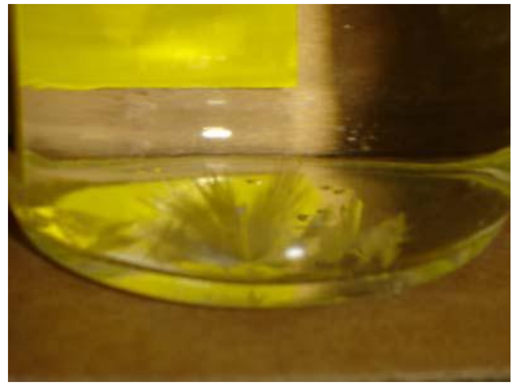
# Peroxide-Forming Chemicals

## Overview

Peroxide-forming chemicals are a class of compounds that have the ability to form shock-sensitive explosive peroxide crystals. Many of the organic solvents commonly used in laboratories have the potential to form explosive peroxide crystals. Diethyl ether and tetrahydrofuran are two of the more common peroxide-forming chemicals used today. Therefore, it is extremely important that this procedure be followed regarding the identification, handling, storage, and disposal of peroxide-forming chemicals.



**Peroxide Formation**

Under normal storage conditions the materials listed in this document have the potential to generate and accumulate peroxide crystal formations, which may violently detonate when subjected to thermal or mechanical shock. Peroxide-forming chemicals react with oxygen – even at low concentrations – to form peroxy compounds. The risk associated with peroxide formation increases if the peroxide crystallizes or becomes concentrated by evaporation or distillation. Factors that affect rate of peroxide formation include exposure to air, light and heat, moisture, and contamination from metals.

Manufacturers may add an inhibitor to peroxide forming chemicals to counter peroxide formation. For many peroxide-forming solvents, butylated hydroxy toluene (BHT) is commonly added. BHT 'scavenges' oxygen in the solvent and prevents it from reacting with the solvent to form peroxides. Over time, BHT or other inhibitor in the solvent can become exhausted allowing peroxides to form. Distilling the solvent can completely remove the BHT and make the solvent immediately susceptible to peroxide formation.

Peroxide crystals may form on the container plug or the threads of the lid and detonate when the lid is twisted. Do not open a liquid organic peroxide or peroxide-forming chemical if crystals or a precipitate are present.

## Applicability

This guidance information applies to all chemists and any other employee who is involved with the packaging, inspecting, or using this type of laboratory chemical/reagent.

## Definitions

A peroxide is a chemical that contains a peroxo (O-O) unit, one that has the chemical formula of $O_2^{2-}$. These are shock sensitive compounds, can explode if subject to mechanical shock, intense light, rapid changes in temperature, or heat.

# Peroxide Forming Compound Evaluation Protocol

Upon discovering potential peroxide forming materials, do not remove from the storage location until a thorough evaluation of the material has been completed using the attached evaluation. After the evaluation, review all information to make a decision based on the evaluation criteria. If the compound is determined to be shippable, be sure to include the inspection sheet in the packing envelope of the labpack container. If the material is deemed not shippable, leave a copy with the generator discussing the potential hazards. Bring the original back to the office. The account manager or operations manager will prepare a quote for onsite handling.

Any material from the potential peroxide forming compound list can be approved for transportation and disposal if the following conditions exist:

- The container is unopened and the contents are unexpired
- The container has been opened and the contents are unexpired or there is no expiration date but the date of manufacture is present and the compound falls within the acceptance parameters on the Recommended Storage Time Limits Table.
- The inner container has been confirmed unopened (seal intact) full, contains an inhibitor, the contents are expired, but the container is less than 3 yrs old and none of the conditions exist.
- The compound is on of the solid peroxide formers (potassium metal, potassium amide, sodium amide, or sodium ethoxyacetylide) and is not discolored and has not formed a crust on the surface.
- Generator can confirm testing for peroxides with results of less than 8 ppm and the testing falls within the timeframes for the groups.

Performing the Visual Inspection

Solvents stored in glass bottles can be visually inspected for peroxides. Bottles containing organic solvents are typically made of amber/brown glass, so a flashlight can be used to light the interior of the bottle.

During the inspection, you should look for 2 signs that the material is contaminated:

1. Hard crystal formations in the form of ice like structures, crystals, solid masses or an obscure cloudy medium signify gross contamination.
2. Wisp like structures floating in a clear liquid suspension signify contamination.

Use caution when performing the inspection- peroxide formation may be present anywhere in the container:

- The bottom of the container
- The side of the container
- The threaded cap
- The outside of the container

Peroxide formation in ppm concentrations may not be visually observable and must be identified through appropriate testing procedures.

Employees should not open any containers that do not pass this evaluation without the proper training, engineering controls, and PPE. Consult your HSE Manager for further guidance.

