Safe Operating Procedure

(Revised 11/22)

OXIDIZERS
CHEMICAL HAZARDS & RISK MINIMIZATION

Background

The Globally Harmonized System (GHS) of classification and labeling of chemicals has three separate classifications for oxidizers; gases, liquids, and solids. The definitions are very similar in that all three generally provide oxygen to cause or contribute to the combustion of other materials.

Oxidizers will be identified with the pictogram shown. In addition, Section 2 of the Safety Data Sheet (SDS) will contain one of the following Hazard Statements:

- H270 May cause or intensify fire; oxidizer
- H271 May cause fire or explosion; strong oxidizer
- H272 May intensify fire; oxidizer

General Hazards of Oxidizers

As will be discussed in more detail, oxidizers pose a serious fire hazard because they:

- Intensify combustion
- Widen the flammable range of flammable gases and liquids
- Lower the flashpoints and ignition temperatures of combustible materials so these materials ignite more readily

Oxidizers cause or contribute to the combustion of other materials by providing oxygen to support the combustion process. Combustion requires four factors to occur:

- A combustible (oxidizable) material
- An ignition source
- Oxygen
- An ongoing reaction that generates free radicals

Remove any of one of these four requirements and there is no combustion process. Normal combustion is simply a relatively rapid oxidation reaction that is accompanied by the emission of energy in the forms of heat and light.

As heat is applied to a combustible material, the molecules that compose the material start to vibrate rapidly. If the vibrations become strong enough, the molecules break into fragments known as free radicals. The process of breaking into free radicals is known as pyrolysis and is endothermic (requiring heat from an outside source). The free radicals encounter oxygen in the air. Oxygen has a great attraction for electrons (electronegativity) and reacts with the free radicals. The reaction that occurs is known as oxidation and is simply the forming of a chemical bond between a free radical and oxygen. The bond-forming process is exothermic (heat producing) and is, in essence, combustion. Some of the heat produced radiates back to the fuel and now supplies the energy necessary for pyrolysis to continue. This entire series of events is known as fire.

The rate at which a reaction occurs is, to a great extent, controlled by the concentration of the materials involved. Air is composed of approximately 21% oxygen. This means that during the combustion process for every 100 molecules that a free radical encounters, about 21 of those will be oxygen. Thus only about 21 out of 100, or 1/5 of the encounters will be with oxygen and can result in a reaction. If the concentration of oxygen is increased, as an oxidizer would do, the rate of reaction will also increase. If the concentration of oxygen is 50%, the rate of encounter between a radical and oxygen is 50 out of 100 or ½ of all encounters. Thus, the rate of reaction is greatly increased, which increases the amount of heat produced. The fire will be much more intense.

Oxidizing Gases

In addition to oxygen, the elemental gases chlorine and fluorine have the high electronegativity needed for oxidizing free radicals and producing combustion. Other oxidizing gases include nitrous oxide, dinitrogen tetroxide, oxygen difluoride, and chlorine trifluoride.

For oxidizing compressed gases in cylinders, a unique hazard is that fire can result from the gas passing through a gauge or piping system that is not free of hydrocarbons, even in trace amounts. Spontaneous ignition of the hydrocarbon will occur. This ignition can result in an explosion accompanied by fragmentation of the equipment and possible fire.

A second hazard unique to oxidizing gases is the potential to concentrate in a room or other unvented or poorly vented space. In oxidizer-enriched environments, the flammable range of flammable gases and liquids is widened at both the upper and lower flammable limits. They will burn when normally they would be either too rich or lean. Flash points and ignition temperatures are also lowered. In some cases, flash points and ignition temperatures are lowered to the point that the substance can ignite at room temperature.

Other materials, especially clothing, exposed to an oxidizer-enriched atmosphere can be saturated with the oxidizer. The material involved will retain a good amount of oxidizer for a minimum of 30 minutes after the exposure to the enriched atmosphere. Clothing that is saturated in this manner can easily ignite and burn with great intensity and with great heat output.

All three oxidizing elements (oxygen, chlorine and fluorine) can be found in the liquid form. Chlorine is liquified by pressurizing the gas until its critical pressure is reached (critical pressure is the pressure at which the particular gas turns to a liquid). However, the primary concern with chlorine in a liquid spill is the toxicity of the vapor produced.

Oxygen and fluorine, on the other hand, are liquified by the process of cooling. When oxygen and fluorine are in the liquid state they are cryogenic liquids; oxygen at a temperature of -362°F and fluorine at -370°F. While in the liquid state, these materials are exceedingly dangerous. Liquid oxygen, when spilled on or mixed with any hydrocarbon will likely spontaneously explode. Liquid fluorine makes liquid oxygen look like kid stuff. It is such a strong oxidizer that it is capable of causing concrete to burn.

Oxidizing Solids

Oxidizing solids also have a few unique properties. Oxidizing solids include:

- Oxysalts such as potassium permanganate, sodium nitrate, sodium persulfate, and other nitrates, nitrites and chlorates.
- Inorganic peroxides include alkali metal (Na, K, Rb, Li, Cs, Fr) peroxides and transition metal (e.g., Cu, Zn, Co, Fe, Cr, Se, Ag, Pb, etc.) peroxides. When wetted, alkali metal peroxides can produce sufficient heat to ignite nearby combustibles (or explosively rupture their containers). Transition metal peroxides are less reactive than those of alkali metals.

