Oxidizers

From: Canadian Centre for Occupational Health and Safety

Oxidizing materials are liquids or solids that readily give off oxygen or other oxidizing substances (such as bromine, chlorine, or fluorine). They also include materials that react chemically to oxidize combustible (burnable) materials; this means that oxygen combines chemically with the other material in a way that increases the chance of a fire or explosion. This reaction may be spontaneous at either room temperature or may occur under slight heating. Oxidizing liquids and solids can be severe fire and explosion hazards.

Common oxidizing liquids and solids include:

- bromine
- bromates
- chlorinated isocyanurates
- chlorates
- chromates
- dichromates
- hydroperoxides
- hypochlorites
- inorganic peroxides
- ketone peroxides
- nitrates
- nitric acid
- nitrites
- perborates
- perchlorates
- perchloric acid
- periodates
- permanganates
- peroxides
- peroxyacids
- persulphates

There are other chemicals that are oxidizing materials. For example, liquid air has been involved in many explosions because of its oxidizing properties. Liquid air itself has about 30% oxygen which makes it a powerful oxidant. However, when liquid air evaporates, it becomes richer in oxygen content when more volatile components evaporate slightly faster. Liquid nitrogen is safer and is preferred to liquid oxygen as a cryogenic liquid coolant.

It is wise to treat any unknown material, especially crystals in solvents known to form a peroxide (e.g., ethers), as very hazardous until it is positively identified.

What can oxidizing materials do?

Oxidizing materials can:

- speed up the development of a fire and make it more intense.
- cause substances that do not normally burn readily in air to burn rapidly.
- cause combustible materials to burn spontaneously without the presence of obvious.
- ignition sources such as a spark or flame.

What happens when an oxidizing material comes in contact with a combustible substance largely depends on the chemical stability of the oxidizing material. The less stable an oxidizing material is, the greater the chance that it will react in a dangerous way.

Are there classes of oxidizing materials?

The [U.S.] National Fire Protection Association (NFPA) Code 430 (1995) "Code for the Storage of Liquid and Solid Oxidizers" has classified oxidizing materials classified according to their ability to cause spontaneous combustion and how much they can increase the burning rate.

Class 1 Oxidizers:

- slightly increase the burning rate of combustible materials.
- do not cause spontaneous ignition when they come in contact with them.

Class 2 Oxidizers:

- increase the burning rate of combustible materials moderately with which they come in contact.
- may cause spontaneous ignition when in contact with a combustible material.

Class 3 Oxidizers:

- severely increase the burning rate of combustible materials with which they come in contact.
- will cause sustained and vigorous decomposition if contaminated with a combustible material or if exposed to sufficient heat.

Class 4 Oxidizers:

- can explode when in contact with certain contaminants.
- can explode if exposed to slight heat, shock, or friction.
- will increase the burning rate of combustibles.
- can cause combustibles to ignite spontaneously.

What are some examples of these classes of oxidizing materials?

The National Fire Protection Association (NFPA) Code 430 (1995) "Code for the Storage of Liquid and Solid Oxidizers" provides many examples of typical oxidizing materials listed according to the NFPA classification system. Some of these examples include:

National Fire Protection Association (NFPA) Class 1 Oxidizers

Examples of NFPA Class 1 oxidizers include:

- aluminum nitrate
- ammonium persulfate
- barium peroxide
- hydrogen peroxide solutions (8% to 27.5% by weight)
- magnesium nitrate
- nitric acid (40% concentration or less)
- perchloric acid solutions (less than 50% by weight)
- potassium dichromate
- potassium nitrate
- silver nitrate
- sodium dichloroisocyanurate dihydrate
- sodium dichromate
- sodium nitrate
- sodium nitrite
- sodium perborate (and its monohydrate)
- sodium persulfate
- strontium nitrate
- strontium peroxide
- trichloroisocyanuric acid
- zinc peroxide

NFPA Class 2 Oxidizers

Examples of NFPA Class 2 oxidizers include:

- calcium chlorate
- calcium hypochlorite (50% or less by weight)
- chromic acid (chromium trioxide)
- 1,3-dichloro-5,5-dimethylhydantoin
- hydrogen peroxide (27.5 to 52% by weight)
- magnesium perchlorate
- nitric acid (concentration greater than 40% but less than 86%)
- potassium permanganate
- sodium permanganate
- sodium chlorite (40% or less by weight)
- sodium perchlorate (and its monohydrate)

