ENVIRONMENTAL
HEALTH AND SAFETY
University of Nebraska-Lincoln

Safe Operating Procedure

(Revised 8/24)

SELF-REACTIVE SUBSTANCES & MIXTURES HAZARDS & RISK MINIMIZATION

Background

The United States Occupational and Safety Health Administration (OSHA) defines self-reactive chemicals as follows: self-reactive chemicals are thermally unstable liquid or solid chemicals liable to undergo strongly exothermic decomposition even without the participation of oxygen (air). This definition excludes chemicals classified as explosives, organic peroxides, or as oxidizing liquids or solids.

OSHA established seven types of self-reactive chemicals as summarized in the following table.

Type	Pictogram	Description	Signal Word	Hazard Statement
A		As packaged, can detonate or deflagrate rapidly	Danger	Heating may cause an explosion
B	 	As packaged, will not detonate or deflagrate rapidly but is liable to undergo thermal explosion	Danger	Heating may cause a fire or an explosion
C		As packaged, possesses explosive properties but will not detonate, deflagrate, or thermally explode	Danger	Heating may cause a fire
D		When tested in a lab, can partially detonate or deflagrate slowly and no violent	Danger	Heating may cause a fire

		effect when heated under confinement		
E		When tested in a lab, does not detonate or deflagrate and low or no effect when heated under confinement	Warning	Heating may cause a fire
F		When tested in a lab, does not detonate, deflagrate, no effect when heated under confinement and shows no explosive power	Warning	Heating may cause a fire

Hazards

As indicated by the hazard statements associated with self-reactive chemicals and mixtures, the primary hazards are fire and explosion. These chemicals may be pure products, diluted in other materials to make them more stable or inhibited to delay reactivity.

Self-reactive chemicals may have a Self Accelerating Decomposition Temperature (SADT). SADT represents the lowest temperature at which a particular chemical will undergo self-accelerating decomposition, which could result in intense fire or detonation. The SADT value varies with each self-reactive formulation and the size and shape of its packaging. Some SADTs are well below room temperature. Storage requirements will generally be 10 to 20 degrees C below the SADT.

In addition to SADTs, some self-reactives have temperature below which storage can be hazardous. Some self-reactive compounds dissolved in solvents may crystalize below certain temperatures concentrating them and making them more sensitive. Do not store self-reactives which are diluted with water at temperatures below 0°C (32°F) to avoid separating out the pure chemical.

Some self-reactives may gradually decompose giving off gas. These are shipped in containers with specially vented caps. Check vent caps regularly to ensure that they are working properly. Keep vented containers in an upright position.

Some self-reactive chemicals contain an inhibitor, which functions to scavenge free radicals as they are formed during the product's slow decomposition. Inhibitors may also scavenge air or other contaminants depending on the circumstance. As such, inhibitors are consumed over time. Depending on the self-reactive, refrigeration may slow this process. If an inhibitor is exhausted, the chemical may spontaneously self-react or become sensitized such that any input (e.g., bumping the container, warming the chemical, etc.) can result in an explosion. All inhibited chemicals need to be checked as recommended by the manufacturer and have either inhibitor added or the chemical disposed prior to the inhibitor becoming exhausted.

A similar case exists for diluents. Care must be taken so that the diluent is not lost due to evaporation, etc. If the diluent is lost, the self-reactive may react spontaneously or in response to the slightest disturbance (e.g., the next time it is handled).

In the OSHA definition of self-reactives, the phrases 'as packaged' and 'when tested in a laboratory' are used. The reason for this is that some self-reactive chemicals need a minimum quantity, depending on their environment, in order to become potentially self-reactive. The minimum quantity is that which is needed for heat from slow decomposition to begin to accumulate in the container. Below the minimum quantity, too much heat is lost to the environment. If the heat is not lost to the environment, the rate of the decomposition reaction continuously accelerates. 'As packaged' limits are not published for self-reactive chemicals but are reflected in the classification (e.g., Type C). Purchasing the smallest amount that will work is a prudent practice for minimizing this hazard.

Conducting intentional reactions with these chemicals can be dangerous. The reactions are very exothermic and are subject to a variety of potentially inter-related factors including:

- **Surface area versus volume**. Volume increases by the cube while surface area increases by the square. Thus, the ability to cool a reaction (i.e., draw the heat to the surface of the reaction vessel) falls dramatically as reactions are scaled up. Directly related to this is the need to mix reactants to assure a steady reaction rate and transmit excess heat to the surface of the reaction vessel where it can be dissipated to the environment.

