



# Storage of organic peroxides



**Nouryon**

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55 m<sup>3</sup> total containment tank for large-scale safety testing in Deventer, the Netherlands

## Introduction

In general organic peroxides are unstable chemical compounds, decomposing at relatively low temperatures. They can, however, be handled and stored safely if proper precautions are followed. The prevention of undesired decomposition reactions during handling and storage of organic peroxides requires knowledge of the general properties of organic peroxides and the specific requirements of each individual peroxide. Personnel who understand and pay proper attention will be able to handle organic peroxides confidently and safely.

This brochure gives guidelines for the safe storage of organic peroxides in their original packaging. Organic peroxide storage requires two important considerations:

- minimization of the possibility of a peroxide decomposition
- reduction of the effects of such a decomposition.

This publication includes guidelines to minimize the probability of a peroxide decomposition by limiting the heat exposure of the product and preventing contamination. Measures to reduce effects of a decomposition are also discussed.

General recommendations are given as well as specific measures for temperature controlled products. A possible design of a storage building is given in Appendix 2. These recommendations are based on Nouryon's experience and extensive safety knowledge.

Beyond the scope of this brochure are the local laws and insurance regulations that must be considered in the design of storage facilities. Various countries have published directives with their local laws. A list of these directives is given in Appendix 1.

For more information on the use and the safe handling and storage of organic peroxides, please contact your Nouryon account manager or regional sales office.



Fire of 5,000 kg organic peroxide

# Safety aspects

## Thermal sensitivity

Organic peroxides are thermally unstable due to the relatively weak -O-O- bond in the molecular structure. As a result of this property organic peroxides are sensitive to heat and will decompose significantly above a certain temperature. This temperature is specific to each individual peroxide.

During decomposition heat is released and the rate of this decomposition increases with temperature. If this heat cannot be transferred to the environment due to reduced surface area from stacking or high ambient temperatures, self-heating will accelerate and lead to a violent combustion or thermal explosion.

Every packaged peroxide has a characteristic temperature at which the self-heating accelerates. This temperature is designated as the Self-Accelerating Decomposition Temperature (SADT). At or above this temperature a runaway reaction will take place. For this reason, strict temperature control and high temperature alarms are required for the storage of organic peroxides. For many peroxides refrigerated facilities will be necessary.



Safety testing to determine the sensitiveness of peroxides to the effect of heat under confinement

## Contamination

Contamination may accelerate the decomposition of organic peroxides. Most heavy metal compounds have an accelerating effect on decomposition.

Acids, bases and accelerators based on e.g. cobalt or copper and amines may cause decompositions to occur at temperatures significantly lower than the recommended storage temperature.

Therefore, organic peroxides must be stored separately from other chemical compounds, unless compatibility has been proven.

## Burning properties

Most organic peroxides should be considered highly combustible. Once ignited many organic peroxides burn vigorously. When heated to their decomposition temperature, organic peroxides will generate vapors. Many of these vapors are flammable. Therefore, the presence of potential ignition sources must be avoided. Electrical equipment installed should be explosion-proof to avoid sparks.

Nevertheless, auto-ignition of the vapors may still occur. Consequently, fire-fighting equipment should be present in all storage rooms.

## Pressure build-up

As organic peroxides produce vapors during decomposition, pressure build-up in the package occurs. To prevent excessive pressure rise inside storage rooms due to prolonged decomposition and bursting of the packages, the storage room should be provided with a pressure relief mechanism.

# Storage

One can minimize the probability of a peroxide decomposition by limiting the heat exposure of the product and preventing contamination. Temperature control is the most critical control measure in preserving quality and preventing a runaway reaction.



Although a number of organic peroxides can be safely stored at ambient temperature, most require some form of temperature control. The maximum temperature allowed by the regulatory agencies is the control temperature  $T_c$ .

This temperature together with the emergency temperature ( $T_{em}$ , see section Temperature control and monitoring on this page) are derived from the SADT in next table.