• sodium peroxide

NFPA Class 3 Oxidizers

Examples of NFPA Class 3 oxidizers include:

- ammonium dichromate
- hydrogen peroxide (52 to 91% by weight)
- nitric acid, fuming (concentration greater than 86%)
- perchloric acid solutions (60 to 72% by weight)
- potassium bromate
- potassium chlorate
- potassium dichloroisocyanurate
- sodium chlorate
- sodium chlorite (greater than 40% by weight)
- sodium dichloroisocyanurate

NFPA Class 4 Oxidizers

Examples of NFPA Class 4 oxidizers include:

- ammonium perchlorate (particle size greater than 15 microns)
- ammonium permanganate
- hydrogen peroxide (greater than 91% by weight)
- perchloric acid solutions (greater than 72.5% by weight)
- tetranitromethane

What are the fire and explosion hazards of oxidizing liquids and solids?

Burning involves the oxidation of a combustible (burnable) substance. When a combustible substance burns, a chemical reaction occurs in which the substance (fuel) combines with oxygen, and gives off heat, gases, and often light (flames). The usual source of oxygen for burning is air. However, oxidizing materials can supply combustible substances with oxygen and support a fire even when air is not present.

Although most oxidizing materials do not burn themselves, they can produce very flammable or explosive mixtures when combined with combustible materials like:

- organic (carbon-containing) materials such as paper, wood, flammable and combustible liquids, greases, waxes, many plastics and textiles
- finely divided metals
- other oxidizable substances such as hydrazine, hydrogen, hydrides, sulphur or sulphur compounds, phosphorous, silicon and ammonia or ammonia compounds

Some oxidizing materials are also incompatible with non-combustible materials. These oxidizers can undergo dangerous reactions with water, inorganic acids or even other oxidizing materials.

The SDS for a particular oxidizing material should explain what other substances the oxidizer is incompatible with (reacts in a dangerous fashion) and any other conditions, such as heat, shock or friction, that could result in dangerous chemical reactions.

What are the health hazards of oxidizing materials?

Oxidizing materials may be toxic or corrosive. Depending on the material, route of exposure (inhalation, eye or skin contact, or swallowing) and dose, they could harm the body. Corrosive oxidizers can also attack and destroy metal.

The SDSs and the container labels should explain all of the hazards of the oxidizing materials that you use in the workplace.

An example is ammonium perchlorate. This material is a white or colourless, odourless crystals. It is used in explosives and fireworks; as an oxidizing agent in solid rocket and missile propellants; as an adhesive; as an engraving agent; laboratory (analytical) reagent; chemical intermediate for alkali and alkaline metal perchlorates; animal feed supplement; and in oxygen-generating devices for life-support systems in submarines, spacecraft, bomb shelters and breathing apparatus.

Ammonium perchlorate can decompose at high temperatures forming toxic gases, such as chlorine, hydrogen chloride and nitrogen oxides. Closed containers or tanks may rupture and explode if heated. It does not burn but is a powerful oxidizer and explosive when mixed with combustible materials. It is highly reactive and impact or high temperatures can cause violent decomposition or explosion. It can form shock-sensitive mixtures with finely powdered metals, metal oxides, strong reducing agents, sulfur and phosphorus. It may cause eye irritation.

Does CCOHS have additional information on ammonium perchlorate or other oxidizing agents?

OSH Answers has a separate question-and-answer document on Organic peroxides and their hazards. Another document How do I to Work Safely With Oxidizing Liquids and Solids has information about handling, using, storing, and disposing of oxidizing agents.

CCOHS also has some 50 databases containing different kinds of information. Some are bibliographic databases (e.g., NIOSHTIC, CIS-ILO, HSELINE, Toxline) which provide abstracts from journal articles, books, government reports, etc. There are other databases that have direct, ready-to-use information (e.g., CHEMINFO, HSDB, RIPP, etc). To find out about these databases and which ones have information on chemicals of interest to you, search the CHEMINDEX Database. When you search using a chemical name or synonym or Chemical Abstracts Service Registry Number (CAS RN), the search results list the databases that contain information on the chemical. The search results will also allow you to link to a description of the databases and view sample records.