- **Removing heat/insulation**. Some reactions may need some amount of initial heat input or insulation to initiate the reaction. However, once the reaction begins and becomes exothermic, it may be necessary to quickly remove the heat source and insulation. If this is not done, a runaway reaction can result.

- **Rate of reagent addition**. Small increases in the rate of reagent addition can dramatically increase the reaction rate.

- **Changes in reactant concentrations**. Like changes in the rate of addition, increasing the concentration of reactants can dramatically increase the rate of the reaction.

- **Catalysts**. Not all catalysts are the same even if they are the same chemical. Different vendors, the age of the catalyst, and how the catalyst was stored can affect the reaction rate.

- **Induction periods**. Some reactions start very slowly and only begin to increase once certain conditions are met such as conversion of a pre-catalyst to an active catalyst, creation of products that then become catalysts, or generation of heat as the reaction slowly progresses.

The margin between a stable and a runaway reaction is reported to vary by as little as 10 to 20 degrees C. This margin can be reduced or eliminated by changing one or more of the above factors.

Mitigating the Risks of Self-Reactive Chemicals

A written, comprehensive project-specific risk assessment with additional oversight is required for any experiment involving a Type A, B, or C self-reactive substance or mixture. See the companion EHS SOP, ***Chemical Hazard Assessment and Risk Minimization***. A specific risk assessment with additional oversight may also be required for other Types of self-reactives depending on the specific hazards of an experiment or protocol, as described in the companion EHS SOP referenced above. General risk mitigation measures for self-reactives are as follows:

- Conduct a thorough literature search, including review of Safety Data Sheets, to establish a thorough understanding of the properties of the self-reactives 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***.

- Follow general safe chemical handling practices as described in the EHS SOP, ***General Guidance for Chemical Ordering, Receipt, Distribution, Use and Storage***.

- Observe all specific safety procedures established for the laboratory/procedure.

- Wear appropriate PPE. See EHS SOP, ***Personal Protective Equipment for Chemical Exposures***. When there is risk of explosion, consideration should be given to face shields and heavier than standard lab coats, leather outer garments, or garments and gear specifically designed to provide protection from blasts.

- Keep amounts on-hand to a minimum. Self-reactivity is related to the size of the container in which it is shipped.
- When possible, select the most stable self-reactive chemical suitable for the experiment.
- When possible, purchase self-reactives that contain stabilizing diluents or inhibitors.
- Conduct work on the smallest scale possible. Do not scale up a reaction before discussing it with the responsible faculty member or supervisor.
- If any changes are made to a reaction (e.g., chemicals/catalysts from a different vendor, etc.) conduct the initial reaction at the smallest scale possible to determine if there is a change in the reaction rate.
- Use containers and dispensing equipment such as scoops or spatulas that the chemical supplier recommends. Keep them very clean to avoid contamination.
- Glass containers with screw-cap lids or glass stoppers may not be acceptable for some self-reactives, 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.
- 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.
- Use diluting/carrier solvents strictly in accordance with the chemical supplier's advice or well-established research protocols. Using the wrong solvent or a contaminated solvent could cause a fire or explosion. Using reclaimed solvents of uncertain composition can also be hazardous. They may contain dangerous concentrations of contaminants that are incompatible with the self-reactive compound.
- Design experiments/apparatus such that strict control can be maintained over the temperature of the reaction vessel. Make contingencies should a reaction runaway occur such as proper venting of the apparatus, ventilation (i.e., work conducted in a fume hood), and shielding.

- Only those chemicals involved in the operation should be in the vicinity of the work being conducted. Bottles/containers from which they were dispensed, and other chemicals need to be put away.

- Incorporate risk minimization strategies into the experimental design that account for the unique hazards of self-reactives: surface area versus volume; heat/insulation; rate of reactant addition; reactant concentration; catalysts; and induction periods.

- Check all self-reactives with an added inhibitor or diluent as recommended by the manufacturer and either replenish the inhibitor or diluent as needed or dispose of the chemical via EHS before the inhibitor or diluent is exhausted.

- Store self-reactives with a SADT at the appropriate safe storage temperature (generally 10 to 20 degrees C below the SADT).

- Do not store self-reactives which are diluted with water at temperatures below 0°C (32°F) to avoid separating out the pure chemical.

- If shipped in containers with specially vented caps, check vent caps regularly to ensure that they are working properly. Keep vented containers in an upright position.

- Know what actions to take in the event of an emergency. Ensure that an appropriate fire extinguisher and properly functioning safety shower are readily available.

- See the EHS SOP, ***Fire Safety – General Prevention and Extinguishing*** and the EHS web-based training program titled ***Fire Extinguisher Training***.