

Chemical Storage & Waste Handling Standard

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PURPOSE

Hazardous and potentially hazardous chemicals are routinely used in laboratories across the University of Calgary campuses and have the potential to cause injury to people and/or the environment.

This Standard contains information on the safe handling, use, and storage of chemicals and chemical wastes at the University of Calgary to protect people, assets, and the environment. The information within this document addresses legislated requirements as found in the following regulations, codes, and standards: Hazardous Products Regulations, Alberta Occupational Health and Safety Code, National Fire Code – Alberta Edition, National Fire Protection Association (NFPA) Code, and Transportation of Dangerous Goods (TDG) Act and Regulations. These requirements and guidelines must be reviewed by all workers prior to starting work involving chemicals and may be used in the development of individual site-specific Standard Operating Procedures.

SCOPE

This Standard applies to all persons handling, using, or storing chemicals or chemical wastes under the auspices of the University of Calgary. This includes purchased chemicals, mixed, diluted, or aliquoted chemicals, synthesized chemicals, intermediary, and final waste products within the laboratory, prior to collection by Hazardous Materials (HazMat) Services. For biohazardous and radioactive materials, and disposal processes, please refer to the resources at the end of this document.

PROPERTIES & HAZARDS

WHMIS 2015

The electronic version is the official version of this standard. EHS-LAB-1027 – Chemical Storage & Waste Handling Standard Page 1 of 32

Laboratory Safety Manual Issued: 2022.07.06

Chemicals are classified based on hazard type in the Hazardous Products Act (Schedule 2), the Hazardous Products Regulations (Part 7 – Physical Hazard Classes; Part 8 – Health Hazard Classes), and the Transportation of Dangerous Goods Act and Regulations. These classifications are based on the physical or chemical properties of a product as well as the ability of a product to cause a health effect.

- **Physical Hazards** flammables, combustibles, pyrophorics, water-reactives, organic peroxides, self-reactive substances, self-heating substances, oxidizers, corrosives, and more that are not otherwise classified.
- **Health Hazards** acute toxicity, aspiration, carcinogenicity, reproductive toxicity, germ cell mutagenicity, specific organ toxicity, ototoxicity, skin/eye corrosion, irritation, sensitization, and more which are not otherwise classified.

RESPONSIBILITIES

Managers/Supervisors/Principal Investigators (PIs)

- Facilitate the protection of the health and safety of people within their areas of responsibility.
- Utilize the Hazard Assessment and Control form (HACF) to identify and communicate hazards related to the tasks being performed and implement the necessary controls.
- Develop and maintain written Standard Operating Procedures (SOPs) detailing the specific procedures for the use, handling, and storage of hazardous chemicals used in their laboratory or workspace.
- Ensure that workers are trained and competent prior to commencing work.
- Ensure that safe work practices are followed in their area.

Workers

- Review this standard prior to working with hazardous or potentially hazardous chemicals.
- Review the Safety Data Sheet (SDS) for the chemical in use.
- Follow the guidelines and requirements set out in this standard, and any additional requirements (e.g. SOPs) as determined by the Principal Investigator or supervisor regarding chemical handling, use, and storage for their area.
- Report hazardous conditions immediately to their supervisor.
- Wear and properly maintain the required personal protective equipment (PPE).

Facilities

• Develop and implement design guidelines compliant with appropriate legislation, codes, standards, and best practices affecting construction and renovations in areas where hazardous or potentially hazardous chemicals will be used or stored.

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Environment, Health and Safety (EHS)

- Provide information to lab users on appropriate legislation, codes, standards, and best practices for use, handling, and storage of hazardous or potentially hazardous chemicals.
- Assist departments with interpretation and methods of compliance with this standard.
- Periodic review and revision to this standard.

Table of Contents

Section	Page
Use & Handling	6
Chemical Storage	7
General Storage Guidelines	7
Labelling Requirements	8
Chemical Compatibility	8
Storage Segregation	9
Special Chemical Storage Requirements	
Flammable Liquids	
Pyrophoric and Water-reactive Chemicals	
Time-sensitive Chemicals	
A. Peroxide forming Chemicals	
B. Self-reactive and Explosive Chemicals	
C. Other Time-sensitive Chemicals	
IARC-classified Chemicals	
Waste Handling Guidelines	
General Waste Handling Guidelines	
Special Waste Handling & Storage Requirements	
Oxidizing Chemicals	
Flammable Liquid Wastes	21
Pyrophoric and Water-reactive Chemicals	
Time-sensitive Chemicals	
A. Peroxide forming Chemicals	23
B. Self-reactive and Explosive Chemicals	23
C. Other Time-sensitive Chemicals	23
Emergency Procedures	24
First Aid	24
Spill Response	24

Relate	Related Documents & Programs24		
Refere	References		
Appen	dix	26	
١.	Chemical Storage Flowchart	26	
١١.	Worksite Labels – Examples	28	
III.	Time-sensitive Chemicals	29	

USE & HANDLING

Table 1. Workplace Hazardous Materials Information System (WHMIS 2015) hazard classification and descriptions of the different laboratory chemical hazards.

Hazard Classification	Description		
	Flammable liquids/solids		
	Chemicals with the ability to ignite and cause, or contribute to, fire or explosion.		
	Pyrophoric materials		
	Chemicals which can ignite spontaneously when exposed to air.		
Flammable	water-reactive materials		
\wedge	chemicals which can react with water to release a hammable gas, which may ignite		
	spontaneously.		
\sim	Chemicals which possess explosive properties or can detenate or deflagrate rapidly under		
	contain conditions		
	Solf reactive or solf heating materials (or mixtures)		
	Substances and mixtures which can explode or react, on their own or when heated		
	Substances and mixtures which can self-heat by reaction with air and without energy supply		
	Finlosives		
	Substances or mixtures liable to detonate deflagrate rapidly or show a violent effect when		
Explosivo	subject to external force (shock, friction, sparks).		
	Self-reactive materials (or mixtures)		
	Substances and mixtures which can explode or react, on their own or when heated.		
	Organic Peroxides		
	Chemicals which possess explosive properties or can detonate or deflagrate rapidly under		
	certain conditions.		
Oxidizer			
	Chemicals which can cause, support, or accelerate the combustion of other materials. Can		
	cause explosions.		
V			
Corrosive			
	Chemicals which cause corrosive damage to metal, as well as skin, eyes.		
Тохіс			
	Chemicals which can cause toxicity or death with short exposure to small amounts,		
	including substances that can release toxic gas upon contact with water.		
\			
Health Hazard (serious)			
	Chemicals which can cause, or are suspected to cause, serious health effects.		
	Respiratory, reproductive, target organ toxicity or carcinogenicity.		
Health Hazard			
\wedge	Chemicals which can cause health effects or damage to the ozone layer.		
	Skin and eye irritation/sensitization and target organ toxicity.		
×			
Environmental Hazard*			
¥ .	Chemicals which can cause damage to the aquatic environment.		