TYPE OF RECEPTACLE	SADT	CONTROL TEMPERATURE	EMERGENCY TEMPERATURE
Single packagings and IBCs	20°C or less over 20 to 35°C over 35°C	20°C below SADT 15°C below SADT 10°C below SADT	10°C below SADT 10°C below SADT 5°C below SADT
Portable tanks	≤ 45°C	10°C below SADT	5°C below SADT

However, for a longer shelf life, lower storage temperatures than the control temperature are generally recommended. At this recommended storage temperature ( $T_s$ ), as indicated on the product label, the product will be stable and quality loss will be minimal.

As each organic peroxide has its own specific storage temperature, consult the product catalog or individual Product Data Sheet (PDS) which can be downloaded from polymerchemistry.nouryon.com.

#### Temperature monitoring and control

The temperature must be maintained at or below the recommended storage temperature; consult the product catalog or PDS.

Organic peroxides should be protected from direct sunlight and all other sources of heat.

Particular attention should be given to:

- windows (not recommended or should be blinded),
- heating systems (e.g. radiators, warmwater pipes, etc).

Cooled storage rooms should be provided with at least two independent temperature alarms. An alarm is recommended when the storage temperature is exceeded by 5°C. If this is the case the store should be inspected. The temperature alarm should incorporate some delay device to allow for intermittent short temperature increase which result from inspection, loading and unloading, etc. Any possibility of alarm de-activation should be countered with an automatic alarm re-activation.

Non-cooled storage rooms should be provided with an alarm set at the emergency temperature but not higher than 45°C. It is imperative that a signal from the mentioned alarm systems should not escape notice at any time including nights, weekends, etc. and that appropriately trained personnel are alerted.

There should be dual power supply for the alarm system.



Space between pallets to allow maximum air circulation

#### Fire fighting

A deluge system of large capacity is strongly recommended to fight large fires.

A dry-powder fire extinguisher with a capacity of at least 10 kg should be located outside the storage building, near the entrance. This is used only to fight small fires of organic peroxides. After the fire has been extinguished the peroxide should be cooled to a temperature below the SADT to prevent the peroxide from re-igniting due to self heating.

#### Management

Smoking, open fire and all other sources of ignition must be forbidden in and near the storage rooms. Appropriate warnings should be posted in the storage area.

Unless compatibility has been proven, organic peroxides should be stored separately from other chemical compounds and, under all circumstances, away from accelerators and other reducing agents.

Store organic peroxides in their original closed packages.

Packages should be visually checked for labelling, leakage and damage, etc. at the time of delivery. If necessary the material should be repacked in suitable, clean packages. A suitable packaging material is non-pigmented polyethylene. Never use tightly closed rigid metal containers.

Repacking, weighing, mixing, etc. should be carried out in a separate room. Clean dedicated polyethylene or stainless steel implements should be used to prevent contamination of the peroxide.

Stacking procedures should require that labels and safety information are always visible. Pallets should be configured to allow maximum air circulation, no more than two high with a minimum clearance of 0.1 m from any wall.

Storage on racks may be applied when individual packages are stored. Different products should be stacked separately to avoid confusion.

If liquid organic peroxides are stored, an inert absorbent material, such as vermiculite or perlite, should be available in or near the store to clean up small spillages. Absorbents should be soaked with water afterwards.

Stock should be rotated following the first in, first out principle.

The doors of the storage should be marked with the peroxide label.

The storage building should be kept clean; no litter, rags, etc.

The store should be kept closed with access limited to authorised, trained personnel only.



Small fire extinguishers in the neighborhood of peroxide stores



Use vermiculite or perlite to clean up small spillages

# Design guidelines for a storage building



Storage temperatures near the entrance of the storage rooms

Repair works on the storage building and its control system should only be performed after a written permit, signed by the responsible supervisor of the storage facility.

Written procedures for alarm response should be developed and implemented prior to installation of an organic peroxide storage facility. Only appropriately trained personnel should be involved in any emergency response.

Regular (once a shift) inspections of the organic peroxide storage building are recommended.

The above recommendations should have the regular attention of the personnel who are in charge of the storage of organic peroxides.