**Solvents and Recommended Storage Time Limits Table**

**Category I Materials- recommended shelf life is 3 months whether it is inhibited or uninhibited.**

| Chemical | Synonyms |
|---|---|
| Isopropyl Ether | Diisopropyl Ether, Diisopropyl Oxide |
| Diethyl Ketene | 2-Ethyl-1-butene-1-one |
| Divinyl Ether | Vinyl Ether, Divinyl Oxide |
| Potassium Metal | Potassium |
| Potassium Amide | |
| Sodium Amide | Sodamide |
| Sodium Ethoxyacetylide | |
| Vinylidene Chloride | 1,1-Dichloroethylene, 1,1-Dichloroethane |
| | |

**Category II Materials- recommended shelf life is 12 months if inhibited and 3 months if uninhibited.**

| Chemical | Synonyms |
|---|---|
| **p-Dioxane** | **1,4-Dioxane, Diethylene Dioxide** |
| **Ethyl Ether** | **Ether, Diethyl Ether, Ethoxyethane** |
| **Tetrahydrofuran** | **Butylene Oxide, Diethylene Oxide** |
| **Acetal** | **1,1-Diethoxyethane, Diethyl Acetal** |
| **Acetaldehyde** | **Ethanal, Ethyl Aldehyde** |
| **Cumene** | **Isopropyl Benzene** |
| **Cyclohexene** | **1,2,3,4-Tetrahydrobenzene** |
| **Cyclopentene** | |
| **Diacetylene** | **Beacetylene** |
| **Ethylene Glycol Dimethyl Ether** | **1,2-Dimethoxy Ethane, Glyme, Monoglyme** |
| **Furan** | **Divinylene oxide** |
| **Methyl Acetylene** | **Allylene, Propyne** |
| **Methyl Cyclopentane** | |
| **Tetrahydronapthalene** | **Tetraline** |
| **Vinyl Ethers** | **Ethyl Vinyl Ether, Methyl Vinyl Ether** |
| **Diethylene Glycol Dimethyl Ether** | **Diglyne** |
| **Other unlisted Ethers** | **Contact EHSRM which will contact SET Technical Services for Evaluation** |
| | |
| | |

**Category III Materials- recommended shelf life is 12 months if inhibited and 3 months if uninhibited.** These are hazardous due to peroxide polymerization when stored as a liquid. The peroxide forming potential increases and should be considered as a peroxide hazard on storage.

| Chemical | Synonyms |
|---|---|
| **Chlorobutadiene** | **Chloroprene** |
| **Vinyl Acetate** | |
| **Vinyl Acetylene** | **Buten-3-yne** |
| **Vinyl Chloride** | **Chloroethylene, Ethylene Monochloride** |
| **Vinyl Pyridine** | |
| **Styrene** | |

**Ideal Storage Conditions:**

Keep away from sources of ignition and store in a cool, dry place. Store in tightly closed containers and keep in a marked flammables area. Store protected from moisture, light and air. Containers should be dated when opened and tested periodically for the presence of peroxides. Do not exceed storage time limits.

**Condition of Material / Scenario Requiring Treatment:**
Peroxide formation may be present anywhere in the container, including the sides, bottom, exterior and threaded cap. Peroxide formation in PPM concentrations may not be visually observable and must be identified through the use of appropriate testing procedures. If any of the following conditions exist, the compound may be explosively unstable and will require stabilization prior to transportation.

1. Material appears to be degraded and or contaminated.
2. Material appears to be discolored.
3. Deterioration or distortion of storage container.
4. Gross contamination.
5. Thermal shock (sunlight).
6. Oxidation on exterior of container.
7. Age of material exceeds recommended storage time.

**Hazard Analysis:**
Peroxides are less volatile than solvent and tend to concentrate in solution or in the container threads**. Experiments have determined that a percentage of 0.008% (80 PPM) or greater is enough to initiate explosive decomposition.** Peroxides are sensitive to heat, friction, and shock. Some peroxides may explode without being concentrated. (I.e. Isopropyl Ether)

## *Potential Peroxide Forming Compound Evaluation Sheet*

| | |
|---|---|
| Generator Name:______________________________ | Generator Address:______________________________ |
| Contact Name:______________________________ | Contact Phone#:______________________________ |
| Chemist Reviewing:______________________________ | Date Reviewed:______________________________ |

| | |
|---|---|
| Chemical Name:______________________________ | Virgin or Spent ?:______________________ |
| Material Inhibited: **YES** **NO** | Inhibitor:____________________ %_____________ |

| |
|---|
| **Container Information/ History:** Complete the sections below to the best of your ability. If there is no information for a specific question simply write "None" or "N/A". |
| Has the container ever been opened: Yes No Unknown Date last opened: ____/____/____ |
| Have you received verification that the material has NEVER been opened? Yes No |
| Container Size:______________________________ Volume remaining:______________________________ |
| Container Type: Glass Plastic Metal Other:___________ |
| Container Lid/ Cap Material of Construction: Cork Glass Plastic Metal Other:___________ |
| Describe the condition of the container: (rusted, dented, visible degradation, or bulging) ________________________________________________ |
| Describe the condition of the material if possible: (Evidence of wisp like structures, cloudiness, solid masses, or ice like structures)________________________________________________ |

