



SELF-HEATING SUBSTANCES HAZARDS & RISK MINIMIZATION

Background

The Globally Harmonized System (GHS) of classification and labeling of chemicals defines a self-heating substance as follows: *a solid or liquid substance or mixture, other than a pyrophoric liquid or solid, which, by reaction with air and without energy supply, is liable to self-heat; this substance or mixture 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).*

The GHS establishes two categories for self-heating substances or mixtures. Category 1 materials are more reactive and self-heat more readily and in smaller amounts than Category 2 materials. Self-heating substances will be identified with the pictogram shown below. In addition, Section 2 of the Safety Data Sheet (SDS) will include one of the following hazard statements:



- H251 Self-heating; may catch fire
- H252 Self-heating in large quantities; may catch fire

Fire Hazards

Self-heating of a substance or mixture is a process where the gradual reaction of that substance or mixture with oxygen in air generates heat. If the rate of heat production exceeds the rate of heat loss, then the temperature of the substance or mixture will rise which, after an induction time, may lead to self-ignition and combustion.

The fire hazard presented by self-heating substances is due to four inter-related factors.

- Volume of material present
- Rate at which the material self-reacts
- Temperature of the surroundings/insulating factors
- Availability of oxygen/moisture



In order to self-heat, the material must generate more heat than it loses to the environment. Mathematically, surface area increases by the square while volume increases by the cube. It is for this reason that larger volumes of material are more susceptible to self-heating than smaller volumes; larger volumes have proportionally less surface area over which to lose heat than smaller volumes. This is reflected in the GHS test criteria for defining a self-heating substance, which states that chemicals with a temperature of spontaneous combustion higher than 50° C (122° F) for a volume of 27 m³ shall not be classified as self-heating chemicals.

The configuration of the reacting mass is also important in determining whether sufficient heat could build up to the point of ignition. If the configuration of the material does not allow heat buildup, then combustion will not occur. However, this must be balanced with consideration of increased surface area susceptible to oxidation.

Self-reaction rates vary from one material to the next, and are based on chemical structure and susceptibility of molecular bonds to oxidation. For those that are more susceptible to self-heating, smaller volumes are needed to self-ignite.

The surrounding temperature and insulating factors can influence the rate of reaction. In a well-insulated environment, heat of oxidation is retained rather than dissipated to the surrounding environment and contributes to an increased rate of reaction, which then leads to more heat as the exothermic process of oxidation accelerates. Likewise, heat from the environment can accelerate the rate of reaction sufficiently to induce combustion.

Availability of air is another important factor. There must be enough oxygen present to permit the oxidation process but not so much that any heat produced by the reaction is carried away by convection as rapidly as it is formed. Loose fitting/missing caps and/or failing to inert containers after they have been opened can contribute to the potential for self-heating. By definition, self-heating substances react with air; not moisture. However, moisture can contribute to the reaction rate in some self-heating substances.

Mitigating the Risks of Self-Heating Substances

First and foremost, conduct a general hazard analysis/risk assessment of the work to be conducted and verify that a written, comprehensive project-specific risk/assessment with additional oversight is not in order, as described in the companion EHS SOP, ***Chemical Hazard Assessment and Risk Minimization***. General risk mitigation measures for self-heating substances 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-heating substances to



be handled with particular consideration given to the procedures and tasks to be conducted.

- Review instructions and precautions provided by the manufacturer/distributor with respect to recommended storage and handling instructions, particularly with respect to establishing an inert environment in the container after opening. Store in a cool, dry place and in tightly closed containers.
- 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 laboratory/work attire and Personal Protective Equipment (PPE). Standard lab/work attire consists of closed-toed shoes and long pants. At a minimum, PPE consists of flame-resistant lab coat (or other outer garment, eye protection, and gloves). See EHS SOP, **Personal Protective Equipment for Chemical Exposures**.
- Keep amounts on-hand to a minimum.
- Keep away from light, sources of heat, moisture, and other flammable and combustible materials.
- Avoid the hazards of work at elevated temperatures; implement appropriate risk mitigation measures.
- When risk of self-heating to the point of ignition is high, work in an inert environment.
- Conduct work on the smallest scale possible.
- Design experiments/apparatus so that temperature and rate of reaction is controlled.
- Make contingencies should a reaction runaway such as proper venting of the apparatus, ventilation (i.e., work conducted in a fume hood), and shielding.
- 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**.