

How to Work Safely with – Oxidizing Liquids and Solids – Fact Sheets



WHY SHOULD I TRY TO SUBSTITUTE WHEN POSSIBLE?

Substitution can be the best way to avoid or reduce a hazard. However, finding a suitable non-oxidizing or less powerful oxidizing substitute to do the job effectively and safely is not always easy or even possible. Ask chemical suppliers if safer substitutes are available. Obtain Material Safety Data Sheets (MSDSs) for all possible substitutes. Find out about all of the hazards (health, fire, corrosivity, chemical reactivity, etc.) of these materials before making any changes.

Choose the least hazardous material and process that can do the job effectively and safely. Also, learn how to work safely with the material.

If I cannot substitute, are there some other things that I can do?

Sometimes changing or modifying a process can reduce the hazards from an oxidizing material. In some cases it may be possible to:

- Reduce dust levels by using solutions of oxidizers instead of dry, solid forms.
- Reduce dangerous reactivity by diluting solutions with water.

Other modifications could include the installation of alarms or automatic shut-off switches on equipment to warn of equipment failure, high temperatures or high pressures.

Why is proper ventilation important?

Well-designed and well-maintained ventilation systems remove airborne oxidizing materials from the workplace and reduce their hazards. The amount and type of ventilation needed depends on such things as the type of job, the kind and amount of materials used, and the size and layout of the work area. An assessment of the particular ways a workplace stores, handles, uses and disposes of its oxidizing materials is the best way to find out if existing ventilation controls (and other hazard control methods) are adequate.

Some workplaces may need a complete system of hoods and ducts to provide

acceptable ventilation. Others may only require a single, well-placed exhaust fan. No special ventilation system may be needed for work with small amounts of oxidizers that do not give off airborne contaminants.

Organic materials, such as wood, should not be used in ventilation systems for oxidizing materials. Systems should be free of ignition sources and separate from other systems that might be exhausting incompatible substances. The system may also need to be corrosion-resistant if the material is corrosive. Air cleaning devices such as dust collectors should be made from non-combustible materials.

Ensure that hoods, ducts, fans and air-cleaning devices, such as dust collectors, are made from materials compatible with the oxidizing agents.

Laboratories that use perchloric acid need special fume hoods and fume exhaust systems. These are available from laboratory equipment suppliers.

What should I know about the storage of oxidizing materials?

Store oxidizing materials according to the occupational health and safety regulations and the fire and building codes that apply to your workplace. These laws may specify the kinds of storage areas such as storage rooms or buildings allowed for different oxidizers. They may also specify how to construct these storage areas, and the amounts of oxidizing materials that can be stored in each area.

Before storing, inspect all incoming containers to ensure that they are undamaged and properly labelled. Do not accept delivery of defective containers.

Store oxidizing materials in containers that the chemical supplier recommends. Normally these are the same containers in which the material was shipped. Repackaging can be very dangerous especially when using contaminated or incompatible containers. Protect containers against banging or other physical damage when storing, transferring or using them. Do not use wooden pallets or other combustible pallets for storing containers of oxidizing materials.

Make sure containers are suitably labelled. For oxidizing materials requiring temperature control, the recommended storage temperature range should be plainly marked on the container. It is also a good practice to mark the date that the container was received and the date it was first opened.

Normally keep containers tightly closed when storing unless the supplier's instructions state otherwise. This helps to avoid contamination of the material or evaporation of solvents used to dilute oxidizers, such as organic peroxides, to safer concentrations.

Some oxidizing agents, such as solutions of 8% or higher hydrogen peroxide in water, must be stored with specially vented caps. Hydrogen peroxide gradually decomposes at room temperature to produce oxygen gas and water. The properly working vent will prevent the build-up of pressure inside containers. The normal build-up of pressure could rupture an unvented container. Check vent caps regularly to ensure that they are working properly. Keep vented containers in the upright position. NEVER stack vented containers on top of each other.

What should I know about the storage area for oxidizing materials?

Store oxidizing materials separately away from processing and handling areas and away from other materials. Separate storage can reduce the risk of personal injury and damage in case of fires, spills or leaks. If totally separate storage is not possible, store oxidizing materials away from incompatible materials especially organic or other oxidizable materials (sometimes called reducing materials or reducing agents).

Some oxidizing materials are incompatible or may react with each other, sometimes violently. Do not store them beside each other. Check the reactivity data and storage requirements sections of the MSDS for details about what materials are incompatible with a specific oxidizer.

