Self-Reactive and Self-Heating Chemicals

Standard Operating Procedure

Revision Date: 11/20/2023

Laboratory Director (LD) Approval is Required Prior to Performing this Procedure

This standard operating procedure (SOP) outlines the handling and use of Self-Reactive and Self-Heating Chemicals. Review this document and supply the information required in order to make it specific to your laboratory. In accordance with this document, laboratories should use appropriate controls, personal protective equipment, and disposal techniques when handling reactive chemicals. All laboratory workers must read and understand the [*Laboratory Emergencies SOP*](https://ehs.umich.edu/wp-content/uploads/2022/05/LaboratoryEmergencyProceduresSOP.docx) prior to commencing any work in a laboratory.

# Description [Provide additional information as it pertains to your research protocol]

**Self-reactive chemicals** are thermally unstable liquid or solid chemicals liable to undergo a strongly exothermic decomposition even without participation of oxygen (air). A self-reactive chemical is regarded as possessing explosive properties when in laboratory testing the formulation is liable to detonate, to deflagrate rapidly or to show a violent effect when heated under confinement.([1](https://www.schc.org/assets/docs/ghs_info_sheets/Self-Reacting%20Chemicals%20_Final-2017-10_.pdf))

Classes of chemicals often identified as self-reactive include, but are not limited to:

* Those with weak and/or strained bonds
  + Azo, Diazo, Azido, Hydrazine, and Azide Compounds
  + Acetylides (acetylene)
  + Epoxides
  + High nitrogen compounds/tetrazoles
  + Nitrides
  + Nitroso compounds
* Chemicals that can polymerize (monomers)
  + Unsaturated carbon bonds
  + Nitrile groups
  + Vinyl groups
  + Cyanate groups
* Chemicals with high oxygen content
  + Nitro-group substituted organics
  + Organic nitrates o Organic nitrites

A **self-heating chemical** is a solid or liquid chemical, other than a pyrophoric liquid or solid, which, by reaction with air and without energy supply, is liable to self-heat; this chemical differs from a pyrophoric liquid or solid in that it will ignite only when in large amounts (kilograms) and after long periods of time (hours or days).([2](https://www.schc.org/assets/docs/ghs_info_sheets/Self-Heating%20_Final%202017-03_.pdf))

Self-reactive and self-heating chemicals may be indicated by one or more of the following Globally Harmonized System (GHS) hazard categories.

|  |  |  |
| --- | --- | --- |
| **Pictogram** | **Hazard Classification** | **Hazard Statement** |
| https://www.drs.illinois.edu/site-documents/images/Flame.png and/orhttps://www.drs.illinois.edu/site-documents/images/Explosive.png | Self-Reactive Chemicals | Heating may cause an explosion (Type A)  Heating may cause a fire or explosion (Type B)  Heating may cause a fire (Type C-F) |
| https://www.drs.illinois.edu/site-documents/images/Flame.png | Self-Heating Chemicals | Self-heating; may catch fire (Category 1)  Self-heating in large quantities; may catch  fire (Category 2) |

U-M EHS maintains separate SOP documents for other highly reactive substances including [explosives](https://ehs.umich.edu/wp-content/uploads/2016/02/Explosives.docx), [pyrophoric materials](https://ehs.umich.edu/wp-content/uploads/2016/02/PyrophoricMaterials.docx), [water sensitive chemicals](https://ehs.umich.edu/wp-content/uploads/2016/02/WaterSensitiveChemicals.docx), [peroxide forming chemicals](https://ehs.umich.edu/wp-content/uploads/2016/02/PeroxideFormingChemicals.docx), and [oxidizing chemicals](https://ehs.umich.edu/wp-content/uploads/2016/02/OxidizingChemicals.docx). These hazards are not covered in the scope of this SOP; users should reference all appropriate SOPs.

