How to Work Safely with -Organic Peroxides – Fact Sheet



IS IT POSSIBLE TO SUBSTITUTE FOR ORGANIC PEROXIDES?

Substitution can be the best way to avoid or reduce a hazard. However, it is not always easy or even possible to find a suitable substitute for a particular organic peroxide used for a certain job. Speak to chemical suppliers to find out if safer substitutes are available. Obtain Material Safety Data Sheets (MSDSs) for all possible substitutes. Find out about all hazards (health, fire, corrosivity, chemical reactivity) of these materials before making any changes.

Sometimes changing or modifying a process can reduce the hazards of working with organic peroxides. These 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 ventilation important?

Well-designed and -maintained ventilation systems remove airborne organic peroxides 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 organic peroxides 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 organic peroxides which do not give off airborne contaminants.

Design and build ventilation systems for organic peroxides so that they do not result in an unintended hazard. Avoid using organic materials, such as wood for the construction of the ventilation system. Use explosion-proof electrical equipment, and hoods, fans, shrouds, duct work and air-cleaners made from materials compatible with the organic peroxides. Keep systems used for organic peroxides separate from systems exhausting incompatible substances.

Use non-combustible materials for air cleaning devices like dust collectors.

How should I store organic peroxides?

Store organic peroxides 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 or separate organic peroxide only storage buildings. They may also specify how to construct these storage areas, and the amounts of organic peroxides that can be stored in each area.

What should I know about storing organic peroxide?

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

Store organic peroxides in the 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.

Make sure containers are suitably labelled. For organic peroxides 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. Store according to self accelerating decomposition requirements (SADT) as well.

Protect containers against impact or other physical damage, when storing, transferring or using them. Do not use combustible pallets, such as wood, for storing organic peroxide containers.

Normally, keep containers tightly closed to avoid contamination in storage except when the supplier’s instructions state otherwise.

Storing open or partly open containers of peroxides diluted with solvents, including water, can lead to evaporation of the solvent. This can expose the more hazardous dry peroxide.

Some liquid organic peroxides, however, such as methyl ethyl ketone peroxide, gradually decompose giving off gas. These peroxides are shipped in containers with specially vented caps. Use no other type of cap for containers of these organic peroxides. The vent caps relieve the normal buildup of gas pressure that could shatter an unvented container. Check vent caps regularly to ensure that they are working properly. Keep vented containers in an upright position. NEVER stack vented containers on top of each other.

What should I be aware of in the organic peroxide storage area?

Store organic peroxides separately, away from processing and handling areas. Keep them away from incompatible materials such as strong acids and bases, other oxidizing materials, flammable or combustible liquids and materials that can be oxidized (often called reducing materials or agents). Separate storage can reduce personal injury and damage caused in case of fires, spills or leaks.

Check the reactivity data and storage requirements sections of the MSDS for

details about what materials are incompatible with a specific organic peroxide.

Construct walls, floors, shelving and fittings in storage areas from non-combustible materials that are compatible with the organic peroxides.

Ensure that floors are resistant to penetration by the organic peroxides in storage. Floors should have no cracks in which chemicals could lodge if spilled.

Since liquid organic peroxides flow easily, provide dikes around large liquid storage areas and sills or ramps at door openings. Store smaller amounts in trays made from compatible materials to contain spills or leaks.

Store 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 organic peroxides in areas which are:

- Well ventilated.
- Out of direct sunlight and away from steam pipes, boilers or other heat sources.
- At temperature as recommended by manufacturer/supplier. Always keep the storage area within the recommended temperature range.
- Supplied with adequate firefighting equipment, including sprinklers.
- Supplied with suitable spill clean-up equipment and materials.
- Free of ignition sources such as open flames, hot surfaces, burning tobacco and spark-producing tools and devices.
- Accessible at all times.
- Labelled with suitable warning signs.

At all times:

- Allow only trained, authorized people into storage areas.
- Keep the amount of organic peroxides 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 organic peroxide storage temperatures?

Follow the chemical supplier’s recommendations for maximum and minimum temperatures for storage and use. Higher temperatures can be hazardous since they speed up the decomposition rate of organic peroxides. Where appropriate, keep the maximum storage temperature less than 38°C (100°F) but the supplier may recommend a lower temperature for specific organic peroxides.

