

# Safety of organic peroxides



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Dutch Pressure  
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# Safety: Our top priority



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

For nearly everyone who makes decisions in the process industry, safety has become one of the primary points of consideration. The extensive safety efforts put forth by many companies have already resulted in a low statistical number of casualties in the chemical industry.

To this achievement simple protective measures for the workers (helmet, clothing, etc.), improved process control, proper safeguarding and comprehensive plant designs greatly contributed. Most companies perform Hazard and Operability studies and other techniques such as Quantitative Risk Analyses to assess the safety of a plant.

Such studies require a thorough knowledge of various intricate aspects, such as the process variables and the characteristics of the raw materials. For an estimation of the extent of the hazards, acquaintance with the effects of runaway reactions, gas/dust explosions, flammability, etc. is also a requisite. Therefore, these items are subject of continuing studies to get an even better understanding of the hazards.

As the global leader in organic peroxide safety we are committed to the safe handling and storage of our products. We at AkzoNobel always place safety as our top priority.

This brochure presents our view of the safety aspects of organic peroxides including the latest insights into their behavior and overall safety.

# Our expertise is your expertise



AkzoNobel has a long history in organic peroxides, starting with dibenzoyl peroxide used for the bleaching of flour in the early 1920s. Since then we have added many new organic peroxides to our product portfolio, with the growth of plastics in everyday life.

Today, we are the worlds leading producer of organic peroxides. Each year, millions of tons of PVC, LDPE, acrylics, styrenics, CR-PP and other thermoplastics are manufactured with our products. Not to forget our range of organic peroxides for the curing of thermoset resins and the crosslinking of elastomers.

Organic peroxides are in principle thermally unstable compounds which require extensive safeguarding. Their behavior is different from that of many other organic chemicals and they are in fact thermally explosive.

Much of our success is due to our long-term commitment to developing and maintaining the highest safety standards. Our thorough understanding of organic peroxide chemistry is the basis for the development of safe processes and products, adapted to customers' needs with respect to storage, handling and supply facilities. Sharing our experience in safety is one of the most important resources we offer.



From a safety point of view, reduction of the hazardous effects is not the only parameter influencing the risk when operating with organic peroxides. Modern hazard and operability studies formulate risks as follows:

$$\text{risk} = \text{probability} \times \text{effect (eq.1)}$$

By this definition the probability that an accident will happen is an independent variable determining the risk involved in an operation. As a matter of fact, every industry working with hazardous materials, e.g. liquefied gases, or carrying out hazardous processes, e.g. polymerization at high pressures, tries to prevent undesirable events by reducing the probability of their occurrence.

The probability of a peroxide accident is reduced or in some cases even eliminated by a number of ways.

For example dry dibenzoyl peroxide which is shock-sensitive, so that the probability of an explosion effect being initiated by mechanical treatment is very high.

The same product wetted with 25% water is practically insensitive to shock and thus has a much lower probability of being ignited. A more common way to reduce the probability of accidents is proper handling of the product. The effect parameter is reduced to an acceptable level by eliminating from the product list those peroxides which show extreme- or avoidable hazards in our extensive safety tests.



# Peroxide safety

The essential feature of organic peroxides is their ability to form free radicals at specific temperatures. These free radicals initiate the desired chemical process. For polymerization a typical process can schematically be given as:



where, in practice, the peroxide concentrations in the monomer vary between 5 and 0.05%.

The main safety aspect of organic peroxides is inherently connected with their function as polymerization initiator. In the absence of monomer the above reaction proceeds as follows:



The reaction is strongly exothermic, which gives rise to dangerous phenomena similar to those observed for many polymerization reactions, namely a runaway. In the case of peroxides the runaway is commonly called a thermal explosion.

Details about the exceptional thermal instability of peroxides are thoroughly discussed in the following chapters. It is an essential part of their thermal behavior, which makes peroxides different from most other substances. Most other safety aspects of peroxides resemble those of common organic substances. In terms of risk assessment (see eq. 1) the specific hazard of peroxides can be described as follows:

**The probability parameter** reflects the chance that a peroxide will be subjected to an unwanted temperature increase as expressed by eq. 3. The thermal activation of the peroxide is functionally only in the polymerization process as indicated in eq. 2, but has to be avoided at any earlier stage.

**The effect parameter** reflects the magnitude of the thermal explosion effect. The degrees of violence vary widely. Aqueous peroxide suspensions and emulsions for instance, have a violence of decomposition which is almost negligible. For most peroxides the effect is sizable and appropriate precautions are required. On the other hand, it has to be noted that peroxides exhibiting properties similar to those of explosives, are not marketed by AkzoNobel.