Solid oxidizers in solution may be too dilute to react with combustible materials to produce a fire. However, if a combustible material (e.g., a paper towel or a lab coat) is contaminated with a solution containing an oxidizer, as the solution dries, the oxidizer is concentrated. This can cause the combustible material to spontaneously ignite and burn intensely. Solid oxidizers saturated with combustible materials can be explosive. An example is the explosive behavior of ammonium nitrate combined with fuel oil.

Toxicity of Oxidizing Compounds

The combustion products of oxidizer-fed fires are generally much more toxic than the combustion products of the combustible material itself in air. For example, methane (i.e., natural gas) burned in air will produce carbon dioxide and water. Burned in a chlorine atmosphere, the combustion products are hydrogen chloride gas and carbon tetrachloride vapor. Inhaled, hydrogen chloride gas will go into solution as hydrochloric acid and corrode lung tissue and other mucous membranes. This can result in chemical pulmonary edema with symptoms not becoming evident for several hours. Other oxidizers have similar hazards.

Since the purpose of oxidizers is to oxidize, tissues such as lung, skin and eyes are at risk. In the case of oxidizing acids, the hazard is very high and the EHS SOP, ***Corrosive Chemical Hazards & Risk Minimization*** should be followed as well. The hazards to tissues from other oxidizers will vary depending on the oxidizer and its concentration. Skin exposure can result in dangerous burns, but dermatitis (i.e., drying of the skin) is more common. Eyes are much more sensitive to exposure.
The health hazard with oxidizing gases is inhalation. With the exception of oxygen, oxidizing gases are very toxic and cause potentially lethal chemical pulmonary edema even with brief exposures.

Extinguishing Agents for Oxidizer Fires

Extinguishing fires involving an oxidizer is difficult. A carbon dioxide extinguisher is not an effective choice for an oxidizer-fed fire because it works on the principle of excluding atmospheric oxygen, and atmospheric oxygen is not required for an oxidizer-fed fire. Dry chemical extinguishing agents will also be ineffective for the most part. They act to interrupt the chemical chain reaction, but will be overcome by the oxidizer in all but the smallest fires.

Water may be the only extinguishing agent that may be effective. Energy/heat generated during combustion must first drive off the water as steam and then reheat the surface of material to a sufficient temperature to support ignition. Some combustible materials (e.g., wood) can retain a lot of heat energy once they are hot. Adding water until the fire is out may not end the potential for fire. Instead, the combustible material may have the energy to drive off the water and still have enough residual heat to re-ignite. Camp fires re-igniting after being extinguished with water are an example of this. Therefore, water must be used in drenching quantities.

Water can also result in the fire spreading if it involves a non-miscible flammable liquid. In this situation evacuation and isolation of the fire may be the only option.

If the fire involves an oxidizing gas, then the gas supply should be shut-off (if it can be done so safely). This is the reason hospitals have remote oxygen shutoffs in hallways outside of rooms where the gas is used.

Mitigating the Risks of Oxidizers

First and foremost, verify that a written, comprehensive project-specific hazard analysis/risk assessment with additional oversight is not in order, as described in the companion EHS SOP, ***Chemical Hazard Assessment and Risk Minimization***. General risk mitigation measures are as follows:

- Conduct a thorough literature search, including review of Safety Data Sheets, to establish a thorough understanding of the properties of the oxidizers to be handled with particular consideration given to the procedures and tasks to be conducted. See also the Laboratory Safety Colloquium archive presentation titled ***Unstable, Reactive, and Energetic Compounds***.
- Follow general safe chemical handling practices as described in the EHS SOP, ***General Guidance for Chemical Ordering, Receipt, Distribution, Use and Storage***.
- Observe all specific safety procedures established for the laboratory/procedure.
- Keep away from combustible materials, such as paper, wood, flammable and combustible liquids, oils, greases, finely divided metals, other oxidizable substances (e.g., hydrides, phosphorus, etc.), and incompatible substances (as listed in the SDS). Remove all unnecessary materials from the work area.
- Wear appropriate PPE. See EHS SOP, ***Personal Protective Equipment for Chemical Exposures***. Flame retardant lab coats are recommended.
- Conduct work on the smallest scale possible.
- For compressed oxidizing gases, ensure that gages, valves, and piping are designed for use with the specific gas and are free of contaminants, particularly hydrocarbon based materials (oil, grease, etc.).
- Use oxidizing gases in hoods or well ventilated spaces.
- Where possible, use dilute solutions of oxidizers to reduce reactivity and degree of health hazards.
- Do not let combustible solids such as paper towels, lab coats, and clothing become contaminated with oxidizers. Should this happen, immediately soak and rinse with water to remove the oxidizer.
- Combine oxidizers with other materials only in accordance with established procedures. For novel work, begin with the smallest amount possible to minimize the scale of adverse reactions.
- Do not use potentially reactive oxidizer mixtures outside of accepted temperature ranges. The additional heat may initiate violent or even explosive reactions.

- Ensure an appropriate fire extinguisher and accessible and properly functioning safety shower are readily available. For more guidance see the EHS SOP, ***Fire Safety – General Prevention and Extinguishing*** and the EHS web-based training program titled ***Fire Extinguisher Training***.