

How to Work Safely with – Dangerously Reactive Liquids and Solids – Fact Sheet



WHY SHOULD I TRY TO SUBSTITUTE WITH A LESS HAZARDOUS MATERIAL?

Substitution can be the best way to avoid or reduce a hazard. But it is not always easy or even possible to find a suitable, less hazardous substitute for a particular dangerously reactive material used for a certain job. Speak to the chemical supplier to find out if safer substitutes are available. For materials that polymerize easily, use a product that contains a polymerization inhibitor instead of a pure product whenever possible. Check for any limitations associated with the inhibitor.

Obtain MSDSs for all possible substitutes. Find out about all of the hazards (health, fire, corrosivity, chemical reactivity) of these materials before making any changes.

Sometimes process changes or modification can improve control of the hazards from working with a dangerously reactive material. These could include the installation of alarms or automatic shut-off switches on equipment to warn of equipment failure, high temperatures or high pressures.

Choose the least hazardous materials and process that can do the job effectively and safely. Learn how to work safely with them, too.

Why is proper ventilation important?

Well designed and maintained ventilation systems remove airborne, dangerously reactive 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 specific ways a workplace stores, handles, uses and disposes of its dangerously reactive 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, ducts and fans to provide acceptable ventilation. Others may require a single, well-placed exhaust fan. No special ventilation system may be needed to work with small amounts of dangerously reactive materials which do not give off airborne contaminants.

Make sure ventilation systems for dangerously reactive materials are designed and built so that they do not result in an unintended hazard. Ensure that hoods, ducts, air cleaners and fans are made from materials compatible with the dangerously reactive substance. Systems may require explosion-proof electrical equipment.

Ensure that the system is designed to avoid buildups of dusts or condensation of vapours. The vapours of inhibited liquids are not inhibited. When they condense, the liquid could polymerize or decompose easily.

Keep systems for dangerously reactive materials separate from other systems exhausting incompatible substances. Periodic inspection of ventilation systems will help maintain them in good operating condition.

How should I store dangerously reactive liquids and solids?

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

The following provides some general guidelines for storing dangerously reactive liquids and solids safely.

What should I know about containers for dangerously reactive materials?

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

Store dangerously reactive materials in containers that the chemical supplier recommends. Normally, these are the same containers in which the material was shipped. Repackaging can be dangerous especially if contaminated or incompatible containers are used. For example, strong hydrogen peroxide solutions can decompose explosively if placed in a container with rusty surfaces. Bottles for light-sensitive materials are often made of dark blue or brown glass to protect the contents from light. Containers for water-sensitive compounds should be waterproof and tightly sealed to prevent moisture in the air from reacting with the material.

Make sure containers are suitably labelled. For 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.

Protect containers against impact or other physical damage that might cause shock. Do not use combustible pallets, such as wood, for storing oxidizing materials or organic peroxides.

Normally keep stored containers tightly closed. This helps to avoid contamination of the material or evaporation of solvents used to dilute substances, such as some organic peroxides, to safer concentrations.

Some dangerously reactive liquids, such as strong hydrogen peroxide solutions or

certain organic peroxide products, gradually decompose at room temperature and give off gas. These liquids are shipped in containers with specially vented caps. These vent caps relieve the normal buildup of gas pressure that 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 dangerously reactive liquids and solids?

Store dangerously reactive liquids and solids separately away from processing and handling areas and from incompatible materials. Some dangerously reactive materials are incompatible with each other. Do not store these beside each other. Separate storage can minimize personal injury and damage caused by fires, spills or leaks.

Check the reactivity data and storage requirements sections of the MSDS for details about what substances are incompatible with a specific dangerously reactive material.

Construct walls, floors, shelving, and fittings in storage areas from suitable materials. For example, use non-combustible building materials in storage areas for dangerously reactive oxidizers or organic peroxides. Use corrosion-resistant materials for dangerously reactive corrosives.

Ensure that floors in storage areas are watertight and without cracks in which spilled materials can lodge. Contain spills or leaks by storing smaller containers in trays made of compatible materials. For larger containers, such as drums or barrels, provide dikes around storage areas, and sills or ramps at door openings.