*The Environmental Hazard group and its classes were not adopted in WHMIS 2015. The class might still be listed on labels and in SDSs. WHMIS 2015 allows including information about Environmental Hazards.

Workers must be familiar with the hazards of the chemicals they handle and must be trained by competent laboratory personnel in the proper handling and storage of these materials. Improper handling or storage can result in spills, incompatibilities, uncontrolled reactions, injury, illness or environmental release. Refer to Table 1 for the hazard classifications of different types of chemicals, common examples, and a general description. Always review the SDS for the chemical in use and ensure the HACF appropriately identifies the hazards and controls in place.

CHEMICAL STORAGE

General Storage Guidelines

- Ensure all containers of hazardous materials are properly identified and labelled (see below for labelling requirements).
- Read chemical labels and the SDS for specific storage requirements.
- Label storage unit/area with the appropriate warning label.
- Appropriately segregate chemicals based on hazard class and compatibility (see Table 2)
 - Use secondary containment to separate incompatible chemicals stored in the same area.
- All chemicals, including wastes, must be capped, and stored in an upright position.
- Do not accumulate materials or wastes in excess within fume hoods, which restricts airflow.
- Minimize storage of hazardous waste, dispose of waste regularly.
- Never keep hazardous chemicals or waste in a public area or corridor.
- Avoid storing any hazardous chemicals higher than eye level, particularly corrosives.
- Do not store chemicals in direct sunlight or near heat sources.
- Do not store chemicals on the floor, if unavoidable you must use secondary containment.
- Flammable liquids, including waste, are to be stored in a certified flammable storage cabinet.
 - Flammable liquids within approved safety containers are exempt, as these containers afford fire protection even when outside a certified flammable storage cabinet.
- If flammables need to be chilled, store them in a spark-proof refrigerator, not in a standard refrigerator.
- No flammable storage is permitted in an exit corridor or within 1.5 m of an exit.
- Hazardous chemicals must be inventoried, and this inventory reconciled annually.
- Store highly toxic chemicals (LD 50 < 50 mg/kg) in a dedicated, locked cabinet.
- Follow recommended timelines on assessments and disposal of chemical as per SDSs and as outlined in this document.
- Date peroxide forming chemicals upon receipt as well as upon opening.

Properties and potential hazards of newly synthesized compounds or research samples are best understood by research groups. Storage guidelines and requirements as described in this standard should be followed based on their estimation of potential hazards of the material.

Refer to the *Chemical Storage Flowchart* in the Appendix to determine the best storage solution based on hazard classifications.

Labelling Requirements

Containers with decanted hazardous products and with synthesized compounds where the hazards are known that are stored (i.e. not immediately used) in laboratories must have a worksite label in place. This includes samples used for educational or demonstration purposes.

Outdated (e.g. WHMIS 1988 labels), damaged or illegible supplier labels on a container must be replaced with a worksite label.

A worksite label must contain the following information:

- Product identifier (name of the hazardous compound)
- Safe Handling Precautions
 - Precautionary statements
 - May also include: Hazard Statements, signal word and/or WHMIS 2015 pictograms
- Reference to the SDS, if available.

See Appendix for examples of worksite labels.

Containers with substances produced or samples collected in a laboratory for research and development purposes are exempt from WHMIS labelling requirements. Examples are diagnostic specimen, e.g. blood samples, soil or water samples containing hazardous material, or mixtures of hazardous products that are being developed. Containers must be less than 10 kg in size.

Clear identification is still required for these newly synthesized substances or research samples, which can be in form of a reference to a laboratory notebook or a chemical identifier/acronym that all lab personnel is familiar with.

Chemical Compatibility

Chemical containers should not be organized alphabetically, but by hazard class and compatibility.

Mixing of incompatible materials (chemicals or wastes) can result in excessive heat, fires, explosions, over-pressurization, generation of toxic and/or flammable vapors, formation of toxic compounds or friction-sensitive compounds, or other dangerous situations. If you plan to mix chemicals, you must first determine whether any dangerous situations may result. This determination also applies to wastes; when mixing wastes within a waste container or grouping them in a bag or tray, you must first

determine their compatibility.

Consult the SDS to determine the hazard identification (Section 2), storage requirements (Section 7) and any potential incompatibility (Section 10). Keep in mind that some chemicals have secondary hazards as well that need to be considered in segregation decisions.

Storage Segregation

Recommended storage and general incompatibilities for the different hazard classes are listed in Table 2. Some conflicting and notable incompatibilities are further described below.

Table 2. Recommended storage and incompatibilities of the different hazard classes. Refer to the Chemical Storage Flowchart in the Appendix for further guidance.

Class of Chemical Recommended Storage		Examples	Incompatibles
Flammable	Certified flammable storage cabinet.	Acetone Ethanol Toluene	Oxidizers
Pyrophoric	Under inert atmosphere or in sealed container.	Organometallic reagents Phosphorus	Atmosphere/ air
Water-Reactive	Dry, cool location. Away from a water source. Protect from fire suppression sprinklers and splashes.	Sodium metal Potassium metal	Water Aqueous solutions Oxidizers
Self-reactive/ Explosive	Separate from all other chemicals.	Organic azides	Flammable liquids Oxidizers Corrosives
Oxidizer	Separate from flammable and combustible material.	Peroxides Perchlorates Nitrates	Reducing agents Flammables Combustibles
Corrosive – Acid	Corrosive storage cabinet, away from bases.	Hydrochloric acid	Bases Cyanides
Corrosive – Base	Corrosive storage cabinet, away from acids.	Metal hydroxides Amines	Acids
Τοχίς	Certain toxic materials require a locked cabinet. Refer to SDS.	Cyanides	No general incompatibilities. Refer to SDS

Conflicting compatibilities:

- Concentrated Acetic acid and Formic acid are flammable and incompatible with other acids. These acids must be stored in a flammable cabinet with secondary containment.
- If only one corrosive cabinet is available and storage is required for both acids and bases, use separate compartments and secondary containment for each.