| | |
|---|---|
| **Manufacturer Information:** | |
| Manufacturer:______________________________ | Catalog #:______________________________ |
| Purchase Date:______________________________ | Lot#:______________________________ |
| Expiration Date:______________________________ | |

| | | |
|---|---|---|
| **Storage Conditions:** | | |
| Was the chemical subject to fire? | Y | N |
| Was the chemical subject to temperature fluctuations? | Y | N |
| Was the chemical subject to humidity fluctuations? | Y | N |
| Was the chemical subject to storage: | Indoors only | Outdoors |
| Was the chemical subject to thermal or physical shock? | Y | N |
| Was the chemical subject to direct sunlight? | Y | N |

| | |
|---|---|
| Customer:______________________________ | EHSRM Representative:__________________________ |
| *Print* | *Print* |
| ______________________________ | ______________________________ |
| *Signature* | *Signature* |

# Borane-Tetrahydrofuran Complex

Borane-Tetrahydrofuran (BTHF) complex is a reagent used for the reduction of functional groups and for hydroboration reactions with carbon-carbon double and triple bonds. Functional groups that are readily reduced by BTHF include aldehyde, ketone, carboxiylic acid, amide, oxime, imine, and nitrile. Groups that are less easily reduced by BTHF complex are epoxide, lactone, ester, and acyl chloride. The material is highly toxic, Pyrophoric, water reactive and extremely flammable.

The tetrahydrofuran (THF) component of the complex is often the focus when considering potential hazards due to anticipated formation of peroxides. However, due to the presence of the borane it is theoretically unlikely for peroxides to form. The primary hazard of concern with this material given closed container handling, needs to be the potential for undetected decomposition and for the material to spontaneously rupture its container.

Unstabilized or improperly stored BTHF complexes may become unstable and can explode spontaneously or if subjected to mechanical shock, rapid changes in temperature, or heat. Thermal decomposition of BTHF complex occurs by ether cleavage of the tetrahydrofuran ring. Storage above $5^{o}$C ($41^{o}$F) can lead to appreciable decomposition in a matter of weeks. Higher boranes form during decomposition and the process is continued through the hydrogenation of the boranes over time. This process increases exponentially if the material has not been refrigerated or stabilized.

In order to decrease the rate of product decomposition, most materials are purchased from the manufacturer with an added stabilizer. Examples of chemical stabilizers are sodium tetrahydroborate, and 1,2,2,6,6-pentamethylpiperidine (PMP), or N-isopropyl-N-methyl-tert-butylamine (NIMBA), to name a few.

***(Note: Given the known generation of hydrogen in tetrahydroborate, it is postulated that the tetrahydroborate stabilizer may in fact, destabilize the borane. Expired materials stabilized with this particular stabilizer should be managed with extreme care.)***

1) If handling is necessary, the container must not be opened and should be managed using clean, dry Nitrile gloves.
2) Fully evaluate to determine if the BTHF can be disposed of based upon the **ALL** of the following criteria:

    - **Original manufactures container** (Aldrich Sure Seal bottle, etc.), AND
    - If possible, identify an expiration or manufacturer's date. If the manufacturer's date is present and the compound falls within the manufacturer's accepted timeline (generally, it is one year if stabilized and stored properly) and the **material has not exceeded the expiration date**, AND
    - The material has been **stored in temperature-controlled conditions** between $0^{o}$C ($32^{o}$ F) and $5^{o}$C ($41^{o}$F) to decrease the rate of decomposition, AND proper storage and the **presence of a stabilizer** according to the material manufacturer's requirements can be confirmed.

BTHF complexes stored in glass bottles can be inspected for discoloration or the presence of solids. However, glass containers will not display signs of over-pressurization from the build-up of hydrogen and subsequently should not be handled. These containers may spontaneously rupture do to the presence of hydrogen and higher borane compounds as a result of decomposition.

Other containers may show visible signs of over-pressurization. These containers must not be handled at all and may pose a significant health and safety risk. Ensure that the HSE Manager is informed of the pressurized container and its location.

3) If the following conditions exist, the material could be potentially explosive or shock sensitive. Materials with the following conditions will not be approved – Do not move or handle the container:

- The container has been opened and the contents are expired and the generator has no additional knowledge about the material (how the chemical was stored, if it contains a stabilizer, etc;)
- The container was stored in direct sunlight or the chemical was heated,
- The chemical was stored where it may have been subject to uncontrolled fluctuations in temperature,
- The chemical appears discolored or unusually viscous,
- There is evidence of solids in the container,
- There are wisp like structures floating in a clear liquid suspension,
- Evidence of any of the following: chips, clouding, solids, crystals, and ice like structures.