Store smaller containers at a convenient height for handling below eye level if possible to reduce the risk of dropping them. 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 dangerously reactive materials in areas which are:

- Well ventilated.
- Supplied with adequate firefighting equipment including sprinklers (sprinklers may not be allowed in areas where materials that react dangerously with water are present).
- Supplied with suitable spill clean-up equipment and materials.
- Free of ignition sources such as sparks, flames, burning tobacco or hot surfaces.
- Accessible at all times.
- Labelled with suitable warning signs.

Why is storage temperature important?

Store dangerously reactive materials in dry, cool areas, out of direct sunlight,

and away from steam pipes, boilers or other heat sources. Follow the chemical supplier's recommendations for maximum and minimum temperatures for storage and handling. Higher temperatures can be hazardous since they can start and speed up hazardous chemical reactions. In many cases, inhibitors can be rapidly depleted at higher-than-recommended storage temperatures. Loss of inhibitor can result in dangerous reactions.

Some dangerously reactive materials must be kept at low temperatures in refrigerators or freezers. Use only approved or specially modified units. These are generally known as "laboratory safe". Standard domestic refrigerators and freezers contain many ignition sources inside the cabinet.

It can also be hazardous to store dangerously reactive materials at less than the recommended temperature. For example, acrylic acid is normally supplied with an inhibitor to prevent polymerization. Acrylic acid freezes at 13°C (55°F). At temperatures less than this, it will partly solidify. The solid part contains little or no inhibitor; the inhibitor remains in the liquid portion. The uninhibited acrylic acid can be safely stored below the freezing point but it may polymerize violently if it is heated to warmer temperatures.

Some organic peroxides are sold dissolved or dispersed in solvents, including water, to make them less shock-sensitive. If these are cooled to below their freezing points, crystals of the pure, very sensitive organic peroxide may be formed.

Alarms that indicate when storage temperatures are higher or lower than required may be needed.

Follow the chemical supplier's directions about inhibitors used in a particular product. Where appropriate, check inhibitor and oxygen levels and add more as needed according to the supplier's instructions.

Do not keep a material for longer than the chemical supplier recommends.

What are some general precautions about storing dangerously reactive solids and liquids?

At all times:

- Allow only trained, authorized people into storage areas.
- Keep the amount of dangerously reactive 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 is important to know when dispensing or using dangerously reactive materials?

Open and dispense containers of dangerously reactive materials in a special room or area outside the storage area. Do not allow any ignition sources in the vicinity. Take care that the dangerously reactive materials do not contact incompatible substances. Use containers and dispensing equipment, such as drum pumps, scoops or spatulas, that the chemical supplier recommends. These items must be made from materials compatible with the chemicals they are used with.

Keep them clean to avoid contamination.

When transferring materials from one container to another, avoid spilling material and contaminating your skin or clothing. Spills from open, unstable or breakable containers during material transfer have caused serious accidents.

NEVER transfer liquids by pressurizing their usual shipping containers with air or inert gas. The pressure may damage ordinary drums and barrels. If air is used, it may also create a flammable atmosphere inside containers of flammable or combustible liquids.

Glass containers with screw-cap lids or glass stoppers may not be acceptable for friction-sensitive materials. Avoid using ordinary screw-cap bottles with a cardboard liner in the cap for moisture-sensitive chemicals. Airborne moisture can diffuse slowly but steadily through the liner. NEVER transfer materials stored in a vented container into a tightly-sealed, non-vented container. The buildup of gas pressure could rupture it.

Dispense from only one container at a time. Finish dispensing and labelling 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.

NEVER return any unused material, even if it does not seem to be contaminated, to the original container.

If a dangerously reactive material freezes, do not chip or grind it to break up lumps, or heat it to thaw it out. Follow the chemical supplier's advice.

Avoid dropping, sliding or skidding heavy metal containers such as drums or barrels of friction- or shock-sensitive material.

What are safe techniques to use when handling dangerously reactive materials?

Make sure that all areas where dangerously reactive liquids and solids are used are clean and free of incompatible materials and ignition sources. Do not allow temperatures in these areas to become hot enough to cause a hazardous reaction.