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Laboratory Safety Manual Issued: 2022.07.06 Notable incompatible situations:

- Bleach incompatible with alcohols, acids, ammonia, metals, organic solvents
- Hydrogen peroxide incompatible with combustible materials, alcohols, acetone
- Acetic acid incompatible with nitric acid, perchloric acid, peroxides
- Acetone incompatible with concentrated nitric acid, sulfuric acid
- Acids *incompatible with* azides
- Perchloric acid incompatible with organic material (including paper, wood)

Special Chemical Storage Requirements

Oxidizing Materials: refer to UCalgary Oxidizing Materials Standard Corrosive Materials: refer to UCalgary Corrosive Materials Standard Toxic Materials: refer to UCalgary Toxic Materials Standard Compressed Gas Cylinders: refer to UCalgary Compressed Gas Cylinder Standard Cryogenic Materials: refer to UCalgary Cryogenic Materials Standard

Flammable Liquids

Within this standard, the term flammable liquid includes any dangerous goods that are classified as flammable or combustible liquid as determined by their flashpoint. Generally, flammable liquids can ignite and burn easily at normal working temperatures, while combustible liquids burn at temperatures that are usually above working temperatures. Some examples for commonly used flammable and combustible liquids are listed in Table 3. To apply segregation requirements, combustible liquids are always to be treated as flammable liquids.

Flammable liquids may have associated secondary hazards. Refer to SDS for information on any secondary hazards and additional storage or segregation requirements.

Flammable liquids must be stored in certified flammable storage cabinets or storage rooms designed for flammable materials. The maximum quantity stored in an approved cabinet(s) must not exceed 500 L. Storage of flammable liquids outside of a certified flammable storage cabinet or storage room is permitted provided such storage does not exceed 5 L total volume in a single room. All quantity limits include any flammable liquid wastes in the laboratory.

Exempt: The storage quantity limits do not apply to those products containing not more than 50% by volume of water-miscible flammable liquids with the remainder of the solution being non-flammable, when in closed containers having a capacity of not more than 5 L.

Flammable liquids within approved safety containers are also exempt, as these containers afford fire protection even when outside a certified flammable storage cabinet.

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Laboratory Safety Manual Issued: 2022.07.06 Table 3. Common flammable and combustible liquids (non-exhaustive).

	Examples
	Ethers: diethyl ether, diisopropyl ether, tetrahydrofuran, dioxanes
	Aliphatic alcohols: methanol, ethanol, 2-propanol (isopropanol), 2-butanol
Elemente la literatul	Alkanes: propane, (iso)pentane, (cyclo)hexane, heptane
	Ketones: Acetone, methyl ethyl ketone (2-butanone)
(hashpoint below 37.8C)	Aromatics: Benzene, chlorobenzene, toluene, xylenes
	Acetonitrile
	Ethyl acetate
	Organic acids: Acetic acid, formic acid
Combustible liquid	Aromatics: benzaldehyde, benzyl alcohol, bromobenzene
(flashpoint above 37.8 and	Dimethyl sulfoxide
below 93.3 C)	Ethylene glycol
	Glycerin

Containers of flammable liquids must be kept closed when not in use. Glass or plastic containers are allowed for volumes up to 5 L. Containers with a capacity larger than 5 L must be approved safety containers (e.g. approved "safety can", Figure 1). Containers larger than 25 L are not allowed to be stored in a laboratory.

Flammable liquids must be kept away from ignition sources such as open flames, hot surfaces, sparks from welding or cutting, operation of electrical equipment, and static electricity.



Figure 1. Example of an approved safety can for flammable liquids.

Flammable liquids must not be stored in areas where they may be subject to temperature extremes or pressures that could cause their containers to become deformed or rupture, or physical impact, or to temperature extremes that could cause a chemical reaction or chemical instability such that a fire could occur.

Flammable liquids must not be stored in or adjacent to exits, elevators or principal routes that provide access to exits. Where fridges or freezers are used to store flammable liquids, they must be designed to be spark-proof and CSA-approved.

All dispensing and processing of flammable liquids must be performed inside a fume hood or wellventilated area. Electrical equipment used in fume hoods where flammable liquids are handled must be CSA-approved for hazardous locations (i.e. spark-proof equipment, e.g. blenders and stirring motors).

Flammable liquids that are moved in glass vessels must be carried in an appropriately moulded rubber, plastic or styrofoam container to prevent accidental breakage. Follow UCalgary Movement of Hazardous Materials Guidelines.

Pyrophoric and Water-reactive Chemicals

Pyrophoric chemicals can ignite spontaneously when exposed to air. Water-reactive chemicals can react with water to release a flammable gas which may ignite spontaneously. Note that some chemicals might become pyrophoric after their use in reactions. Consult SDS for details on stability, reactivity, and conditions to avoid prior to handling and prepare accordingly.

Note: This section describes some general requirements and guidance on the storage of pyrophoric and water-reactive chemicals. Detailed step-by-step instructions must be provided in lab-specific SOPs and on-site training in labs for the specific pyrophoric or water-reactive chemical in use.

Pyrophoric and water-reactive chemicals must be stored in a sealed container in a dry location and segregated based on their properties as described in the SDS. Pyrophoric and water-reactive chemicals in gloveboxes must be kept in sealed containers when not in use. This will prevent undesired reactions if the inert atmosphere inside the glovebox is compromised and oxygen or water vapor are able to enter the glovebox.

Pyrophoric and water-reactive chemicals that need to be refrigerated shall be stored in a spark-proof refrigerator. Containers are not to be stored in the door of the fridge.

Pyrophoric and water-reactive chemicals must be handled and stored under an inert atmosphere and should be kept in a liquid that is inert to the chemical, if possible. When stored in an inert liquid, a sufficient amount of such protective solvent must be kept in the storage container to fully submerge the material or ensure it remains fully solubilized.

Excess pyrophoric or water-reactive chemicals should not be returned to the original storage container to avoid the introduction of impurities which can lead to reaction with the uncontaminated chemical.