Walls, floors, shelving, and fittings in storage areas should be constructed of non-combustible materials. Wood impregnated with a fire-retardant material is not fully protected against the increased fire hazard caused by contact with oxidizers. Protect metal construction materials against corrosion by painting them with a compatible coating.

Ensure that floors in areas where oxidizers are stored are watertight, do not have cracks where these materials can lodge. Contain spills or leaks by storing in trays made from compatible materials. For larger containers, such as drums or barrels, provide dikes around storage areas, and sills or ramps at door openings.

Store oxidizer containers at a convenient height for handling, below eye level if possible, to reduce the risk of dropping containers. Avoid overcrowding in storage areas. Do not store containers in out-of-the-way locations where they could be forgotten.

Store containers away from doors. Although it is convenient to place frequently-used materials next to the door, they could cut off the escape route if an emergency occurs.

Store oxidizing materials in areas that are:

- Labelled with suitable warning signs.
- Well-ventilated.
- Supplied with adequate firefighting equipment including sprinklers, where appropriate.
- Supplied with suitable spill clean-up equipment and materials.
- Free of ignition sources.
- Accessible at all times.

Is storage temperature important?

Store oxidizing materials in dry, cool areas, out of direct sunlight and away from steam pipes, boilers or other sources of heat. Follow the chemical supplier's recommendations for storage temperatures. Some dangerously reactive oxidizing materials start to decompose at temperatures only a little above normal room temperatures. The decomposition can lead to an explosion under some conditions. For these oxidizers, ensure that the storage temperature is kept at least 14°C (25°F) below their decomposition temperature. Avoid storing any oxidizer at temperatures above 49°C (120°F).

Storage areas may need alarms that provide a warning when storage temperatures

are higher or lower than required.

What are general precautions for storing oxidizing materials?

At all times:

- Allow only trained, authorized people into storage areas.
- Keep the amount of oxidizing materials in storage as small as possible.
- Inspect storage areas regularly for any deficiencies including damaged or leaking containers and poor housekeeping.
- Correct all deficiencies as soon as possible.

What should I know about dispensing and using oxidizing liquids and solids?

Be very careful when dispensing oxidizers from storage containers into other containers. Avoid spilling material and contaminating your skin or clothing. Spills from open, unstable or, breakable containers during material transfer have caused serious accidents.

Dispense from only one container at a time. Finish all the dispensing of one material before starting to dispense another. Dispense the smallest amount possible, preferably only enough for immediate use. Keep containers closed after dispensing to reduce the risk of contaminating their contents.

Take care that the oxidizing materials do not contact combustible or other incompatible materials when they are dispensed. Use containers and dispensing equipment, such as drum pumps, scoops or spatulas, that the chemical supplier recommends. These items must be made from materials that are compatible with the oxidizing materials you are using. Keep them clean to avoid contamination.

NEVER transfer liquids by pressurizing their usual shipping containers with air or inert gas. Ordinary barrels or drums may be damaged by the pressure. Moreover, if air is used, it may create a flammable atmosphere inside the container. NEVER pipette oxidizing liquids (or other chemicals) by mouth. Use a pipette bulb or aspirator instead.

Since some solid oxidizers may be shock sensitive, do not chip or grind lumps to break them up. If crystals have precipitated in containers of an oxidizing agent, contact your health and safety officer about their safe handling and disposal. Follow the chemical supplier's advice. Avoid sliding or skidding heavy metal containers such as drums or barrels across floors.

Can I add oxidizers to water?

Follow the chemical supplier's directions for mixing oxidizers with water. Some oxidizers including nitric acid and perchloric acid generate large amounts of heat when they are mixed with water. This reaction can cause the solution to froth and boil or even erupt violently from the container. For this reason, always add these oxidizers to cold water slowly and in small amounts with frequent stirring.

What should I know about handling oxidizing materials?

Make sure that all areas where oxidizing materials are used are free of combustible and other incompatible materials. Do not allow tobacco smoking or

any other ignition sources around oxidizing materials.

Ensure that temperatures in these areas do not become high enough to cause rapid decomposition of the materials. For example, hydrogen peroxide decomposes almost twice as fast for every 5.6°C (10°F) temperature rise.

In laboratories, do not use corks, rubber stoppers or stopcock grease to seal containers of strong oxidizing materials. Use fibreglass heating mantles or sand baths instead of oil baths to heat reaction vessels containing significant amounts of oxidizing materials.

Follow the chemical producer's instructions regarding the handling of oxidizing agents.