Always:

- Inspect containers for damage or leaks before handling them.
- Handle containers carefully to avoid damaging them.
- Keep containers tightly closed except when actually using the material.
- Avoid returning used chemicals to containers of unused materials.
- Keep only the smallest amounts possible (never more than one day's supply) of dangerously reactive materials in the work area.
- Return unopened containers to the proper storage area at the end of the day and opened containers to a dispensing area at the end of the day.
- Check that all containers are properly labelled, and handle containers so that the label remains undamaged and easy to read.

Regular workplace inspections can help to spot situations in which dangerously reactive materials are stored, handled or used in potentially hazardous ways.

What are basic safe practices when working with dangerously reactive liquids and solids?

Following these basic safe practices will help protect you from the hazards of dangerously reactive liquids and solids:

- Read the Material Safety Data Sheets (MSDSs) and labels for all of the materials you work with.
- Know all of the hazards (fire, explosion, health, corrosivity, chemical reactivity) of the materials you work with.
- Know which of the materials you work with are dangerously reactive.
- Store dangerously reactive materials in suitable, labelled containers (usually their shipping containers) in a cool, dry area.
- Store, handle and use dangerously reactive materials in well-ventilated areas and away from incompatible materials.
- Follow the chemical supplier's advice on maximum and minimum temperatures for storage and use.
- Follow the chemical supplier's advice on checking and maintaining inhibitor and dissolved oxygen levels where appropriate.
- Eliminate ignition sources (sparks, smoking, flames, hot surfaces) when working with dangerously reactive materials.
- Handle containers carefully to avoid damaging them or shocking their contents.
- Keep containers closed when not in use.
- Keep only the smallest amount possible (not more than one day's supply) in the work area.
- Dispense dangerously reactive materials carefully into acceptable containers, using compatible equipment.
- Do not subject dangerously reactive materials to any type of friction or impact.
- Be careful when performing operations such as separations or distillations, that concentrate dangerously reactive materials.
- Practice good housekeeping, personal cleanliness and equipment maintenance.
- Handle and dispose of dangerously reactive wastes safely.
- Wear the proper personal protective equipment for each of the jobs you do.
- Know how to handle emergencies (fires, spills, personal injury) involving the dangerously reactive materials you work with.
- Follow the health and safety rules that apply to your job.

What should I know about the equipment I use with dangerously reactive materials?

Ensure that processing equipment is clean, properly designed and made from materials compatible with the dangerously reactive material used. Find out from the chemical supplier what materials are suitable for the specific chemical. For example, some steels and aluminum alloys, zinc and galvanized metal can cause rapid decomposition of certain organic peroxides.

Accidents have happened when reactive materials came in contact with incompatible heat exchange fluids or fluids used in instruments to monitor processes.

Reactive substances have, on occasion, leaked and soaked into equipment insulating materials. Insulators have good heat-keeping ability. Once a reaction

begins within the insulating material, the heat given off from the reaction can rapidly build up to hazardous levels and may result in fire.

What should I know about diluting dangerously reactive materials?

Some jobs require that dangerously reactive materials be diluted prior to use. Always strictly follow the chemical supplier's advice. Using the wrong solvent or a contaminated solvent could cause an explosion. Using reclaimed solvents of unknown purity can be hazardous. They might contain dangerous concentrations of contaminants that are incompatible with the dangerously reactive material.

What should I be aware of during hazardous operations?

Some operations involving dangerously reactive materials can be especially hazardous. Many accidents have occurred during distillation, extraction or crystallization because these processes involve concentrating reactive substances. Sieving dry, unstable materials might result in static electricity sparks which could cause ignition.

Filtering friction- or shock-sensitive chemicals with materials and devices that produce frictional heat, such as sintered glass filters, can be hazardous.

Before using a new material in an operation, find out as much as possible about the potential hazards of the particular chemical and operation.

How should I dispose of these materials and the containers?

Dangerously reactive wastes are hazardous. Dispose of unwanted or contaminated reactive chemicals promptly using a method the chemical supplier recommends. Consider any reactive materials accidentally mixed with an unknown or foreign material as contaminated, and dispose of them. NEVER attempt to salvage spilled or contaminated dangerously reactive materials.