Glass bottles of pyrophoric and water-reactive chemicals must not be handled or stored unprotected. An appropriate secondary containment (i.e. corrosion and shatter resistant) must be used as a protective container for moving and storage.

If pyrophoric and water-reactive chemicals are received in a specially designed container (e.g. Aldrich Sure-Seal), ensure that the integrity of the container and seal is maintained. If an unused portion of the chemical is to be stored for an extended length of time, the chemical should be transferred from the Sure-Seal bottle to a suitable storage vessel (e.g. glass storage flask with PFTE tap or PTFE tap adapter, Figure 2). Ensure proper labelling of those storage vessel (i.e. according to WHMIS – see above).

Any excess of chemical that is pyrophoric and/or water-reactive must be properly inactivated prior to disposal. Refer to the Waste Handling section below for details.



Figure 2. Examples of a storage flask and adapter suitable for storage of pyrophoric and water-reactive chemicals.¹

Time-sensitive Chemicals

Time-sensitive chemicals are defined as any chemicals that have the potential to develop additional hazards upon prolonged storage which are different from their hazards in the original formulation.

These include:

- Potentially explosive chemicals (PECs)
 - Chemicals that form peroxides in the presence of air making them heat-/shock-sensitive or highly reactive.

¹ Sigma - Technical Bulletin AL-134

- Chemicals that become shock-, friction or heat-sensitive over time by other means than peroxide formation, e.g. due to evaporation of a stabilizer/protective solvent and/or crystal/salt formation.
- Chemicals that undergo slow chemical reactions to form a gas that could lead to overpressurization of storage container.
- Chemicals that undergo slow chemical reactions creating additional hazards other than explosion hazard, e.g. decomposition to form toxic or corrosive gases.

Containers of time-sensitive chemicals must be dated when received and when first opened, and they must be properly managed thereafter. Proper management includes defining those chemicals that are time-sensitive, each time-sensitive chemical's inspection frequency and inspection methodologies (see below). The methodologies should include defined pass and fail criteria to determine the relative hazard of the time-sensitive chemical. Keep record of received, opening and inspection dates by recording results in a lab logbook or on a label on the container.

Always dispose of time-sensitive chemicals past their expiry date. Check shipment documentation for a certificate of analysis provided by the manufacturer which might state an expiry date. The certificate of analysis can also be obtained from manufacturer using the chemical's LOT or batch number.

Disposal requirements for unopened and opened containers of certain time-sensitive chemicals are listed in the following sections.

EHS provides stickers for containers of time-sensitive chemicals for easier identification (Figure 3). Please contact EHS at <u>ucsafety@ucalgary.ca</u> to obtain stickers.





A. Peroxide forming Chemicals

A wide range of organic chemicals can form peroxides in the presence of oxygen *via* an auto-oxidation process. The formed products are heat/shock-sensitive or highly reactive and can lead to violent explosions. Common organic structural functionalities known to form peroxides include ethers, certain vinyl alkene derivatives, some alkynes and acrylates. Figure 4 in the Appendix displays 14 structural functionalities that have been identified as prone to peroxide formation.

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Laboratory Safety Manual Issued: 2022.07.06 Peroxide forming chemicals are further separated into different classes depending on the properties of the peroxides being formed over time (Table 4). Table 6 in the Appendix provides a list of commonly used peroxide forming chemicals based on their class.

Class	Description	Inspection and Disposal Guidelines	Examples
A	Chemicals that form explosive levels of peroxides without concentration. Severe peroxide hazard after prolonged storage, especially after exposure to air.	Test for peroxide formation before each use. Discard opened container after 3 months. Dispose when peroxides levels above 20 ppm are detected.	Diisopropyl ether Potassium
В	Chemicals that form explosive levels of peroxides on concentration (when evaporated, distilled, or concentrated) Test for peroxide formation before evaporation, distillation or concentrat Discard opened container after 12 mor Dispose when peroxides levels above 20 are detected.		Diethyl ether Tetrahydrofuran Some secondary alcohols Dioxanes
с	Chemicals that are highly reactive and may autopolymerize as a result of peroxide formation and accumulation.	Test for peroxide formation before each use. Discard opened container after 12 months. For uninhibited chemicals in this Class: dispose after 24 h. Dispose when peroxides levels above 20 ppm are detected.	Acrylic acid Methyl methacrylate Styrene Vinyl pyridine
D	Other peroxidizable chemicals which cannot be placed into the other categories but nevertheless require handling with precautions.	Test for peroxide formation before each use. Discard opened container after 12 months. Dispose when peroxides levels above 20 ppm are detected.	Acrolein Anisaldehyde Benzyl ether

 Table 4. Classes of peroxide forming chemicals including inspection and disposal guidelines

Always aim to purchase peroxide-forming chemicals in the smallest amount possible and those that contain inhibitors to prevent peroxide formation unless the inhibitor will interfere with its intended use. Note that inhibitors will deplete over time and peroxide formation may increase after prolonged storage. Those chemicals should then be treated as uninhibited.

Peroxide forming chemicals must be stored in their original container away from light and heat. They must be kept under inert atmosphere in tightly sealed containers to reduce potential peroxide formation due to exposure to air/oxygen, except for those chemicals that contain an inhibitor that requires oxygen to be effective. Refer to SDS for further details on appropriate storage conditions.

Refrigeration can reduce peroxide formation but also slow down peroxide decomposition leading to accumulation of peroxides and precipitation of shock-sensitive compounds. Always refer to SDS for recommended storage conditions. Only use spark-proof refrigerators to store peroxide forming chemicals if cold storage is required.

Inspection frequency and disposal guidelines for opened containers of the different classes of peroxide forming chemicals are listed in Table 4. The inspection of peroxide forming chemicals and their

containers includes:

 Visual inspection: Check for crystal formation, visible precipitates, discoloration of liquids/solids and/or an oily viscous layer in container and around cap if possible. Check integrity of container and cap. Crystal formation could occur in cap threads which poses a serious hazard when opening containers since friction can lead to explosion. If in doubt, the visual inspection has failed.

