ENVIRONMENTAL HEALTH AND SAFETY
University of Nebraska-Lincoln

Safe Operating Procedure

(Revised 11/22)

ORGANIC PEROXIDES
CHEMICAL HAZARDS & RISK MINIMIZATION

Background

This SOP is primarily for commercially manufactured organic peroxides. Some concepts may be applicable to organic peroxides created in the lab. For chemicals that can form peroxides, see EHS SOP, ***Use and Storage of Peroxide-Forming Chemicals***.

This SOP supports other EHS training. To determine what training is applicable to your job, please refer to the document: Training Needs Assessment for EHS-Related Topics.

The Globally Harmonized System (GHS) of classification and labeling of chemicals has seven categories for organic peroxides, which are described below.

- Type A – An organic peroxide as packaged that can detonate or deflagrate rapidly;
- Type B – An organic peroxide as packaged that does not detonate or deflagrate rapidly but is capable of undergoing a thermal explosion;
- Type C – An organic peroxide as packaged that possesses explosive properties but will not detonate, deflagrate or thermally explode; and
- Types D through F – Organic peroxides that have shown hazards such as partial detonation, etc., when tested in a laboratory but do not possess these hazards as packaged.

Organic peroxides will be identified with either the exploding bomb or flame pictogram (as shown). In addition, Section 2 of the Safety Data Sheet (SDS) will include one of the following Hazard Statements:

- 240 Heating may cause an explosion (Type A; Exploding Bomb pictogram)
- H241 Heating may cause a fire or explosion (Type B; Exploding Bomb or Flame pictogram)
- H242 Heating may cause fire (Types C – F; Flame pictogram)

Hazards

An organic peroxide is a carbon-based compound containing a “peroxy” group (two oxygen atoms joined together R-O-O-R). It is the double oxygen of the "peroxy" group that makes organic peroxides both useful and hazardous. The peroxy group is chemically unstable, and can decompose with varying degrees of severity. All organic peroxides will burn vigorously, and once ignited will be difficult to extinguish. Some organic peroxides decompose very rapidly or explosively when exposed to heat, friction, mechanical shock, or contamination with incompatible materials. Other organic peroxides will decompose at a slower rate and give off heat as a result of the exothermic reaction, and the rate of reaction can increase to dangerous levels if the heat accumulates. Many organic peroxides give off flammable vapors when they decompose.

Organic peroxides are characterized by a Self-Accelerating Decomposition Temperature (SADT). SADT is the lowest temperature at which a material will undergo self-accelerating decomposition, which could result in an intense fire or detonation. The SADT value will vary with each organic peroxide formulation and the size and shape of its packaging. Some SADTs are well below room temperature. Safe storage requirements will generally be 10 to 20 degrees Celsius below the SADT.

Be aware of lower limits of safe storage as well. Some peroxides have temperature below which storage can be hazardous. 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 in the solution. 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.

Organic peroxides can also be strong oxidizing agents. Combustible materials contaminated with most organic peroxides can catch fire very easily, even spontaneously, and burn very intensely. Extinguishing organic peroxide-fed fires is extremely difficult since the chemical provides the necessary oxygen to support combustion.

Organic peroxide decomposition can also be initiated by chemical contaminants, particularly oxidizing and reducing agents, metal salts, and strong mineral acids. Heavy metals and alloys are another contaminant of concern.

While the main hazards related to organic peroxides are their fire and explosion hazards, they may also be toxic or corrosive. Depending on the material, route of exposure (inhalation, eye or skin contact, or ingestion) and dose or amount of exposure, they can harm the body. Corrosive organic peroxides can also attack and destroy metals.

Organic peroxides are available as solids (usually fine powders), liquids, or pastes. Some materials, such as water, odorless mineral spirits, and some phthalate esters are stable when mixed with organic peroxides and are often used to dilute them. Diluted mixtures or formulations are less likely to explode when exposed to heat or physical shock than undiluted organic peroxide formulations.

Some liquid organic peroxides such as methyl ethyl ketone peroxide gradually decompose giving off gas. These peroxides are shipped in containers with specially vented caps.

Mitigating the Risks of Organic Peroxides

A written, comprehensive project-specific risk assessment with additional oversight is required for any experiment involving "Organic Peroxides- GHS Types A through C." See the companion EHS SOP, ***Chemical Hazard Assessment and Risk Minimization***. A written, comprehensive project-specific risk assessment with additional oversight may also be required for other types of "Organic Peroxides" depending on the specific hazards of an experiment or protocol, as described in the companion EHS SOP referenced above. 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 organic peroxides 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***.
- Purchase the most stable organic peroxide that will do the job.
- Keep amounts on-hand to a minimum.
- Purchase organic peroxides that contain stabilizing diluents.
- Conduct work on the smallest scale possible.
- Store out of direct sunlight and away from steam pipes, boilers or other heat sources, sparks, flames, and other potential ignition sources. Store at a safe temperature range (both upper and lower), as stated by the manufacturer or supplier.
- Use containers and tools/supplies/equipment made from non-metal materials and which are compatible with the peroxides used. Keep them very clean to avoid contamination.
- Never reuse containers that once held organic peroxides.
- Glass containers with screw-cap lids or glass stoppers may not be acceptable for some organic peroxides, especially those sensitive to friction and grinding.
- Do not store organic peroxides that give off gas as they decompose in a tightly sealed, non-vented container. The buildup of gas pressure could rupture it. 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.

- Do not permit open flames and other sources of heat near operations involving organic peroxides. Avoid friction, grinding, and other forms of impact that could initiate a reaction. Avoid operations that might vaporize inert solvents used to reduce the sensitivity of an organic peroxide compound.
- 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.
- Dilute organic peroxides strictly in 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.
- Conduct distillation, extraction or crystallization, and other processes that concentrate the organic peroxides only when it is explicitly known safe to do so. Filtering friction- or shock-sensitive chemicals with materials and devices that produce heat, such as sintered glass filters, can also be hazardous. If the reactivity is not known but must be done, conduct these activities as if the organic peroxide is an explosive.
- Wear appropriate PPE. See EHS SOP, ***Personal Protective Equipment for Chemical Exposures***. At a minimum, laboratory PPE consists of appropriate lab attire (e.g., closed-toed shoes, long pants, non-synthetic blends, etc.) supplemented with flame-retardant lab coats, protective eyewear, and gloves.
- Do not let combustible solids such as paper towels and lab coats become contaminated with organic peroxides. Should this happen, immediately soak and rinse with water to remove the organic peroxide.
- Any observable gassing or distortion of the container should be treated very carefully. Visible gassing of organic peroxide containers may be an indication of imminent, possibly violent decomposition.
- Ensure that an appropriate fire extinguisher 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***.