"Empty" drums, bottles, bags and other containers usually contain hazardous residues. NEVER use these "empty" containers for anything else, no matter how clean they seem to be. Treat them as dangerously reactive wastes. Follow the chemical supplier's advice for safely handling or decontaminating "empty" containers.

Store reactive waste in the same way as unused dangerously reactive materials. Use only compatible containers for wastes. Identify their contents with suitable labels.

NEVER dispose of these wastes in ordinary garbage or down sinks or drains. Dispose of them according to the supplier's advice, or through hazardous waste collection and disposal companies. In all cases, dispose of dangerously reactive wastes according to the environmental laws that apply to your jurisdiction. Contact the appropriate environmental officials for details.

Why is good housekeeping important?

Maintain good housekeeping at all times in the workplace:

- Clean-up any spills promptly and safely according to directions in the MSDS.
- Use suitable clean-up materials.*

- Properly dispose of unlabelled or contaminated materials.
- Promptly remove combustible wastes, including wood, paper or rags from work area.
- Avoid any buildup of chemical dusts on ledges or other surfaces.
- Ensure that all waste containers used are compatible with the reactive materials, properly marked and located close to the job.

*Note: For example, some commercial sorbent materials used for spill clean-up may initiate polymerization in some monomers. Do not use sawdust or other combustible sweeping compounds to clean up spills of oxidizers or organic peroxides.

Why is personal cleanliness important?

Personal cleanliness helps protect people working with dangerously reactive materials:

- Wash hands before eating, drinking, smoking or going to the toilet.
- Remove contaminated clothing and footwear since they can be a severe fire or health hazard.
- Wash contaminated clothing and footwear thoroughly before rewearing or discarding. Check the MSDS or contact the chemical supplier for details.
- Do not wear or carry contaminated items into areas having ignition sources or where smoking is allowed.
- Store food and tobacco products in uncontaminated areas.
- Clean yourself thoroughly at the end of the workday.

Why is equipment maintenance necessary?

Regular equipment maintenance can prevent hazardous conditions in the workplace:

- Ensure that maintenance personnel know the possible hazards of the materials they may encounter and any special procedures and precautions needed before they begin work.
- Prevent leaks of grease or other lubricants from equipment where dangerously reactive materials are used.
- Do not allow materials, such as cleaning liquids, paints or thinners, to come into contact with dangerously reactive materials.
- Check to ensure that the job can be done safely before performing shock-, heat- or friction-generating operations, such as hammering, grinding, cutting or welding, on containers or equipment used for dangerously reactive materials.
- Comply with applicable regulations and contact the chemical supplier for advice.

What should I know about Personal Protective Equipment?

If other methods, such as engineering controls, are not available or effective in controlling exposure to dangerously reactive 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 someone who knows how to evaluate the hazards of a specific job and how to select the proper PPE.

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 penetration or damage by the chemical. 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 dangerously reactive chemicals. 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 current Canadian Standards Association (CSA) Standard Z94.3, "Industrial Eye and Face Protectors," provides advice on selection and use of eye and face protectors.

Avoid Breathing Dust, Vapour or Mist

If respirators must be used for breathing protection, there should be a written respiratory protection program to follow. The current CSA Standard Z94.4, "Selection, Care, and Use of Respirators," gives guidance for developing a program. 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 oxidizers or organic peroxides 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.

What should I do in an emergency?

Act fast in emergencies like chemical leaks, spills and fires:

- Evacuate the area at once if you are not trained to handle the problem or if it is clearly 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.

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 help people to know what they must do. Prepare a written emergency plan. Update it whenever conditions in the workplace change.

The MSDSs for the materials used 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 not clear or seem incomplete, contact the material's supplier for help.

It is very important to know the best ways to fight fires involving dangerously reactive materials. For example, using water on water-reactive chemicals can cause the rapid release of lethal gas or, in some cases, violent explosions.

There are numerous other sources to turn to for help in developing your emergency plans. The local fire department can provide assistance in this area, as well as training.

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