Note: DO NOT inspect containers with peroxide forming chemicals of unknown age, origin or in unknown condition. Such containers and those with a failed visual inspection should not be touched, moved or opened – special precautions for extra protection are required. Secure area and post appropriate warning signs (e.g. "Do not move, touch, or open chemical container") if safe to do so. Contact EHS (<u>ucsafety@ucalgary.ca</u>) or HazMat (<u>hazmat@ucalgary.ca</u>) without delay.

 Testing of peroxide levels (solvents only): Only test for peroxide levels after containers have passed the visual inspection. Test peroxide levels using an established method such as Peroxide Test Strips.

Commercially available test drip strips can be used for semi-quantitative analysis of peroxide levels. Ensure that the purchased strips cover a certain peroxide ppm range. A range up to at least 100 ppm is recommended. Use test strips according to manufacturer instructions. Contact <u>hazmat@ucalgary.ca</u> to obtain information on suitable testing strips.

Dispose of peroxide forming chemicals with peroxide levels above 20 ppm. Those chemicals with levels below 20 ppm can be kept if prior to their expiry date; however, containers must be inspected more frequently. Update the expiry date in the inventory database. Refer to Table 4 for guidance on inspection and testing intervals.

Dispose of any opened container according to guidelines for the different classes given in Table 4. Always dispose of containers past their expiry date. Dispose of any unopened containers after 18 months or after the expiry date has passed, whichever is earlier. Perform an inspection prior to discarding of any peroxide forming chemical if possible.

B. Self-reactive and Explosive Chemicals

Self-reactive and explosive chemicals are defined as those that are unstable and susceptible to reactions, such self-accelerating decomposition initiated by heat, shock, vibration, light, an increase in pressure, or sound waves. They are capable of a rapid release of energy by themselves and can lead to severe fires or explosions. Examples include nitrocellulose, some (in)organic peroxides, peracids, peroxy

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Laboratory Safety Manual Issued: 2022.07.06 compounds, perhalogen compounds (perchlorates), some azides, hydrazines, and polynitro compounds (e.g. di- and tri-nitro compounds, picrate salts). See Table 7 in the Appendix for self-reactive and explosive chemicals commonly found in laboratories.

Purchase self-reactive and explosive chemicals in minimum practical quantities and with stabilizers. Explosive chemicals can only be procured in Canada in a desensitized state where the chemical is wetted or dissolved (e.g. with/in water or alcohol) to suppress its explosive properties. This makes them safe to transport and handle. Care must be taken to avoid the evaporation of the stabilizing or desensitizing agent/solvent. Container conditions must be carefully and regularly monitored for both self-reactive and explosive chemicals (see below).

Self-reactive and explosive chemicals must be stored separated from all other chemicals in a location and manner that will prevent the undesired conditions to occur. Always store containers tightly closed away from heat and light. Self-reactive and explosive chemicals can be extremely sensitive to moisture/water, shock and/or friction, and could cause a severe reaction in contact with metals. Never return any unused material to original container as this might introduce contaminations that could accelerate their decomposition. Refer to SDS for additional information and guidance on proper storage and conditions to avoid.

For organic peroxides, aim to store containers at the lowest temperature possible in agreement with their solubility and freezing point to avoid precipitation. Containers with organic peroxides must be vented and kept upright to avoid leakage of liquids through the vented cap. Containers should be made of plastic. Do not use glass containers with screw caps or ground glass closure since friction during opening can cause detonation.

At minimum, a regular visual inspection of containers holding self-reactive and explosive chemicals must be completed and documented. Check containers frequently for any signs of decomposition, such as crystal formation, visible precipitates, discoloration of solids and/or an oily viscous layer in container or on cap. When self-reactive and explosive chemicals contain water or an inert solvent for stabilization, check frequently to prevent the chemical from drying out and becoming a more severe explosion hazard. Refer to Table 7 for common self-reactive and explosive chemicals found in labs, their associated hazards, and inspection and disposal criteria.

Dispose of any contaminated, partially decomposed or expired self-reactive and explosive chemicals immediately. Always dispose when past their expiry date. Refer to Waste Handling section below.

Note: DO NOT touch, move or open any containers of self-reactive and explosive chemicals of unknown age, origin or in unknown conditions. Secure area and post appropriate warning signs (e.g. "Do not move, touch, or open chemical container") if safe to do so. Contact EHS (ucsafety@ucalgary.ca) or HazMat (hazmat@ucalgary.ca) without delay.

C. Other Time-sensitive Chemicals

Other time-sensitive chemicals include those known to develop hazardous conditions via a slow chemical reaction other than peroxide formation. Commonly used chemicals in this category include the following:

- Chloroform
- Certain corrosive compressed gases (e.g. HF, HCN, H₂S)
- Formic acid

Inspection criteria and disposal guidelines vary depending on the chemical and potential additional hazards. At minimum, a regular visual inspection of the container must be completed. A list of commonly used chemicals that fall into this category and their inspection criteria, as well as disposal guidelines are listed in Table 5. Always dispose of chemicals past the expiry date provided by the manufacturer. Refer to Waste Handling section below.

Note: DO NOT inspect time-sensitive chemicals of unknown age, origin or in unknown condition. Containers should not be touched, moved or opened. Secure area and post appropriate warning signs (e.g. "Do not move, touch, or open chemical container") if safe to do so. Contact EHS (<u>ucsafety@ucalgary.ca</u>) or HazMat (<u>hazmat@ucalgary.ca</u>) without delay.

Chemical (CAS)	Hazard	Inspection Details, Frequency and Disposal Guidelines
Chloroform (67-66-3)	Decomposes to form toxic phosgene gas over time.	Dispose after 12 months or after expiry date has passed whichever is earlier.
Formic acid (64-18-6)	Decomposes over time to gaseous products which can lead to explosion of container due to pressure build-up.	Inspect containers regularly for pressure build-up or any signs of decomposition. Vent periodically. Dispose after expiry date.
Corrosive compressed gases	Potential corrosion of container material in contact with gas over extended period of time.	Dispose of cylinder according to expiry date provided by supplier.

Table 5. List of other common time-sensitive chemicals including inspection and disposal guidelines.

IARC-classified Chemicals

Chemicals that are carcinogenic to humans are classified into different groups by the International Agency for Research on Cancer (IARC).

- Group 1: Carcinogenic to humans.
- Group 2A: Probably carcinogenic to humans.
- Group 2B: Possibly carcinogenic to humans.
- Group 3: Not classifiable as to its carcinogenicity to humans.