# Safety parameters

Dust explosion testing  
of solid organic peroxide



Decomposition of contaminated peroxide



The safe handling and housekeeping of organic peroxides, and a proper prevention of undesired events, is possible only if the hazards are known. In this chapter, the hazards, including those which organic peroxides have in common with most other chemicals, are presented.

#### Fire

Most peroxides burn violently. The reason is that the high temperatures at the flame front induce decomposition in the peroxide surface layer. Therefore, the burning rate is high, which in combination with the presence of flammable decomposition products gives rise to heavy fires. Selection of site and construction of organic peroxide storage buildings is mainly based on fire hazard (see chapter Storage on page 14). Some peroxide formulations, aqueous peroxide suspensions and emulsions are an exception to this rule.

#### Ignitability

Due to their low vapor pressure the flashpoint of organic peroxides is generally higher than their decomposition temperature. Explosive gas mixtures will therefore not be present in peroxide storage rooms. A noticeable exception is di-tert-butyl peroxide, which has a flashpoint of 6°C.

On the other hand, the decomposition vapors of organic peroxides are of course combustible. Ignition of peroxides may take place due to external fire, hot surfaces or the decomposition of the peroxides themselves.

#### Decomposition temperature

The lowest temperature at which a runaway can take place with a substance in the packaging as used in transport, is called Self-Accelerating Decomposition Temperature (SADT). SADT values can be found in our product catalog or Product Data Sheets (PDS) which can be downloaded from [www.akzonobel.com/polymer](http://www.akzonobel.com/polymer).

More information about this important aspect of peroxide safety is given in chapter Thermal stability on page 8. For SADT values of peroxides

in containers other than the commercial packing units, e.g. storage tanks and supply vessels, please consult your supplier.

#### Thermal explosion

The effect of a decomposition varies from mild to violent. Peroxides are subjected to a series of tests to classify the hazard (see chapter The thermal explosion hazard on page 11). Do not put peroxides in closed metal containers or glass bottles without having installed appropriate venting devices.

#### Contamination

Contamination constitutes a hazard, because many chemicals seriously reduce the decomposition temperature (SADT) of organic peroxides. Notorious examples are metal salts, amines, acids, bases and construction materials such as iron, copper and other heavy metals. Compatibility must have been proved before foreign materials are mixed with peroxides. Solvents sometimes reduce the thermal stability as well.

#### Mechanical sensitivity

Friction, shock and impact can cause decomposition mainly due to the high local temperatures they create. The decomposition can propagate through the peroxide.

Most commercially available organic peroxides show a low degree of mechanical sensitivity. Nevertheless, this item needs attention when severe mechanical treatment is applied, as occurs during grinding, pumping, intensive mixing and in the rolling mill.

#### Physiological effects

In general, peroxides are moderately toxic upon inhalation and ingestion. Because of their low

vapor pressure at handling temperatures no special precautions for inhalation are required during regular handling. Proper ventilation is strongly advised. In case of dust formation, dust masks are recommended. Do not ingest peroxides as they may affect the internal organs.

A noticeable physiological hazard is the contact of the liquid peroxide with the eyes and skin. Particularly, ketone peroxides and hydroperoxides can lead to serious eye damage and sometimes blindness, if the eyes are not immediately rinsed with copious amounts of water.

Contact with the skin may cause lesions or irritation. For this reason, personal means of protection, such as safety goggles and protective gloves are recommended.

Detailed information on a specific peroxide can be found in the Material Safety Data Sheet (MSDS) available at [www.akzonobel.com/polymer](http://www.akzonobel.com/polymer).

Free radicals are obtained by thermal activation of the peroxide. For strongly diluted peroxides the rate of free radical formation at various temperatures can be determined from the half-life chart or Arrhenius equation on page 30 of our product catalog.

# Thermal stability



Thermal Activity Monitor for accurate measurement of the decomposition rate of organic peroxides

AkzoNobel offers a wide range of organic peroxides for the polymerization of various monomers at temperatures from 250°C to as low as 40°C. However, formation of free radicals should be avoided during storage, transport and handling because of quality and safety reasons.

The safety aspect is assessed by thermal stability studies of the concentrated peroxide at low temperatures. This results in SADT charts to be used for the handling of the peroxides.

