amounts of acids and bases. However, in the field, facing a large spill of a corrosive material, neutralization may not be feasible. The neutralization reaction requires a large amount of neutralizing agent. For the same spill of 2000 gallons of concentrated hydrochloric acid mentioned in the previous example, it would require 8.7 tons of sodium bicarbonate, 5.5 tons of sodium carbonate, or 4.15 tons of sodium hydroxide to neutralize the spill. The latter would not be recommended, because sodium hydroxide is a strong base and would be dangerous to work with by itself without trying to add it to a concentrated acid. There would also be a need for a method to apply the neutralizing agent. The reaction that occurs will be a violent one, producing heat, vapor, and splattering of product. Neutralization may not work well for emergency responders at the scene of an incident with a large spill. The method of choice may turn out to be one of cleaning up the product by a hazardous waste contractor. They may use vacuum trucks; absorbent, gelling materials; or neutralization to accomplish the task.

The main danger of corrosive materials to responders is the contact of these materials with the body. Corrosive materials destroy living tissue. Destruction begins immediately upon contact. Many strong acids and bases will cause severe damage upon contact with the skin. Weaker corrosives may not cause noticeable damage for several hours after exposure. A chemical burn is nine times more damaging than a thermal burn. There are four basic methods of reducing the chemical action of corrosives on the skin: physical removal, neutralization, dilution, and flushing. Flushing is the method of choice. Removal of a corrosive material is difficult to accomplish and may leave a residue behind. Neutralization is a chemical reaction that may be violent and produce heat. This type of reaction on body tissues may cause more damage than it prevents. Neutralization should not be attempted on personnel wearing chemical suits, for the same reason as mentioned above. The layer of chemical protection is thin, and the heat from the neutralization may melt the suit and cause burns to the skin below the suit.

Dilution takes a large amount of water to lower the pH to a neutral position. While dilution may be similar to flushing, the intended outcome is different. With dilution, the goal is to reduce the pH number to as near neutral as possible. With flushing, the goal is to remove as much of the material as possible with a large volume of water.

Flushing should be started as soon as possible to reduce the amount of chemical damage and should continue for a minimum of 15 min. This also applies to the eyes. Most corrosives are highly water-soluble. Contact lenses should not be worn by personnel at HazMat incident scenes. Contact with acids can “weld” the contact to the eye, which almost always produces blindness. The person being treated may be in a great deal of pain and may have to be restrained during the flushing operation. Treatment after flushing involves standard first-aid for burns.

Corrosives are transported in MC/DOT 312/412 tanker trucks. These trucks have a small-diameter tank with heavy reinforcing rings around the circumference of the tank. The tank diameter is small because most corrosives are heavy. No other type of hazardous material is carried in this type of tanker. The 312/412 is a corrosives tanker regardless of how it is placarded. The placard may indicate a poison, an

MC/DOT 312/412 tanker for heavy corrosive materials.

oxidizer, or a flammable; but do not forget the “hidden hazard”: the tank identifies corrosives. Lighter corrosives may also be found in MC/DOT 307/407 tankers and may be placarded corrosive, flammable, poison, and oxidizer. Corrosives may also be found in tank cars, intermodal containers, and varying sizes of portable containers. Portable containers may range from pint and gallon glass bottles to stainless steel carboys and 55-gal drums. Some are also shipped in plastic containers.

## INCIDENTS

Emergency responders should have a thorough knowledge of corrosive materials. After flammable liquids and gases, corrosives are the most frequently encountered hazardous material. Responders should have proper chemical protective equipment and SCBA to deal safely with corrosive materials. Firefighter turnouts will not provide protection from corrosives. The most common exposures are contact with the hands and feet, and inhalation of the vapors. Make sure that the chemical suits chosen for use are compatible with the corrosive material. No suit will protect you from chemicals indefinitely; they all have breakthrough times. Make sure personnel are rotated to avoid prolonged exposure, and make sure they do not contact the material unless absolutely necessary. Safety should be your primary concern.

In California, an MC/DOT 312/412 tanker truck developed a leak along an interstate highway. On arrival, responders found a reddish-brown vapor cloud coming from the tank. The shipping papers indicated that the load was spent sulfuric acid; however, the color of the vapor coming from the trailer was in conflict with that information. As it turns out, the driver was hauling spent sulfuric acid, but had room to pick up some nitric acid and put it in the same tank with the sulfuric acid. The nitric acid was not compatible with the tank and ate through it quickly. The entire load of acid was spilled onto the highway when the tank failed. Certain hazardous materials have specific colors, and responders should be aware of these colors.

A tank car placarded "empty," which contained an estimated 800 gal of anhydrous hydrogen fluoride, a corrosive liquid, was found leaking in a rail yard. "Empty" or "residue" placarded tank cars, as they are now called, can have as much as 3000 gallons of product still in the tank if it has not been purged. Responders attempted to control the leak over a 4-hour period. In the meantime, a vapor cloud formed and traveled approximately 2.5 miles downwind. This forced the evacuation of 1500 people from a 1.1-sq-mile radius around the leaking tank car for 9 hours. Local hospitals treated approximately 75 people for minor skin and eye irritations.

## REVIEW QUESTIONS FOR CHAPTER 10

1. List the two types of chemicals that make up the DOT corrosive class.
2. List the two types of acids.
3. The strength of an acid is a result of passing a gas through water. Which of the following terms reflects the name of the process?
   A. Radiation
   B. Sublimation
   C. Ionization
   D. Cationazation
4. Concentration of an acid is an expression of the relationship between acid and what other material?
   A. Alcohol
   B. Water
   C. Gas
   D. Dissolved solid
5. A corrosive hazardous material with a pH of 7.0 is considered to be:
   A. Weak
   B. Acidic
   C. Basic
   D. Neutral
6. A corrosive hazardous material with a pH of 2.3 is considered to be:
   A. Acidic
   B. Basic
   C. Neutral
   D. Weak
7. A corrosive hazardous material with a pH of 8.7 is considered to be:
   A. Neutral
   B. Acidic
   C. Basic
   D. Weak
8. List two procedures that can be used to reduce the corrosive effects of an acid.
9. Provide the names and structures for the following organic acids.

   $CH_3COOH$ $C_2H_5COOH$ $C_3H_7COOH$

10. List the formulas and names for the following organic acid structures.

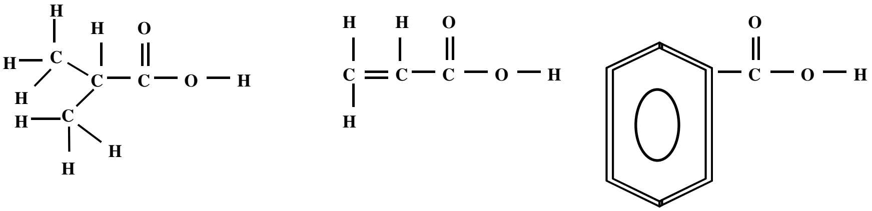


Figure 10.11