Always:

- Inspect containers for damage or leaks before handling them.
- Handle containers of oxidizers carefully to avoid damaging them.
- Keep containers of oxidizers tightly closed, except when actually using the material, to help avoid spillage or contamination of the container contents.
- Keep only the smallest amounts possible (not more than one day's supply) of oxidizers in work areas.
- Return unopened containers to the proper storage area and opened containers to a dispensing area at the end of the day.
- Check that all containers are properly labelled, and handle the containers so that the label remains undamaged and easy to read.
- Never return "used" or unused oxidizers to original containers of uncontaminated material. Trace amounts of contaminant might cause a dangerous decomposition.

Regular workplace inspections can help to spot situations where oxidizers are stored or handled in potentially hazardous ways.

What should I know about disposal of oxidizing wastes?

Oxidizing wastes are hazardous. Always handle them safely. Consider oxidizing materials accidentally mixed with an unknown or foreign material as contaminated and do not use. Dispose of contaminated material immediately.

"Empty" drums, bottles, bags, sacks and other "oxidizing agent" containers usually have hazardous oxidizing residues inside them. NEVER use these containers for anything else, no matter how clean they seem. Treat them as oxidizing wastes. The chemical supplier can give advice about how to safely handle or decontaminate "empty" containers or other packaging material.

Store oxidizing wastes, including contaminated empty combustible containers, in the same way as unused oxidizing materials. Only use compatible containers for oxidizing wastes. Identify their contents with suitable labels.

NEVER dispose of oxidizers in ordinary garbage or down sinks or drains that connect to sanitary or storm sewers. Dispose of them according to the supplier's directions, or through hazardous waste collection and disposal companies. In all cases, dispose of oxidizing wastes according to the environmental laws that apply to your jurisdiction. Contact the appropriate environmental officials for

details.

Why is good housekeeping important?

Maintain cleanliness and order at all times in the workplace:

- Clean up any spills and build-ups of oxidizers promptly and safely according to directions in the Material Safety Data Sheet (MSDS) and additional guidelines from the producer.
- Be careful not to contaminate anything with the oxidizing agent that can burn when cleaning up.
- Do not use sawdust or other combustible sweeping compounds to clean up spills of oxidizing materials.
- Rewash the area if a powdery residue remains after an area has dried out.
- Properly dispose of unlabelled or contaminated chemicals.
- Promptly remove combustible wastes, including wood, paper and rags, from work areas.
- Avoid any build-up of oxidizer dusts on ledges or other surfaces.
- Ensure that all waste containers are compatible with the oxidizing material used, properly marked and easily located.

Why is personal cleanliness important?

Personal cleanliness helps protect you when you are working with oxidizers:

- Wash hands before eating, drinking, smoking or going to the toilet.
- Remove contaminated clothing and leather shoes or boots since they can be a severe fire hazard.
- Wash contaminated items immediately and thoroughly in water before re-wearing or discarding.
- Do not wear or carry contaminated clothing or footwear into areas having ignition sources or where smoking is allowed.
- Store food and tobacco products in uncontaminated areas.
- Avoid touching yourself (e.g., scratching your nose or rubbing your eyes) with contaminated hands.
- Wash thoroughly at the end of the workday even though you have done everything mentioned before.

Why should I know about equipment maintenance?

Regular equipment maintenance can prevent leaks or emissions of oxidizers into the workplace:

- Ensure maintenance personnel know the hazards of the materials they may encounter and any special procedures and precautions needed before they work begins.
- Prevent leaks of grease or other lubricants from equipment where oxidizers are used.
- Do not allow materials such as cleaning solvents, paints or thinners to contact oxidizers.
- Be very careful when cutting and welding or doing other hot work involving oxidizing material containers or equipment.
- Comply with applicable regulations and contact the chemical supplier for advice.

What should I know about personal protective equipment for oxidizing materials?

If other methods, such as engineering controls, are not available or effective in controlling exposure to oxidizing materials, wear suitable personal protective equipment (PPE). Choosing the right PPE for a particular job is essential. MSDSs should provide general guidance. Also obtain help from a qualified professional who knows how to evaluate the hazards of a specific job, especially those related to oxidizers, and how to select the proper PPE.

Before the oxidizing material is brought into the building:

- The appropriate PPE should be selected and be available.
- Workers should know where the PPE is and be trained to use it for emergencies as well as for normal operations.