In a way the SADT charts are the counterpart of the half-life charts used for the processing. Half-life charts are applicable to low peroxide concentrations. The half-life is an important process parameter in polymerization reactions.

## SADT charts

For concentrated organic peroxides, the occurrence of a runaway reaction is determined by the product temperature. At high temperatures the exothermic decomposition gives rise to self heating. This, in turn, causes an increase in temperature. At the higher product temperature the decomposition becomes even faster and thus a self-accelerating decomposition is attained resulting in phenomena described in chapter The thermal explosion hazard on page 11. The lowest temperature at which self-accelerating occurs is referred to as Self-Accelerating Decomposition Temperature (SADT). At temperatures below the SADT, some decomposition of the peroxide can occur, but it does not lead to self-acceleration and its accompanying hazardous effects.

The behavior of the product temperature as a function of various ambient temperatures is given in a SADT chart. SADT charts of specific peroxides are available upon request. Figure 1 on page 9 displays the experimental results of

the thermal stability study of tert-butyl peroxy-2-ethylhexanoate (Trigonox® 21S).

Four Trigonox 21S samples of about 10°C are placed in ovens at 40°C, 35°C, 30°C and 25°C, respectively. The course of the product temperature in the following days is indicated in the figure. The sample placed in the oven at 40°C decomposes 12 hours after the product has reached its ambient temperature of 40°C. The sample at an ambient temperature of 35°C decomposes about 115 hours after having reached the oven temperature. The third sample exceeds the oven temperature by about 3°C, but does not increase any further.

Seven days after having reached its new ambient temperature of 30°C the peroxide content has deteriorated from 97.2 % to 93.5%. Finally, the product at 25°C reaches the oven temperature and does not show a perceptible extra temperature increase, but suffers some quality loss in the considered time span of 7 days.



The test conditions are such that the samples simulate behavior of 25 kg Trigonox 21S in a 30 l container. The test method used is called the Heat Accumulation Storage Test (Wärmestau). The test has been developed by the German Institute for Material Research (BAM) and is recommended for the determination of SADT values by the United Nations Group of Experts for the Transport of Dangerous Goods. From Figure 1 it can be concluded that the lowest temperature at which tert-butyl peroxy-2-ethylhexanoate shows self-accelerating decomposition within 7 days is 35°C, when measured at multiples of 5°C.

### Thermal conditions

The occurrence of a thermal runaway, i.e. self-accelerating decomposition, is basically determined by the heat balance between the heat generated in the exothermic decomposition reaction and the heat dissipated to the surroundings.

Consequently, SADT values are different for each peroxide and influenced by external conditions such as amount of peroxide, heat transfer coefficient and type of packing. One could argue that it would be advantageous to pack organic peroxides in containers facilitating the heat exchange between product and its surroundings.

This would indeed lead to higher SADT values but not to higher storage temperatures. Although the heat losses have increased, the decomposition, i.e. quality loss, remains.

At the recommended storage temperature the heat produced by the peroxide is so low that it easily dissipates. Details about SADT and heat production data of peroxides can be found in references 1-4.

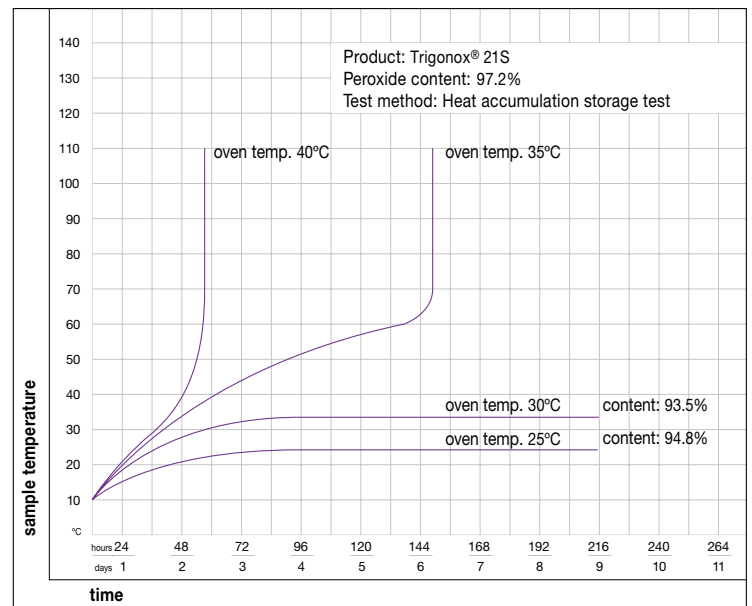
SADT values are influenced by the amount of peroxide per container. Test and calculation methods are available to determine SADT values for peroxides in drums, supply vessels and storage tanks. Since the external conditions in these cases vary, no uniform SADT values can be given (see also Figure 3 and accompanying text on page 10). Contamination of peroxides can drastically reduce the SADT. SADT values of solid organic peroxides can decline considerably when they are dissolved.