4) If the material passes the evaluation and will be going for disposal, please note the following:

- Wrap the cap with Parafilm,
- Pack the BTHF alone
- Use vermiculite as packing media

**PLEASE NOTE THAT THESE COMPOUNDS CAN BE DANGEROUS AND ALL CHEMISTS SHOULD EXERCISE CAUTION AND CARE WHEN ENCOUNTERING THESE MATERIALS**

**Ideal Storage Conditions:**

Do not allow water to get into the container because of violent reaction. Always use spark-proof tools and explosion proof equipment. Use only in a chemical fume hood. Keep away from sources of ignition and store in a cool, dry place. Store in tightly closed containers and keep in a marked flammables area or refrigerator. Store protected from moisture, light and air. Containers should be dated when opened and tested periodically for the presence of peroxides. Regularly check inhibitor levels to maintain peroxide levels below 0.008%. After opening, always purge container with nitrogen before reclosing.

**Condition of Material / Scenario Requiring Treatment:**

Peroxide formation may be present anywhere in the container, including the sides, bottom, exterior and threaded cap. Peroxide formation in PPM concentrations may not be visually observable and must be identified through the use of appropriate testing procedures. If any of the following conditions exist, the compound may be explosively unstable and will require stabilization prior to transportation.

1. Material appears to be degraded and or contaminated.
2. Material appears to be discolored.
3. Deterioration or distortion of storage container.
4. Gross contamination.
5. Thermal shock (sunlight).
6. Oxidation on exterior of container.
7. Age of material exceeds recommended storage time.

**Hazard Analysis:**

Peroxides are less volatile than solvent and tend to concentrate in solution or in the container threads. <u>Experiments have determined that a percentage of 0.008% (80 PPM) or greater is enough to initiate explosive decomposition</u>. Peroxides are sensitive to heat, friction, and shock. Some peroxides may explode without being concentrated. (I.e.. Isopropyl Ether)

Once again, given the known generation of hydrogen in tetrahydroborate, it is postulated that the tetrahydroborate stabilizer may in fact, destabilize the borane. ***Expired materials stabilized with this particular stabilizer should be managed with extreme care.***

# NFPA Class 4 Oxidizers

## Overview

Oxidizing materials may be toxic or corrosive. Depending on the material, route of exposure (inhalation, eye or skin contact, or swallowing) and dose, they could harm the body. Corrosive oxidizers can also attack and destroy metal. Remember to review all MSDSs and the container labels prior to handling them. These documents should explain all of the hazards of the oxidizing materials that you encounter on the job site.

Class 4 oxidizers are a specific class of oxidizer that has special storage requirements and quantity limitations set forth by the National Fire Prevention Association. The total quantity limitation for NFPA Class 4 oxidizers is <10 pounds per facility at any given time. Limitations are placed on these due to the fact that in the right setting they can explode when in contact with certain contaminants, can explode if exposed to slight heat, shock, or friction, will increase the burning rate of combustibles and can cause combustibles to ignite spontaneously.

## Applicability

Due to the reactive nature of Class 4 oxidizers, this subset of chemicals must be considered on a case-by-case basis. Each container should undergo a thorough evaluation prior to shipment.

The following are typical Class 4 oxidizers:
(1) Ammonium perchlorate (particle size greater than 15 microns)
(2) Ammonium permanganate ***(forbidden to ship)***
(3) Guanidine nitrate
(4) Hydrogen peroxide solutions (greater than 91 percent)
(5) Tetranitromethane

This guidance information applies to all chemists and any other employee who is involved with the packaging, inspecting, or using this type of laboratory chemical/reagent. Approved NFPA Class 4 oxidizers can be shipped for disposal if the following criteria has been met:

(1) Material has not been subjected to thermal or physical shock
(2) Material is virgin, opened, and generator has confirmed no incompatibles have been mixed
(3) Material has no discolorations
(4) Material does not exceed disposal facility weight limitations.

If the container does not pass inspection, contact you HSE Manager.

## Definitions

**Class 4 oxidizer** – An oxidizer that can undergo an explosive reaction due to contamination or exposure to thermal or physical shock and will cause a severe increase in the burning rate of combustible materials with which it comes into contact.

**Ideal Storage Conditions:**

Keep away from heat, sparks, and flame. Do not store near combustible materials. Store in a tightly closed container. Store in a cool, dry, well-ventilated area away from incompatible substances.

# Inorganic Azide Materials

## Overview

Sodium Azide, NaN3, is a colorless, odorless, crystalline solid (salt-like) or solution. It is soluble in water or liquid ammonia, slightly soluble in alcohols, and insoluble in ether. It is highly toxic and presents a severe explosion risk when shocked or heated. When heated from 275 to 330°C in dry air, the solid crystals decompose with the evolution of nitrogen gas, leaving a residue of sodium oxide. Sodium hydroxide then forms in moist air. Synonyms and Trade Names are Azide, Azium, and Sodium salt of hydrazoic acid.

Sodium azide is a common preservative of samples and stock solutions in laboratories and a useful reagent in synthetic work. It is not explosive except when heated near its decomposition temperature (300°C) or reacted with metals; heating sodium azide should be avoided. Sodium azide (solid or concentrated solution) should never be flushed down the drain since this practice can cause serious incidents when the azide reacts with lead or copper in the drain lines and explodes. Sodium azide has high acute toxicity as well as high toxicity to bacteria in water treatment plants. Other incompatible materials include: acids, halogens, strong oxidizers, and heavy metal salts.