## Additional recommendations for cooled facilities

A back-up cooling system is recommended. A back-up chiller and emergency generator, alternative buildings, refrigerated transport containers or dry ice are options. Provision for an alarm to sound in case of failure of the cooling unit is required; e.g. low pressure alarm in the cooling medium system.

The storage temperature should be posted near the entrance of the storage room.

The actual temperature in each store should be indicated at the building or storage area entrance.

Before putting a cooled store into use, determination of the rate of temperature increase, after the mechanical cooling has stopped is recommended. This can be done with dummy packages simulating the containers with organic peroxide. It is recommended to test each individual store with different degrees of filling, e.g. empty and half filled, in order to have the temperature-time characteristics available as basic knowledge for an emergency program.

## Site

The floor should be seamless, easy to clean and made from a non-combustible and non-absorbent material. A slight slope is recommended. This will direct liquids and allow for easier clean-up. Exercise extreme caution when collecting this liquid to prevent trapping of organic peroxides. As fire fighting water may carry peroxide, it should be directed from the inside of the storage building through an open gutter to an open basin outside. Another possibility is to direct the water (with peroxide) into a basin underneath the floor with provisions for emptying. The capacity of the basin should be at least equal to the maximum amount of stored products.

Any drainage system should not be in direct contact with the site sewer system to allow control of the peroxide. It should be noted that fire-fighting water may carry burning peroxide with it as it drains away. Observe local regulations with respect to containment of fire-fighting water.

A storage building should be adequately provided with lightning protection. When the store is painted outside, light colors are recommended. Construction materials should be compatible with organic peroxides or coated to prevent contamination.

Ventilation openings (required for volatile non-cooled peroxides) should be covered with gratings and should be at least 0.5% of the floor area with a minimum of 0.01 m<sup>2</sup>.

Placement of organic peroxide stores with respect to essential equipment or services, office buildings, public roads, railways, waterways, etc. must be considered. No definite distances can be stated as generally applicable. Typical distances for most peroxides

with respect to offices are 10 m for storage of 1 ton of peroxide and 20 m for storage of 10 tons of peroxide when safety provisions are made. Local regulations should be consulted.

## Construction

Based on the extensive experience of Nouryon with organic peroxides, the following describes our recommended storage building. The design is such that safety distances reach minimal dimensions. The drawings in Appendix 2 illustrate further details.

As a pressure release mechanism, each storage building should have a venting capacity of 0.5 m<sup>3</sup> per 1000 kg of organic peroxide capacity. The roof, door(s), or wall panels can serve this function. The emergency venting should actuate at a pressure below the design pressure of the storage room. Doors should always be functional from inside the store. The walls should be constructed of non-combustible materials and have a fire resistancy of at least 1 hour.

If there is a risk that the temperature in a non-cooled store can occasionally rise above 30°C a low capacity spray system, installed on the outside of the roof, can be of help to maintain the temperature below 30°C. The roof construction and material should obviously be suitable.

Another possibility may be a double-deck roof: the air layer acts as an insulating layer.



Organic peroxide storage rooms



Actual temperature in a peroxide store



Roof venting in peroxide stores



Two cooling units, alternately operating, fully independent of each other



# Appendix 1

## Regulations on storage



### France

Journal Officiel de la république Française: Arrêté du 6 novembre 2007 relatif à la prévention des risques présentés par les dépôts et ateliers utilisant des peroxydes organiques. NOR: DEVPO765936A

### Germany

BGV B4 Organische Peroxide vom 1. Oktober 1993/Fassung 1. Januar 2011 mit Durchführungsanweisungen vom Oktober 2000

### The Netherlands

Publication Series on Dangerous Substances 8 (PGS 8) Storage of Organic Peroxides, December 2011

### Spain

Instrucción Técnica Complementaria MIE-APQ-9 'Almacenamiento de Peróxidos orgánicos' y de materias autorreactivas, 23-06-2017

### Sweden

Sprängämnesinspektionen föreskrifter om hantering av organiska peroxider, Organiska peroxider, SÅIFS, 1996:4

### United Kingdom

Health and Safety Executive, UK, Chemical Safety Series 21. The Storage and Handling of Organic Peroxides, Guidance Note CS 21, 1991

### United States of America

National Fire Protection Agency, USA, NFPA 400 Hazardous Materials Code, 2016

In addition to this brochure, for legal purposes, consult your national storage regulations.