General storage and segregation requirements apply to IARC-classified chemicals, as well as special storage requirements depending on any additional hazard associated with the chemical. Refer to SDS for details.

WASTE HANDLING GUIDELINES

General Waste Handling Guidelines

Chemical waste containers must be identified according to UCalgary Hazardous Materials Disposal Manual.

UCalgary's Hazardous Materials (HazMat) Services will collect and dispose of most hazardous wastes regularly, safely and efficiently. For further details on waste containers, waste preparation and waste collection, refer to the Hazardous Materials Services webpage and Hazardous Materials Disposal Manual. This section will provide guidance on waste handling and storage within the lab, prior to disposal by Hazmat.

- As with any chemical storage, chemical wastes must be properly segregated.
- All waste containers must be appropriately labelled with full chemical name and concentration.
 - If waste is collected over time, each addition to the waste container must be logged and tracked so that it may be reported accurately for collection, and to avoid incompatible reactions.
- Ensure the container material is compatible with the intended chemical waste.
- Ensure the waste container is kept clean, with no residues on the exterior. Wipe up spills.
- All waste containers must be capped. If over-pressurization is a concern, consider purchasing vented caps.
- Leave room for expansion and gas formation, only fill containers 70-80% full.
- Dispose of waste regularly, do not accumulate waste materials.
- Do not store excessive waste within the fume hood.
- Do not evaporate waste within the fume hood. Evaporation is not an acceptable form of disposal.
- Do not dispose of waste down the drain.

Special Waste Handling & Storage Requirements

In addition to the general waste guidelines described above, the following special waste handling and storage requirements apply to certain groups of chemicals.

Oxidizing Chemicals

Follow the Oxidizing Materials Standard and always refer to SDS for waste disposal guidelines and conditions to avoid.

Dispose of all unused oxidizers and oxidizing waste as hazardous waste. Store oxidizing wastes and

contaminated containers the same way as the unused oxidizing chemical. Ensure container compatibility for wastes and label containers accordingly.

Oxidizers and their waste are not to be mixed with organic material, including paper or wood, or reducing chemicals. Keep away from flammable chemicals.

Empty containers can be discarded in regular trash after triple-rinsing with water and defacing or removal of the label. Treat uncleaned containers like the chemical itself.

Dispose of solid waste such as paper towel, wipes, gloves etc., that have been in contact with oxidizing chemicals as contaminated waste. Do not mix solid wastes (e.g. gloves, paper towel, wipes, tools) contaminated with oxidizing chemicals with flammable or any other incompatible material. Keep those contaminated solid wastes separate and dispose of them immediately. Furthermore, combustible materials, such as paper towels, contaminated with an oxidizing chemical must be thoroughly moistened with water to prevent combustion.

Dispose of expired and contaminated oxidizers immediately.

Flammable Liquid Wastes

Wastes of flammable liquids must be stored in the same way as the unused chemical. Containers must be kept closed and stored in certified flammable storage cabinets or storage rooms. Always segregate containers from incompatible materials.

Containers for liquid flammable wastes with a capacity larger than 5 L must be approved safety containers (e.g. approved "safety can") which can be kept outside a flammable cabinet.

Separation of halogenated from non-halogenated flammable liquids waste is recommended whenever possible to allow submitting them to different waste disposal streams (incineration for halogenated vs. recycling for non-halogenated).

Collect solid waste contaminated or soaked with flammable liquids in an appropriate waste disposal container.

Do not let flammable liquid waste evaporate to the environment (in liquid form or when drying soaked solid materials). This is not an acceptable means of disposal. Waste must be collected in an appropriate container and disposed safely to protect the environment.

Pyrophoric and Water-reactive Chemicals

Always consult SDS for disposal guidelines and conditions to avoid before handling of any pyrophoric or water-reactive chemical to ensure proper waste handling procedures are in place. Note that some chemicals might become pyrophoric after their use in reactions and prepare accordingly (e.g. some hydrogenation catalysts contain adsorbed hydrogen after use, which may ignite when dried in air).

Note: This section describes some general requirements and guidance on the disposal of pyrophoric and water-reactive chemicals. Detailed step-by-step instructions must be provided in lab-specific SOPs and on-site training in labs for the specific pyrophoric or water-reactive chemical in use.

Excess pyrophoric and water-reactive chemicals must be neutralized before disposal. Neutralization must be done in a controlled way and be monitored throughout. Chemicals must be transferred to an appropriate reaction flask for hydrolysis and/or neutralization with adequate cooling under an inert atmosphere.

Containers with residual pyrophoric or water-reactive chemical must be triple-rinsed with a dry and compatible solvent that is inert to the original chemical in the container. All wastes from rinsing processes must also be neutralized prior disposal. Empty, triple-rinsed and dry containers can then be disposed of into the glass waste after a final triple-rinse with water.

Containers with unused or residual amounts of pyrophoric and water-reactive chemicals can also be disposed of as hazardous waste according to the UCalgary Hazardous Materials Disposal Manual and do not require neutralization prior to disposal if kept sealed in original container.

Needles, spatulas, wipes and tools, etc. that have been in contact with pyrophoric and water-reactive chemicals must be stored in an inert atmosphere or neutralized in the same manner as the pure chemical itself.

All collected and neutralized wastes must be disposed of following the UCalgary Hazardous Materials Disposal Manual.

Time-sensitive Chemicals

Follow general disposal guidelines for opened containers of time-sensitive chemicals as listed in Table 4, 5 and 7 and as summarized below.

Note: DO NOT inspect time-sensitive chemicals of unknown age, origin or in unknown condition. Containers of those and those with a failed visual inspection should not be touched, moved or opened. Secure area and post appropriate warning signs (e.g. "Do not move, touch, or open chemical container") if safe to do so. Contact EHS (<u>ucsafety@ucalgary.ca</u>) or HazMat (<u>hazmat@ucalgary.ca</u>) without delay.

A. Peroxide forming Chemicals

Follow disposal requirements as listed in Table 4. Refer to Table 6 for chemicals in the respective class.

- Class A: Discard opened container after 3 months.
- Class B: Discard opened container after 12 months.
- Class C: Discard opened container after 12 months. For uninhibited chemicals in this Class: dispose after 24 h.
- Class C: Discard opened container after 12 months.