Metal shelves and other metal items used to handle sodium azide and potassium azide (i.e., spatulas) can also result in the formation of heavy metal azides and thus should be avoided. Solutions of sodium azide and potassium azide do not pose the danger of shock-sensitivity associated with the solid form; however, the hydrazoic acid generated when the sodium azide is dissolved is extremely toxic. Therefore, the solution is should prepared inside a laboratory chemical hood. If not dissolved, solid sodium azide should be stored in a secured cabinet because of the shock hazards.

## Applicability

This guidance information applies to all chemists and any other employee who is involved with the packaging, inspecting, or using this type of laboratory chemical/reagent.

Approved azide compounds may be shipped as is if one of the following criteria has been met: (1) Material is virgin and has never been opened; (2) material is virgin, opened, and generator has confirmed no incompatibles have been mixed with it and it has not been exposed to high temperatures; (3) material is spent and generator has confirmed no incompatibles have been mixed with it and it has not been exposed to high temperatures.

## Definitions

An Azide is the anion with the formula $N_3^-$.

# ***Azide Evaluation Form***

The following guidelines apply to all containers with an azide in **ANY** concentration. Reference the list of azides and azide chemical families below. By no means is this list all inclusive. Any labpack chemist who encounters a container with an azide in **ANY** concentration needs to complete the following evaluation to assist in the determination of the container stability, so the appropriate handling procedures can be employed.

| **AZIDE CHEMICAL FAMILY** | **AZIDE EXAMPLES** |
|---|---|
| *Alkaline earth metal azides* | *(sodium, potassium, lithium)* |
| *Acyl Azides* | *(t-butyl azidoformate, ethyl azidoformate)* |
| *Alkyl Azides* | *(methyl azide, ethyl azide)* |
| *Aryl Azides* | *(phenyl azide)* |
| *Heavy Metal Azides* | *(silver, lead, copper)* |
| *Hydrazoic Acid* | *(hydrogen azide)* |

***NOTE: DO NOT OPEN ANY PACKAGING OR MOVE THE CONTAINER TO COLLECT INFORMATION***

Generator Name: ____________________ Contact Name: ____________________
Generator Address: ____________________ Contact Phone: ____________________
Generator Phone#: ____________________ ____________________
Chemist Name: ____________________ Date: ____________________

Chemical Name: ____________________ Virgin or Spent Material: (Circle) V S
Description of material: ____________________ Odor: (Circle) Y N
Azide Identity: ____________________ % OF Azide: ____________________
Identity/ Concentration of other Constituents: ____________________
Color (if in glass or see through container): ____________________

**CONTAINER INFORMATION/HISTORY:**

Manufacturer: ____________________ Lot Number: ____________________
Catalog Number: ____________________ Purchase Date: ____________________
Has the container ever been opened: Y N UNK Date last opened: ____________________
Container Size: ____________________ Volume/Wt remaining: ____________________
Container Type: ____________________
Cap Type: ____________________
Condition of the container: ____________________

*Fill in all of the sections. If there is no information listed for a question write the word "NONE"

**Ideal Storage Conditions:**

Always store the azide containers in a cool, dry place away from acids or acidic materials. Store in a tightly closed glass or plastic containers and never store in metal containers.

**Condition of Material / Scenario Requiring Treatment:**

Sodium Azide is colorless to white hexagonal crystals that may hydrolyze to form hydrazoic acid. Lithium Azide is colorless to white in color. The moist or dry salt decomposes explosively above 115-298 C depending on the rate of heating. Conditions that may require stabilization are:

A. Contamination/degradation
B. Discoloration
C. Deterioration or distortion of storage container.
D. Exposed to thermal shock (direct sunlight)
E. Sodium Azide in solution with an unknown pH.
F. Storage container other than plastic or glass.

**Hazard Analysis:**

A. Interactions with heavy metals/salts may produce heavy metal azide products that are explosively unstable when subjected to friction, thermal, and mechanical shock.
   1) Lead Azide PbN3
   2) Silver Azide AgN3
   3) Copper Azide CuN3
   4) Mercury Azide HgN3

B. Interactions with acids may yield hydrogen azide (HN3) which is explosively unstable when subjected to mechanical shock or slight vibrations. Hydrazoic acid solutions with concentrations of 10% or less do not present an explosion hazard, although a toxicity concern still remains.

# Sodium Amide

## Overview

Sodium amide, commonly called sodamide, is the chemical compound with the formula $NaNH_2$. This solid, which is dangerously reactive toward water, is white when pure, but commercial samples are typically gray due to the presence of small quantities of metallic iron from the manufacturing process. Such impurities do not usually affect the utility of the reagent. $NaNH_2$ has been widely employed as a strong base in organic synthesis.