Use of explosion-proof forklifts

An effective fire-fighting system should be installed. An automatic system activated by melting bulbs (57°C) is recommended.

Manual activation of the deluge system should always be possible.

If an organic peroxide storage building is fitted with a heater, the following precautions must be observed:

- the heating system should have a moderate capacity;
- temperature of the heating surface should not exceed 60°C,
- if an electrical heating system is used, the equipment should be explosion-proof,
- if warm air is used, it should be directed away from the packages,
- a high temperature warning system must be installed in the storage room,
- to achieve a safe distance between the organic peroxide packages and the heater, fixed barriers should be installed.

All electrical fittings and other electrical equipment should be explosion-proof.

### Additional requirements for cold storage

Walls, roof and door(s) should be insulated. The insulating material should be non-flammable or flame-retardant. To avoid absorption of moisture and to retain the insulating properties, non-absorbent material (closed cell structure) should be used.

Moreover, the material should preferably be resistant to the solvents used in the products to be stored. If the insulating material is not solvent resistant it should be covered with a cladding material.

Any equipment, including the cooling unit, that may generate heat or sparks should be located outside the storage building, away from the entrance so as to reduce the electrical requirements (if all wall ducts are air tight).

Any electrical equipment having direct contact with the inside air should be explosion-proof.

The cooling agent should be non-flammable and non-reducing; liquid air is unsuitable.

Moving parts and openings should be protected from becoming icebound by atmospheric moisture.

In contrast to non-cooled storage, there should be no ventilation openings in doors or walls. If fresh air ventilation is desired, the following items should be considered:

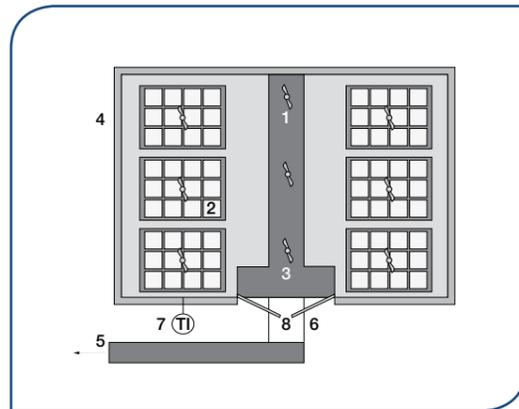
- the replacement rate should be minimized,
- the outside air intake must not be allowed to warm up the stored peroxides.

If a sprinkler or deluge system is used, it should be a dry type system.



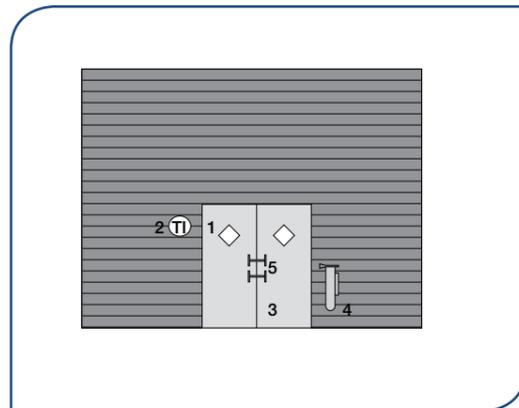
# Appendix 2

Storage building design with the roof as an emergency vent.