Dispose of peroxide forming chemicals in opened containers when peroxide levels exceed 20 ppm. Dispose of any unopened container containing time-sensitive chemicals after 18 months or before expiry date given by manufacturer whichever is earlier.

Perform a container inspection prior to disposal of any peroxide forming chemical if possible and note peroxide levels on container.

B. Self-reactive and Explosive Chemicals

Self-reactive and explosive chemicals, and their wastes, require special handling for disposal. Keep those chemicals in their original container if possible.

Wastes of self-reactive and explosive chemicals must be stored in the same way as the unused chemical, i.e. keep separate and do not mix with other chemicals or wastes. Ensure container compatibility for wastes of self-reactive and explosive chemicals, and label containers accordingly.

Empty containers can be discarded in regular trash after triple-rinsing with water and defacing or removal of the label. Treat uncleaned containers for disposal like the original chemical itself.

Dispose of any self-reactive and explosive chemicals with suspected contamination immediately. Dispose of expired self-reactive and explosive chemicals and those containers that fail a visual inspection immediately. Follow disposal requirements as listed in Table 7.

C. Other Time-sensitive Chemicals

Disposal requirements depend on chemical. Refer to Table 5.

EMERGENCY PROCEDURES

Keep the inventory of hazardous chemicals current and at a minimum, not exceeding the supply that is required for normal operation. This will ensure to reduce loads of hazardous materials in laboratories and lower the risk of potentially serious incidents.

Consider limiting handling of certain higher risk chemicals to working hours only and/or to not be left unattended. Refer to UCalgary Unattended Operations, After Hours Operation and Working Alone Policies and Guidelines.

First Aid

- In case of chemical exposure, provide first aid in accordance with the Safety Data Sheet.
- Call 911 if in critical, life-threatening condition.
- Contact Campus Security at 403-220-5333, if medical attention (non-life threatening condition) is required.
- Contact supervisor and follow the University of Calgary Incident Reporting and Investigation instructions on the EHS website.

Spill Response

- Ensure that you have an adequate spill kit for the chemicals in use.
- Follow the UCalgary Spill Response Procedures in case of chemical spills.

Follow the UCalgary Online Accident Reporting System (OARS) instructions on the EHS website to submit any incident or near miss through OARS.

RELATED DOCUMENTS & PROGRAMS

UCalgary Corrosive Materials Standard UCalgary Toxic Materials Standard UCalgary Oxidizing Materials Standard UCalgary Compressed Gas Cylinder Standard UCalgary Cryogenic Materials Standard UCalgary Movement of Hazardous Materials within Buildings Guidelines UCalgary Hazardous Waste Disposal Infographic UCalgary Hazardous Materials Disposal Manual

UCalgary Chematix Chemical Inventory Instructions UCalgary Chematix Chemical Reconciliation Instructions UCalgary Spill Response Procedure UCalgary Biosafety Program UCalgary Radiation Safety Program UCalgary Standard Operating Procedure Standard & Template UCalgary Personal Protective Equipment Program UCalgary Hearing Conservation Program UCalgary Nanomaterials Program

REFERENCES

Alberta Occupational Health and Safety Code Canadian Centre for Occupational Health and Safety (CCOHS) NFPA 45 – Standard on Fire Protection for Laboratories Using Chemicals National Fire Code – Alberta Edition Sigma Technical Bulletin AL134 Sigma Technical Bulletin AL164 Sigma – Peroxide Forming Solvents Peroxides and peroxide forming compounds, Donald E. Clark, *Chem. Health Saf.* 2001, *8*, 12-22. Review of Safety Guidelines for Peroxidizable Organic Chemicals, Richard R. Kelly, *Chem. Health Saf.* 1996, *3*, 28-36.

APPENDIX

I. Chemical Storage Flowchart

This flowchart provides general guidelines for chemical storage depending on the hazard classifications and it is based on a hazard ranking. Always consult the SDS for information on hazard classification, chemical storage, and storage incompatibilities to ensure proper storage and segregation of chemicals.

To use the flowchart, follow the arrows by starting on the top left (explosive/self-reactive). The flowchart would only need to be followed once for one of the assigned hazard pictograms, found on the container or in the SDS, whichever occurs highest on the chart. Hazard classification and their respective determined storage conditions always overrule those further down in the flowchart. For example, if a chemical is toxic and flammable, the storage conditions for flammable should be followed. Segregation and secondary containment consideration must be given to secondary hazards. Refer to the Storage Segregation above.



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EHS-LAB-1027 – Chemical Storage & Waste Handling Standard Page 27 of 32

II. Worksite Labels – Examples

For containers smaller than 100 mL include

- Product identifier (name of the hazardous compound)
- Reference to SDS, if available.

Acetone, ACS reagent, > 99.5%

Refer to SDS for more information

For containers larger than 100 mL, include

- Product identifier (name of the hazardous compound)
- Safe Handling Precautions
 - Precautionary statements
 - Signal word and pictogram if space on container permits
- Reference to SDS, if available



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Laboratory Safety Manual Issued: 2022.07.06

III. Time-sensitive Chemicals

 Table 6. List of peroxide forming chemicals by class.