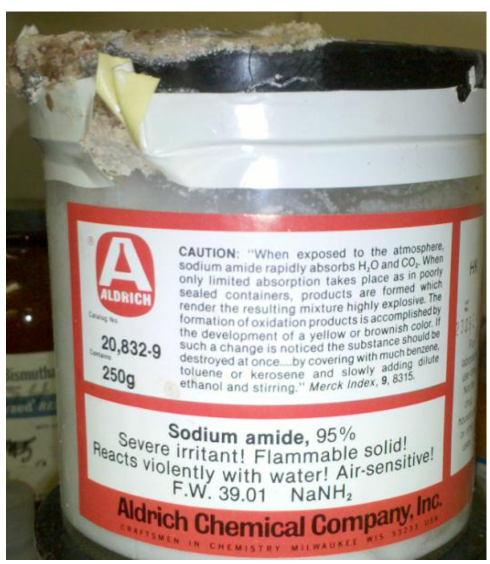
In the presence of limited quantities of air and moisture, such as in a poorly closed container, explosive mixtures of oxidation products can form. This is accompanied by a yellowing or browning of the solid. As such, sodium amide should always be stored in a tightly closed container, if possible under an atmosphere of nitrogen gas. Sodium amide samples which are yellow or brown in color should be destroyed immediately. Explosive peroxides can also form when sodium amide is heated so heating is not recommended.  Sodium amide may be expected to be corrosive to the skin, eyes and mucous membranes. Care should be taken to avoid dispersal of this material in dust form.

## Applicability

This guidance information applies to all chemists and any other employee who is involved with the packaging, inspecting, or using this type of laboratory chemical/reagent.

## Definitions

Amides are the members of a group of organic chemical compounds containing nitrogen.



**Ideal Storage Conditions:**

Always store in a cool, dry place and in a tightly closed container. Keep under a nitrogen blanket if possible and do not exceed storage limitations.

**Condition of Material / Scenario Requiring Treatment:**

Sodium Amide uncontaminated is gray to white in color. It is a crystalline powder with an ammonia odor. Conditions that require stabilization prior to transportation include the following.

A. Material appears to be degraded/contaminated.
B. Material appears to be discolored. ( yellow to brown powder)
C. Deterioration or distortion of storage container.
D. Age of material exceeds recommended storage time.

**Hazard Analysis:**

A. Exposure to air and moisture may produce oxidation products that are explosively unstable
   1) Sodium Hyponitrate
   2) Pentaoxodinitrate
   3) Hexaoxodinitrate

B. Interactions with halocarbons may produce explosive reactions.
   1) Carbon Tetrachloride
   2) Carbon Tetrafluoride

# Potassium Metal

## Overview

Potassium is the second least dense metal; only lithium is less dense. It is a soft, low-melting solid that can easily be cut with a knife. Freshly cut potassium is silvery in appearance, but in air it begins to tarnish toward grey immediately. Due to the highly reactive nature of potassium metal, it must be handled with great care, with full skin and eye protection being used and preferably an explosive resistant barrier between the user and the potassium.

Potassium is usually kept under a hydrocarbon oil such as mineral to stop the metal from reacting with water vapor present in the air**. Potassium should not be stored under kerosene, as it readily reacts and can explode on contact**. Potassium metal reacts very violently with water producing hydrogen gas which then usually catches fire. The reaction evolves much heat and also causes the potassium to melt and splatter as it reacts. As potassium reacts with water, it produces highly flammable hydrogen gas. A potassium fire is only exacerbated by the addition of water, and only a few dry chemicals are effective for putting out such a fire. Potassium also produces potassium hydroxide (KOH) in the reaction with water. Potassium hydroxide is a strong alkali and so is a caustic hazard, causing burns.

Unlike lithium and sodium, however, potassium should not be stored under oil indefinitely. If stored longer than 6 months to a year, a yellow layer of dangerous shock-sensitive peroxides can form on the metal and under the lid of the container, which can detonate upon opening. It is recommended that potassium, rubidium or cesium not be stored for longer than three months unless stored in an inert (oxygen free) atmosphere, or under vacuum.

## Applicability

This guidance information applies to all chemists and any other employee who is involved with the packaging, inspecting, or using this type of laboratory chemical/reagent.

**Ideal Storage Conditions:**

Always store in a cool, dry, well-ventilated place and in a tightly closed container. Keep material away from any possible contact with water and do not allow water to get into container because of violent reaction. This material is moisture and air sensitive. Keep under oil and do not exceed recommended storage limit of 6 months. Promptly dispose of potassium approaching 6 months in age.

**Condition of Material / Scenario Requiring Treatment:**

Potassium Metal, uncontaminated, is silver/white in color. It is a solid normally found in chunks or in the form of sticks. Conditions that require stabilization prior to transportation include the following:

A. Material appears to be degraded/ contaminated.
B. Material appears to be discolored. ( yellow potassium oxide formation)
C. Deterioration or distortion of storage container.
D. Age of material exceeds recommended storage time.