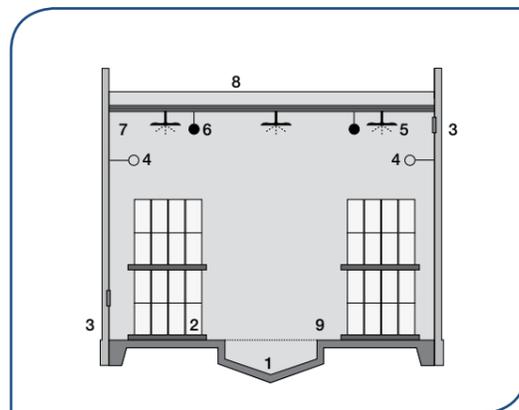
**Floorplan:**

- 1 sprinkler head
- 2 pallet with packages
- 3 gutter/basin system
- 4 fire resistant wall
- 5 gutter system to outside basin
- 6 doors
- 7 temperature indicator
- 8 gutter system to outside gutter



**Front:**

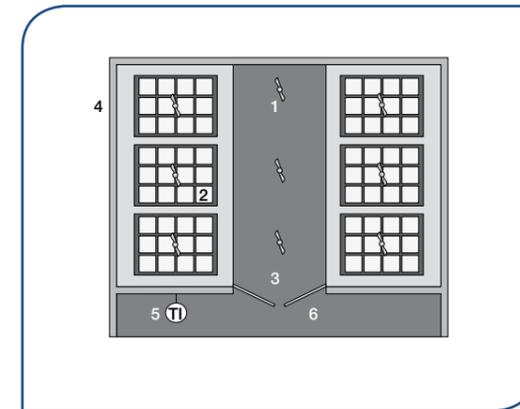
- 1 placarding
- 2 temperature indicator
- 3 doors
- 4 portable fire extinguisher
- 5 locks



**Cross section:**

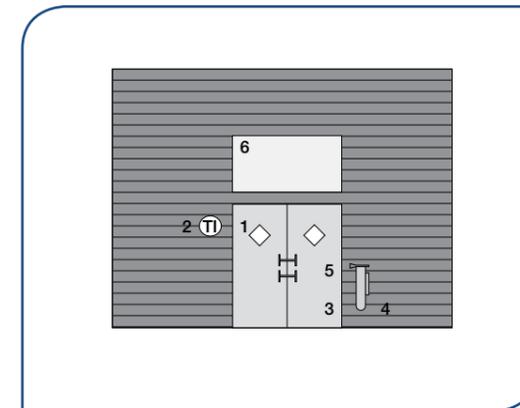
- 1 gutter/basin system
- 2 pallet with packages
- 3 ventilation opening with gratings
- 4 temperature sensor
- 5 sprinkler head
- 6 melting bulb
- 7 steel beam
- 8 loosely constructed roof (emergency vent)
- 9 sloped floor

Storage building design with a venting panel above the doors



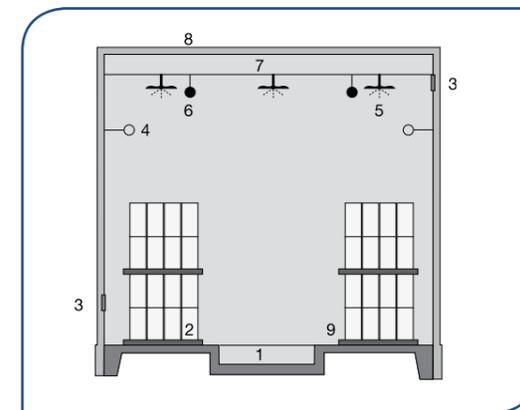
**Floorplan:**

- 1 sprinkler head
- 2 pallet with packages
- 3 gutter/basin system
- 4 fire resistant wall
- 5 temperature indicator
- 6 doors



**Front:**

- 1 placarding
- 2 temperature indicator
- 3 doors
- 4 portable fire extinguisher
- 5 locks
- 6 venting panel



**Cross section:**

- 1 gutter/basin system
- 2 pallet with packages
- 3 ventilation opening with gratings
- 4 temperature sensor
- 5 sprinkler head
- 6 melting bulb
- 7 lower part of double roof
- 8 upper part of double roof, rigid constructed
- 9 sloped floor

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## Additional information

Product Data Sheets (PDS) and Safety Data Sheets (SDS) for our polymerization initiators are available at [nouryon.com](http://nouryon.com)

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