Some organic peroxides must be kept at low temperatures in refrigerators or freezers. Use only approved or specially modified units (generally known as “laboratory safe”). Standard kitchen refrigerators and freezers contain many

ignition sources inside the cabinet. If the storage area requires explosion-proof equipment, keep the refrigeration unit and all electrical equipment outside the area. Make connections between the refrigerator cabinet and the other equipment using tubing that passes through the wall of the storage area.

Locate refrigeration equipment in a well-ventilated area. This is needed to carry away peroxide decomposition products that might result from a refrigeration failure.

It can be hazardous to store organic peroxides below the minimum recommended temperatures. For example, acetyl peroxide, which is very shock-sensitive, is usually sold as a 25 percent solution in dimethyl phthalate to make it less sensitive. At temperatures below about -8°C (17°F), pure crystals of shock-sensitive acetyl peroxide form. Do not store organic peroxides which are diluted with water at temperatures below 0°C (32°F) to avoid separating out the pure organic peroxide.

Storage areas need monitoring and alarms that indicate when storage temperatures are higher or lower than required.

What is important to know about dispensing or transferring organic peroxides?

Open and dispense containers of organic peroxides in a special room or area outside the storage area. Do not allow any ignition sources in the vicinity. Take care that the organic peroxides 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 non-sparking materials compatible with the peroxides used. Keep them very clean to avoid contamination.

When transferring organic peroxides from one container to another, avoid spilling or 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. Moreover, if air is used, it may create a flammable atmosphere inside the container.

Glass containers with screw-cap lids or glass stoppers may not be acceptable for some organic peroxides, especially those sensitive to friction and grinding. 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 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.

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

If a water-based formulation freezes, do not chip or grind it to break up lumps of material, 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 is important to know when handling organic peroxides?

Make sure that all areas where organic peroxides are used are clean and free of combustible and other incompatible materials and any ignition sources. Temperatures in peroxide use areas should be controlled so as to not become high enough to cause rapid decomposition.

Processing Equipment

Ensure that processing equipment is clean, properly designed and made from materials compatible with the organic peroxide being used. Find out from the chemical supplier what materials are suitable for the specific peroxide. Copper, brass or lead equipment is dangerous in contact with some organic peroxides at higher temperatures. Some steels and aluminum alloys, zinc and galvanized metal can also cause rapid decomposition of certain organic peroxides.

Diluting Organic Peroxides

Some jobs require diluting organic peroxides prior to use. Do this strictly according to the chemical supplier’s advice. Using the wrong solvent or a contaminated solvent could cause an explosion. For example, methyl ethyl ketone peroxide and cyclohexanone peroxide may explode if they are mixed with acetone, a common solvent. Using reclaimed solvents of uncertain composition can also be hazardous. They may contain dangerous concentrations of contaminants that are incompatible with the organic peroxide.

Hazardous Operations

Some operations involving organic peroxides can be especially hazardous. Accidents have occurred during distillation, extraction or crystallization, because these processes concentrated the organic peroxides. Filtering friction- or shock-sensitive chemicals with materials and devices that produce 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 peroxide and operation.

Using Organic Peroxides with Resins

Organic peroxides are often used as catalysts to activate resins in plastics production. Never mix organic peroxides directly with any accelerators or promoters. A violent explosion may result. Thoroughly mix the accelerator or promoter in the resin mixture before adding the organic peroxide.

It is dangerous to dissolve peroxides in very small amounts of monomer (such as styrene) before adding them to the resin mixture. These “small quantity” mixtures can undergo rapid polymerization giving off a lot of heat. This may result in a fire.

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

How should I dispose of organic peroxides?

Organic peroxide wastes are hazardous. Dispose of unwanted or contaminated organic peroxides promptly using a method the chemical supplier recommends. Consider organic peroxides accidentally mixed with an unknown or foreign material as contaminated. Never attempt to salvage spilled or contaminated organic peroxides.

Dispose of unused peroxide-resin mixes also. Allow partly cured wastes to set and cool in safe, open areas. Doing this helps to prevent the heat produced during the curing reaction from starting a fire in waste containers.

“Empty” drums, bottles, bags and other containers usually contain hazardous residues. Never use these containers for anything else, no matter how clean they seem. Treat them as organic peroxide wastes. Follow the chemical supplier’s advice about how to safely handle or decontaminate “empty” containers.

Store organic peroxide waste in the same way as unused organic peroxides. Use only compatible containers for wastes. Identify their contents with suitable labels.