## Process [Write the steps for using the chemical in your research protocol]

# Potential Hazards [Provide additional information as it pertains to your research protocol]

Self-reactive and self-heating chemicals are liable to explode, catch fire, or initiate combustion or deflagration as result of an unwanted, self-sustained reaction.

The **Self-Accelerating Decomposition Temperature (SADT)** is the lowest temperature for self-accelerating decomposition in organic peroxides and self-reactive substances (used in transportation packaging). At or above the SADT, heat evolution from the self-sustained reaction exceeds the heat removal rate from the package and an uncontrolled reaction may occur. This reaction may become violent after a variable period of time after reaching the SADT. SADTs are determined by laboratory testing protocols and are assigned by the manufacturer, specific to the chemical, volume, and packaging. ([3](https://pubs.acs.org/doi/10.1021/acsomega.1c06481))

**Self-heating** occurs when a chemical substance gradually reacts with atmospheric oxygen and generates heat. Over time, the heat production can exceed the dissipation of heat from the reaction, resulting in a fire. This differs from pyrophoric chemicals, which by MIOSHA definition, are liable to ignite within five minutes of coming in contact with air. Large amounts (kilograms) and long periods of time (hours or days) are often required for ignition of self-heating chemicals.

# Engineering Controls [Provide additional information as it pertains to your research protocol]

Chemical inhibitors or diluents are sometimes added by the supplier to reduce the reactivity of chemicals in this class. Pure products are common also; it is critical to understand which, if any additives are present. Uninhibited and undiluted reagents pose a much greater reactivity risk. Always order reagents with inhibitors or diluents if available and compatible with the research.

A critical hazard control measure for self-reactive and self-heating substances is to ensure the material is maintained at a safe temperature, both while in storage and while in use. Store under appropriate refrigeration and utilize cooling measures when conducting reactions to effectively dissipate heat from the reaction.

The **maximum storage temperature** is the temperature below which the product can be stored safely, but at which it may lose assay if stored for long periods. The **minimum temperature** is the temperature above which the product can be stored safely, and below which freezing, crystallization or phase separation of the peroxide from the safety diluent increases the hazard. It is customarily listed only for those products that will exhibit this phenomenon. The **recommended storage temperature** is the best temperature for safe, longer-term storage and for preserving product quality.

The **Emergency Temperature** is 10°C / 18°F below the SADT. Under no circumstances should products be exposed to temperatures at or above the emergency temperature. Planned, preventive action should occur when this temperature is reached. If the SADT is reached, immediately evacuate the area and implement the facility emergency response plan. If decomposition occurs, it should be observed from a safe distance, taking only those measures necessary to preserve life and nearby property

Always work in a fume hood, glove box, or other containment device when handling self-reactive or self-heating chemicals. Special ventilation may be required if these materials are used outside a fume hood. If your research does not permit the handing of reactive chemicals in a fume hood you must contact Environment, Health & Safety (EHS) to review the adequacy of all special ventilation.

Self-heating, but not self-reactive, chemicals require oxygen to undergo a self-heating reaction. Working under an inert atmosphere or using air-free techniques will help eliminate potential reaction with atmospheric oxygen.

Where the eyes or body of any person may be exposed to reactive chemicals, suitable facilities for quick drenching or flushing of the eyes and body shall be provided within the work area for immediate emergency use. Bottle type eyewash stations are not acceptable.

# Work Practice Controls [Provide additional information as it pertains to your research protocol]

Thoroughly review the safety data sheet and product literature to understand the specific properties of any self-reactive or self-heating substance.

Strictly follow the recommended and maximum storage temperatures provided by the manufacturer.

Whenever possible, utilize the least reactive reagents possible for the necessary procedure.

Minimize quantities, both in reaction size and storage quantity. The mathematical principle of the square-cube law dictates that as a shape grows in size, its volume grows faster than its surface area. In practice, this means that the substance’s ability to adequately release heat into the environment is inversely proportional to the volume of the substance. Exercise caution when scaling up a reaction and ensure cooling measures account for this principle.

Designate areas where reactive chemicals are stored and manipulated.