**Hazard Analysis:**

A. Exposure to air and moisture may produce oxidation products that are explosively unstable.
   1) Potassium oxide
   2) Potassium superoxide

* <u>Potassium metal will form the peroxide and the superoxide at room temperature even when stored under mineral oil. Disposal within 6 months of purchase is recommended.</u>

# Benzoyl Peroxide ($\geq$50%)

## Overview

Dibenzoyl peroxide, commonly called benzoyl peroxide, is a chemical compound with the formula $(C_6H_5CO)_2O_2$. This solid is white, granular, and crystalline in appearance and is listed as an organic peroxide. It has no taste and has a faint odor of benzaldehyde. Benzoyl peroxide is soluble in nearly all organic solvents and slightly soluble in alcohols and water.

This dust of this chemical compound is highly toxic by inhalation, but the hazard of explosion doesn't exist until the product begins to dry. Benzoyl peroxide > 50% should be handled with care.

## Applicability

This guidance information applies to all chemists and any other employee who is involved with the packaging, inspecting, or using this type of laboratory chemical/reagent.

## Definitions

Peroxides are compounds containing a bivalent O-O group. Such compounds release atomic oxygen readily and are strong oxidizing agents.

**Ideal Storage Conditions:**

Always store in a cool, dry, well-ventilated place and in a tightly closed container separate from acids, alkalis, reducing agents and combustibles. See NFPA 43A, Code for the Storage of Liquid and Solid Oxidizers. Do not store above 40°C (104°F).

**Condition of Material / Scenario Requiring Treatment:**

Benzoyl Peroxide uncontaminated, is white in color. It is a crystalline powder with a slight benzaldehyde odor. Conditions that require stabilization/dilution prior to transportation include the following:

A. Material appears to be degraded/contaminated.
B. Material appears to be discolored. ( Off-white discolorations)
C. Exceeds percentage legally shippable without explosive classification

**Hazard Analysis:**

A. Exposure to heat, friction, or organic materials may produce:
   1) Explosive conditions
   2) Fire
   3) Chemical instability

B. Interactions with halocarbons may produce explosive reactions.
   1) Carbon Tetrachloride
   2) Methyl Methacrylate
   3) N,N-Dimethylaniline

# Picric Acid Stabilization

**Material Description:**

Picric Acid
Stabilization of lab pack quantities

**Background Info:**

Picric acid is the chemical compound formally called 2,4,6-trinitrophenol (TNP). This, a yellow crystalline solid, is one of the most acidic phenols. Like other highly nitrated compounds such as TNT, picric acid is an explosive. Its name comes from Greek πικρος (*pik' ros*), meaning "bitter", reflecting the bitter taste of picric acid. Other synonyms include: Trinitrophenol; Picronitric acid; Nitroxanthic acid; 2-Hydroxy-1,3,5-trinitrobenzene; Phenol trinitrate.

By far the largest use has been in munitions and explosives. In microscopy, picric acid is a reagent for staining samples, e.g., Gram staining. It has found some use in organic chemistry for the preparation of crystalline salts of organic bases (picrates) for the purpose of identification and characterization. Bouin's picro-formol is a preservative solution used for biological specimens. In addition to these uses, it is also used in workplace drug testing for the Jaffe Reaction to test for creatinine. It forms a colored complex that can be measured using spectroscopy.

Much less commonly, wet picric acid has been used as a skin dye or temporary branding agent. It reacts with proteins in the skin to give a dark brown color that may last as long as a month. In the early 20th century, picric acid was stocked in pharmacies as an antiseptic and as a treatment for burns, malaria, herpes, and smallpox.

**Ideal Storage Conditions:**

Always store in a cool, dry, well-ventilated place and in a tightly closed container. Store the containers in a segregated, approved and labeled area away from acute fire hazards and powerful oxidizing materials. Isolate from organic materials and never store in metal containers. Do not allow this material to dry out. Keep Picric acid wetted with a minimum of 30% water. Avoid all possible sources of ignition (spark or flame).

Dry picric acid is explosive. Dried crystals may be present within threads of screw top containers and present a detonation hazard when opening. If a bottle of picric acid is old and has a metal cap, care must be exercised as highly shock sensitive metal picrates may have formed. Do not store on concrete and protect from freezing.

**Condition of Material / Scenario Requiring Treatment:**

Picric acid in anhydrous form is shock, friction, and heat-sensitive. Care should be used when handling it due to the fact that it is highly unstable in crystalline form. While it is classified by the Department of Transportation as a flammable solid, it also causes severe eye and skin irritation with possible burns and is harmful if swallowed. Moisture content may not be visually observable and old materials older than 1 year should be wetted further prior to shipments.

Material may be shock sensitive. Any external energy input may cause high or low order detonation if any of the following conditions exist:.

1. Material appears to be degraded and or contaminated.
2. Material appears to be dry and contains <30% water or discolored
3. Deterioration or distortion of storage container.
4. Mechanical shock or friction
5. Age of material exceeds recommended storage time.