Chemical	CAS	Chemical	CAS	
Class A				
Butadiene (liquid monomer)	106-99-0	Vinylidene chloride	75-35-4	
Chloroprene (liquid	126.00.8	Tetrahydrofuran (no	100.00.0	
monomer)	120-99-8	inhibitor)	109-99-9	
Diisopropyl ether	108-20-3	Potassium metal	7440-09-7	
Divinyl acetylene	820-54-2	Potassium amide	17242-52-3	
Tetrafluoroethylene (liquid	110 14 2	Codiumo omido	7702 02 5	
monomer)	110-14-3	Sodium amide	//82-92-5	
Class B				
Acotal	105 57 7	Ethylene glycol ether	110 71 4	
Acetai	103-37-7	(Glyme)	110-71-4	
Acetaldehyde	75-07-0	Furan	110-00-9	
Benzyl alcohol	100-51-6	4-Heptanol	589-55-9	
2-Butanol	78-92-2	2-Hexanol	626-93-7	
Chlorofluoroethylene	2317-91-1	Methyl acetylene	74-99-7	
Cumene (Isopropylbenzene)	98-82-8	3-Methyl-1-butanol	123-51-3	
Cyclohexanol	108-93-0	Methyl cyclopentane	96-37-7	
Cyclohexene	110-83-8	Methyl isobutyl ketone	108-10-1	
2-Cyclohexen-1-ol	98-82-8	4-Methyl-2-pentanol	108-11-2	
Cyclopentene	142-29-0	2-Pentanol	6032-29-7	
Decahydronaphthalene	102 01 6 102 02 7 01 17 9	1 Ponton 1 ol	821 00 0	
(Decalin)	495-01-0, 495-02-7, 91-17-8	4-renten-1-01	821-09-0	
Diacetylene (Butadiyne)	460-12-8	1-Phenylethanol	98-85-1	
Dicyclopentadiene	77-73-6	2-Phenylethanol	60-12-8	
Diethyl ether	60-29-7	2-Propanol*	67-63-0	
Diethylene glycol dimethyl	111-96-6	Tetrahydrofuran (THF)	109-99-9	
ether (Diglyme)	111 50 0	retranyaroraran (rrn)	105 55 5	
1,3-Dioxane	505-22-6	Tetrahydronaphthalene	119-64-2	
1 4-Dioxane	123-91-1	Vinvl ethers	109-92-2 (ethyl)	
	123 31 1	Villyretiters	111-34-2 (butyl)	
Class C				
Acrylic acid	79-10-7	Styrene	100-42-5	
Acrylonitrile	107-13-1	Tetrafluoroethylene (gas)	116-14-3	
Butadiene (gas)	106-99-0	Vinyl acetate (gas)	108-05-4	
Chloroprene	126-99-8	Vinyl chloride (gas)	75-01-4	
Chlorotrifluoroethylene	79-38-9	Vinyl pyridine	100-69-6 (2-)	
(gas)	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		100-43-6 (4-)	
Methyl methacrylate	80-62-6	Vinylidene chloride	75-35-4	

*NOTE: Lab personnel should be aware that 2-propanol (isopropanol) is recognized as a peroxide former and listed in the Class B PEC section. Always keep inventories of 2-propanol as low as possible to allow for timely consumption and to avoid accumulation of old containers with unused 2-propanol. Risks are considered moderate to low if handled, tested and disposed of properly as outlined in the SDSs and in Table 4.

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Laboratory Safety Manual Issued: 2022.07.06

EHS-LAB-1027 – Chemical Storage & Waste Handling Standard Page 29 of 32



Figure 4. Organic structural functionalities (highlighted in orange) commonly known to form peroxides via auto-oxidation.

 Table 7. List of commonly used self-reactive or explosive chemicals (non-exhaustive).

Chemical	CAS	Hazard	Inspection and Disposal
Chemical		Παζαι υ	Guidelines
			Inspect visually every 12 months.
		Explosive when dry, can form	Monitor for water content:
Picric acid		shock-sensitive compounds	add water every six months as
(wetted and in solution)	88-89-1	with metal impurities	needed. Rotate containers to
(wetted and in solution)		Keep wetted with water. Do not	distribute water every
		allow material to become dry.	three months. Dispose of any
			within two years of purchase
			Inspect visually every 12 months
		Strong oxidizer	for crystal/precipitate formation
Perchloric acid	7601-00-3	Can form shock-sensitive	and discoloration. Dispose within
r er chion c aciu	7001-30-3	compounds with metal	10 days of use or if any
		impurities	discoloration occurs (highly
			concentrated).
Porchloratos	Ammonium perchlorate	Strong oxidizer	Inspect containers regularly.
Ferciliorates	(7790-98-9)	Explosive - shock-sensitive	Dispose past expiry date.
		Explosive when dry	
Picrato	Ammonium picrate (131-74-8)	Can form more shock-sensitive	Inspect containers regularly.
Piciale		compounds with metal	Dispose past expiry date.
		impurities	
4 Nitrophonyl hydrozino	100 16 2	Explosive when dry	Inspect containers regularly.
4-INICOPTIENT INVUTAZITE	100-10-2	Heating may cause an explosion	Dispose past expiry date.
Dinitrotoluono	121 14 2	Explosive heat- and shock-	Inspect containers regularly.
Dilitiotoldene	121-14-2	sensitive	Dispose past expiry date.
Dinitrophonol	51-28-5	Explosive when dry	Inspect containers regularly.
Dinitiophenoi			Dispose past expiry date.
2.4 Dinitronhonyl	119-26-6	Explosive when dry	Inspect containers regularly
2,4-Diniti Opnenyi		Risk of explosion if heated	Dispose past expire date
nyurazine		under confinement	Dispose past expiry date.
2,4,6-Trinitrotoluene	119.06.7	Explosive when dry	Inspect containers regularly.
(TNT)	118-50-7		Dispose past expiry date.
2,2-Diphenyl-1-	1909 66 4	Explosive – shock-sensitive	Inspect containers regularly.
picrylhydrazyl	1090-00-4	Light-sensitive	Dispose past expiry date.
Hovanitradinhanylamina	121 72 7	Shock-sensitive and potentially	Inspect containers regularly.
nexamitroupnenyiamine	151-75-7	explosive	Dispose past expiry date.
Hydrazino (nuro)	202 01 2	Fuelesius avera hartina	Inspect containers regularly.
(pule)	502-01-2	Explosive upon heating	Dispose past expiry date.
Organic Porovidos	Benzoyl peroxide	Heat-sensitive	Inspect containers regularly.
Organic Peroxides	(94-36-0)	Explosive when dry	Dispose past expiry date.
	Calcium peroxide		
Dorovideo	(78403-22-2)	Strong suidings	Inspect containers regularly.
Peroxides	Hydrogen peroxide	Strong oxidizer	Dispose past expiry date.
	(7722-84-1)		

Table 7. Continued.

Chemical	CAS	Hazard	Inspection and Disposal Guidelines
Azides	Silver azide	Explosive – light- and shock-	Inspect containers regularly.
Azides	(13863-88-2)	sensitive	Dispose past expiry date.
Nitro cellulose Collodion solution	9004-70-0	Heat-sensitive Store away from sources of ignition, oxidizers and	Inspect containers regularly. Dispose past expiry date.
		combustible material	
Nitro guanidine	556-88-7	Explosive when dry	Inspect containers regularly. Dispose past expiry date.