**Containers:** All reactive chemicals must be clearly labeled with the correct chemical name. Handwritten labels are acceptable; chemical formulas and structural formulas are not acceptable.

Hazard assessment of work involving reactive chemicals should address proper use and handling techniques, fire safety (including the need for Class D fire extinguishers), storage, the specific reactive nature of the material (such as water and air reactivity), and waste disposal issues.

# Personal Protective Equipment [Provide additional information as it pertains to your research protocol]

Safety shielding is required any time there is a risk of explosion, splash hazard or a highly exothermic reaction. All manipulations of reactive chemicals that pose this risk should occur in a fume hood with the sash in the lowest feasible position. Portable shields, which provide protection to all laboratory occupants, may be acceptable.

Lab coats, closed toe shoes, long pants, and long sleeved clothing must be worn when handling reactive chemicals. Additional protective clothing should be worn if the possibility of skin contact is likely.

Gloves must be worn when handling reactive chemicals. Disposable nitrile gloves provide adequate protection against accidental hand contact with small quantities of most laboratory chemicals. Lab workers should contact EHS for advice on chemical resistant glove selection when direct or prolonged contact with hazardous chemicals is anticipated.

Adequate safety glasses with side shields that meet the requirements of ANSI Z87.1 must been worn. Safety glasses with side shields do not provide adequate protection from splashes; therefore, when the potential for splash hazard exists, a face shield (with safety glasses) or splash goggles must be worn.

# Transportation and Storage [Provide additional information as it pertains to your research protocol]

Reactive chemicals should be stored in a cool and dry location. Keep reactive chemicals segregated from all other chemicals in the laboratory. Minimize the quantities of reactive chemicals stored in the laboratory.

Ensure appropriate temperature control at all times.

Store away from acids, bases, oxidizers, or any other incompatible chemicals. Incompatible chemicals may initiate an unwanted reactions.

Store chemicals under inert atmosphere if prescribed.

Date all containers upon receipt. Examine storage containers frequently. Dispose of any container that exhibits salt build up on its exterior. Dispose of all reactive chemicals whenever they are no longer required for current research.

Never return excess chemicals to the original container. Small amounts of impurities may be introduced into the container that may cause a fire or explosion.

# Waste Disposal [Provide additional information as it pertains to your research protocol]

All materials contaminated with reactive chemicals should be disposed of as hazardous waste. Because most spent, unused, and expired chemicals/materials are considered hazardous wastes, they must be properly disposed of. **Do not dispose of chemical wastes by dumping them down a sink, flushing in a toilet or discarding in regular trash containers, unless authorized by EHS Hazardous Materials Management (HMM)**. Contact EHS-HMM at (734) 763-4568 for waste containers, labels, manifests, waste collection and for any questions regarding proper waste disposal. Also, refer to the EHS [Hazardous Waste](http://ehs.umich.edu/haz-waste/) Web page for more information.

# Training of Personnel

All personnel shall read and fully adhere to this SOP when handling self-reactive or self-heating chemicals.

# Certification

I have read and understand the above SOP. I have received approval from my Lab Director to perform this procedure. I agree to contact my Lab Director if I plan to modify this procedure.

|  |  |  |  |
| --- | --- | --- | --- |
| Name | Signature | UMID # | Date |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |

|  |  |
| --- | --- |
| Lab Director | Revision Date |

### Major Revisions (Tracking purposes only -- Do not print as part of SOP)

|  |  |
| --- | --- |
| Date | Revision |
| 03-23-18 | Put into EHS format, changed department name, and fixed links. Revised Spill Procedure section (AJK). |
| 02-25-19 | Updated links, certification and formatting (DML) |
| 05-18-20 | Updated editing rights to headings (RSH) |
| 08-22-22 | Updated document to cover self-reactive and self-heating chemicals, expanded document sections with additional details, and removed emergency procedures (JMW). |
| 11/20/23 | Minor phrasing edits (JMW) |