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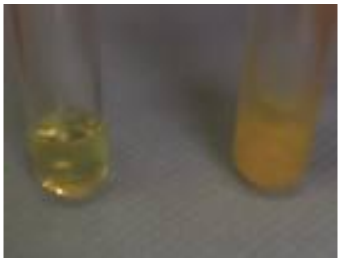
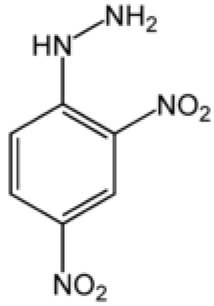
# 2,4-Dinitrophenylhydrazine Stabilization






**Material Description:**

2,4-Dinitrophenylhydrazine
Stabilization of lab pack quantities

**Background Info:**

2,4-Dinitrophenylhydrazine (DNPH, Brady's reagent) is the chemical compound $C_6H_3(NO_2)_2NHNH_2$. Dinitrophenylhydrazine is relatively sensitive to shock and friction; it is a shock explosive so care must be taken with its use. It is a red to orange solid, usually supplied wet to reduce its explosive hazard. It is a substituted hydrazine, and is often used to qualitatively test for carbonyl groups associated with aldehydes and ketones. The hydrazone derivatives can also be used as evidence toward the identity of the original compound.

**Condition of Material / Scenario Requiring Treatment:**

2,4-Dinitrophenylhydrazine in anhydrous form is shock, friction, and heat-sensitive. Care should be used when handling it due to the fact that it is highly unstable in crystalline form. While it is classified by the Department of Transportation as a flammable solid, it also causes severe eye and skin irritation and is harmful if swallowed. Lengthy exposures may affect the ability of blood to carry oxygen (methemoglobinemia), resulting in bluish discoloration of lips and tongue (cyanosis). Moisture content may not be visually observable and old materials older than 1 year should be wetted further prior to shipments.

Material may be shock sensitive. Any external energy input may cause high or low order detonation if any of the following conditions exist:

1. Material appears to be degraded and or contaminated.
2. Material appears to be dry and contains $<30\%$ water or discolored
3. Deterioration or distortion of storage container.
4. Mechanical shock or friction
5. Age of material exceeds recommended storage time.

**Ideal Storage Conditions:**

Protect containers against physical damage and store them in a cool, dry well-ventilated location, away from any area where the fire hazard may be acute. Outside or detached storage is preferred. 2,4-Dinitrophenylhydrazine should be stored separate from incompatibles and larger containers should be bonded and grounded for transfers to avoid static sparks. Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product. Do not attempt to clean empty containers since residue is difficult to remove. Do not pressurize, cut, weld, braze, solder, drill, grind or expose such containers to heat, sparks, flame, static electricity or other sources of ignition: they may explode and cause injury or death. Maintain the material's water content at a minimum of 30%.

## Perchloric Acid (>72%)


### Overview

Perchloric acid is the inorganic compound with the formula $HClO_4$. Usually encountered as an aqueous solution, this colourless compound is a strong acid comparable in strength to sulfuric and nitric acids. It is a powerful oxidizer, but its aqueous solutions up to appr. 70% are remarkably inert, only showing strong acid properties and no other oxidizing properties. Above concentrations of appr. 70% the speed of oxidizing reactions rapidly increases with increasing acid concentration. It is useful for preparing perchlorate salts, especially ammonium perchlorate, an important rocket fuel. Perchloric acid is also dangerously corrosive and readily forms explosive mixtures.

Anhydrous perchloric acid is an oily liquid at room temperature. It forms at least five hydrates, several of which have been characterized crystallographically. These solids consist of the perchlorate anion linked via hydrogen bonds to $H_2O$ and $H_3O^+$ centers Perchloric acid forms an azeotrope with water, consisting of about 72.5% perchloric acid. This form of the acid is stable indefinitely and is commercially available. Such solutions are hygroscopic. Thus, if left open to the air, concentrated perchloric acid dilutes itself by absorbing water from the air.

### Applicability

This guidance information applies to all labpack chemists and any other employee who is involved with the packaging, inspecting, or using this type of laboratory chemical/reagent.

**Ideal Storage Conditions:**

Keep container tightly closed in a dry, cool, and well-ventilated place. Containers which are opened must be carefully resealed and kept upright to prevent leakage. Separate from acids, alkalis, reducing agents and combustibles. See NFPA 43A, Code for the Storage of Liquid and Solid Oxidizers.

**Conditions of Material/Scenario Requiring Treatment:**

Perchloric Acid uncontaminated is a colorless, fuming, hygroscopic liquid. Conditions that require stabilization prior to transportation include the following.

A. Material appears to be degraded/ contaminated.
B. Material appears to be discolored.
C. Deterioration or distortion of storage container.
D. Exposed to thermal shock. (Direct sunlight)
E. Concentration above 72%.
F. Age of material exceeds recommended storage time.

**Hazard Analysis:**

A. Interactions with metals may produce metal perchlorates, which are explosively unstable when subjected to friction, mechanical shock, and thermal shock.
B. Perchloric Acid is highly corrosive and oxidizing material. Interactions with organic material may explode on contact, most notably acetic acid, acetic anhydride, alcohols, aniline, formaldehyde, paper, wood, carbon, glycols, and ethers.
C. Concentrations of Perchloric Acid above 72% are explosively unstable and DOT forbidden to transport.