Never dispose of organic peroxides in ordinary garbage or down sinks or drains that connect to sanitary or storm sewers. Dispose of them according to the supplier’s advice, or through hazardous waste collection and disposal companies. In all cases, dispose of organic peroxide 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.
- Be careful not to contaminate anything that can burn. A serious fire resulted when the same cotton rag was used to clean up both spilled organic peroxide and accelerator.
- Do not use sawdust or other burnable sweeping compounds to clean up organic peroxide spills.
- Properly dispose of unlabelled or contaminated materials containing peroxides.
- Promptly remove combustible wastes, including wood, paper and rags, from work areas.
- Avoid any build-up of organic peroxide dusts on ledges or other surfaces.
- Ensure that all containers for waste are compatible with the organic peroxides used, properly marked and located close to the job.

Why is personal cleanliness important?

Personal cleanliness helps protect you when you are working with organic peroxides:

- Wash hands before eating, drinking, smoking or going to the toilet.
- Remove contaminated clothing and footwear, 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 items into areas having ignition sources or where smoking is allowed.
- Store food and tobacco products in uncontaminated areas.
- Avoid touching yourself with contaminated hands.
- Wash thoroughly at the end of the workday.

Why is equipment maintenance important?

Regular equipment maintenance can prevent leaks or emissions of organic peroxides into 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 organic peroxides are used.
- Do not allow materials such as cleaning solvents, paints or thinners to contact organic peroxides.
- Be very careful when cutting, welding or doing other hot work on organic peroxide containers or equipment.
- Comply with applicable regulations and contact the chemical supplier for advice.

What should I know about Personal Protective Equipment and organic peroxides?

If other methods, such as engineering controls, are not available or effective in controlling exposure to organic peroxides, 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 organic peroxides. 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. T

Avoid Breathing Dust, Vapours or Mists

If respirators must be used for breathing protection, there should be a written respiratory protection program to follow. 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 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.

How should I handle emergencies?

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

- 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.

Check that emergency eyewash stations and safety showers are available wherever accidental exposure to organic peroxides that can damage skin or eyes might occur.

Only specially trained and properly equipped people should handle emergencies. 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 unclear or seem incomplete, contact the material’s supplier for help.

It is very important to know the best ways to fight fires involving organic peroxides. The “built-in” supply of oxidizing gas in organic peroxides makes extinguishing methods based on smothering ineffective (for example, foam or carbon dioxide). Often, cooling with large amounts of water is the only suitable method.

Many other sources can also help develop emergency plans. Local fire departments can assist with fire emergency plans and training.

What are basic safe practices concerning organic peroxides?

Following these basic safe practices will help protect you from the hazards of organic peroxides:

- Read the Material Safety Data Sheets (MSDSs) for all of the materials used

in your work.
- Know all of the hazards (fire/explosion, health, corrosivity, chemical reactivity) of the materials used in your work.
- Know which of the materials you work with are organic peroxides.
- Always follow safe work practices for temperature, avoiding contamination, storage, and quantity (of use).
- Store organic peroxides in suitable, labelled containers (usually their shipping containers).
- Follow the chemical supplier’s advice about maximum and minimum storage and use temperatures.
- Know the SADT “danger temperature” and what to do if the organic peroxide is reaching this temperature.
- Inspect containers for damage or leaks before handling them.
- Store, handle and use organic peroxides in well-ventilated areas and away from incompatible materials.
- Eliminate ignition sources (sparks, smoking, flames, hot surfaces) when working with organic peroxides.
- Handle containers safely to avoid damaging them.
- Keep containers closed when not in use.
- Keep only the smallest amounts possible (not more than one day’s supply) in the work area.
- Dispense organic peroxides carefully, using compatible equipment, into acceptable containers.
- Do not grind or subject organic peroxides to any type of friction or impact.
- Be careful when performing operations such as distillations or separations that concentrate organic peroxides.
- Never return unused or contaminated organic peroxides to their original containers.
- Return unopened containers to the proper storage area and opened containers to a dispensing or premixing area at the end of the day.
- Practice good housekeeping, personal cleanliness and equipment maintenance.
- Handle and dispose of organic peroxide 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 organic peroxides you work with. Have trained personnel and planned emergency procedures specific to organic peroxides.
- Follow the health and safety rules that apply to your job.

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