Avoid Skin Contact

When using materials that are harmful by skin contact, wear protective gloves, aprons, boots, hoods or other clothing, depending on the risk of skin contact. Choose clothing made of materials that resist permeation, penetration or damage by the chemical. The Chemical Protective Clothing question-and-answer document has general information on selecting gloves and other chemical protective clothing. The MSDS should recommend appropriate materials. If it does not, contact the chemical supplier for specific information.

Protect Your Eyes and Face

Always wear eye protection when working with oxidizers. Avoid ordinary safety glasses. Use chemical safety goggles instead. In some cases, you should also wear a face shield (with safety goggles) to protect your face from splashes. The Safety Glasses question-and-answer document has information on selecting PPE for protecting the eyes and face.

Avoid Breathing Dusts, Mists or Vapours

If respirators must be used for breathing protection, develop and follow a written respiratory protection program, as described in the Respirator Selection question-and-answer document. Further guidance for developing a program can be found in the current CSA Standard Z94.4, "Selection, Care, and Use of Respirators." Follow all legal requirements for respirator use and approvals. These may vary between jurisdictions in Canada.

Sorbents in respirator cartridges or canisters must be compatible with the chemical they are supposed to protect against. For example, oxidizable sorbents, such as activated charcoal, may not be acceptable if high airborne concentrations of strong oxidizers are present. A hazardous reaction might occur.

Know and be familiar with the right PPE for emergencies, as well as normal operations.

Wear the PPE needed for doing a particular job. It cannot provide protection if it is not worn.

How should I handle emergencies?

Act fast in emergencies such as chemical fires, leaks and spills:

- Evacuate the area at once if you are not trained to handle the problem or if it is beyond your control.
- Alert other people in the area to the emergency.
- Call the fire department immediately.
- Report the problem to the people responsible for handling emergencies where you work.
- Obtain first aid if you have been exposed to harmful chemicals and remove all contaminated clothes.

Prepare a written emergency plan. All of the above procedures plus any others specific to your workplace should be included. Update it whenever conditions in the workplace change.

Check that emergency eyewash stations and safety showers are available and are in proper operating order, wherever accidental exposure to oxidizers that can damage the skin or eyes might occur.

Only specially trained and properly equipped people should handle the emergency. Nobody else should go near the area until it is declared safe.

Planning, training, and practicing for emergencies are necessary and help people to know what they must do.

The MSDSs for the materials used on each job are a starting point for drawing up an emergency plan. MSDSs have specific sections on spill clean-up procedures, first aid instructions, and fire and explosion hazards including suitable fire extinguishing equipment and methods. If the directions in each MSDS section are unclear or seem incomplete, contact the material's supplier or manufacturer for help, including technical bulletins that they may provide.

It is very important to know the best ways to fight fires involving oxidizing materials. The "built-in" supply of oxidizing gas in oxidizing materials makes extinguishing methods based on smothering, such as foam or carbon dioxide, ineffective. Often, cooling with large amounts of water is the only suitable method. But water on fires involving water-reactive oxidizers can lead to serious problems, including violent explosions.

Many other sources can also help develop emergency plans. Local fire departments can assist with fire emergency plans and training. If your workplace uses significant amounts of oxidizing agents, you should advise your local fire department (if it is required in your jurisdiction). Check with local officials.

What are basic safe practices for working with oxidizing liquids and solids?

Following these basic safe practices will help protect you from the hazards of oxidizing materials:

- Read the Material Safety Data Sheets (MSDSs) for all of the materials used in your work.
- Know the hazards (fire/explosion, health, corrosivity, chemical reactivity) of the materials used in your work.
- Know which materials you work with are oxidizing materials.
- Store oxidizing materials in suitable labelled containers, in a cool, dry

place, and according to any other conditions that may be required.

- Avoid or eliminate ignition sources (sparks, smoking, flames, hot surfaces) when working with oxidizing materials.
- Store, handle and use oxidizing materials in well-ventilated areas away from combustible and other incompatible materials.
- Handle containers safely to avoid damaging them.
- Dispense oxidizing materials carefully, using compatible equipment and containers.
- Keep containers closed when not in use.
- Keep only the smallest amounts possible (not more than one day's supply) in the work area.
- Do not return contaminated or unused oxidizers back to the original container.
- Practice good housekeeping, personal cleanliness and proper equipment maintenance.
- Handle and dispose of oxidizing wastes safely.
- Wear the appropriate personal protective equipment for each of the jobs you do.
- Know how to handle emergencies (fires, spills, personal injury) involving the oxidizing materials you work with.
- Follow the health and safety rules that apply to your job.

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