Peroxide packing and storage rooms are designed to keep the product temperature constant, not to cool a product of too high temperature to normal. Considerable misconception exists with regard to this matter, which frequently results in unwanted decompositions.

Peroxides of too high temperature can indeed be cooled down. However, extra means of cooling are necessary, e.g. ice, liquid N<sub>2</sub> or solid CO<sub>2</sub> (dry ice).

'Peroxides of too high temperature' are products which have reached the maximum storage temperature but not yet the SADT.

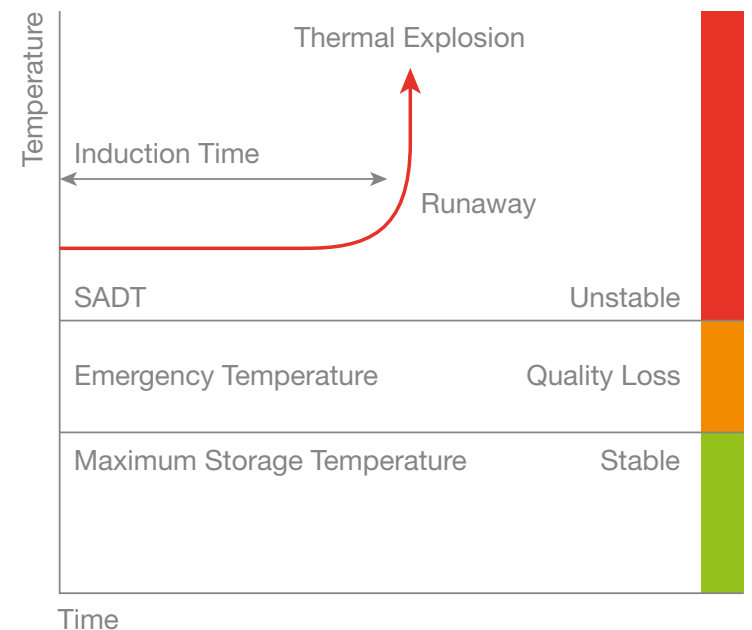
Figure 1: SADT chart of Trigonox 21S



SADT: lowest ambient (oven) temperature at which decomposition results in a temperature rise of more than 6°C.

Emergency temperature: temperature at which the planned emergency action must be executed.

Figure 2: Thermal stability of organic peroxides



### References:

- 'Thermal properties of peroxides' by J.J. de Groot and F. Hupkens van der Elst in 'Runaway Reactions', I. Chem. E. Symposium Series No. 68, 3/VII
- 'Thermal stability of tert-butyl peroxy pivalate' by A.C. Hordijk, J. Verhoeff, J.J. de Groot in 'Thermochimica Acta', 43 (1981)
- 'Experimental data on the thermal kinetics of organic peroxides' by A.C. Hordijk and J.J. de Groot in 'Thermochimica Acta', 101 (1986) 45-63.
- 'Evaluation of the validity of the UN SADT H.4 test for solid organic peroxides and self-reactive substances' by M. Steensma, P. Schuurman, M. Malow, U. Krause, K.D. Wehrstedt in 'Journal of Hazardous Materials' A117 (2005) 89-102.

Once ignited, organic peroxides burn more violently than common solvent like, for example, acetone



### Induction times

Peroxides can be handled for a limited period of time at temperatures close to and even above their SADT values. Firstly see Figure 1 on page 9, because it takes some time for the peroxide to reach the new ambient temperature; secondly, because the self-heating process takes some time, which is called induction time.

The first time-lag can be used for transferring cooled peroxides from one room to another, the second time-lag for the supply of the peroxide into the polymerization process.

Handling of the peroxide during the induction time requires careful engineering. Figure 3 on this page also illustrates the induction times for Trigonox 21S in 30 l packages: 12 hours at 40°C and 11 hours at 35°C, ambient temperatures. The graph on page 15 illustrates another use of induction times: peroxides in supply vessels. For a 600 l supply vessel filled with a 25% Trigonox 25 solution the induction times have been calculated.

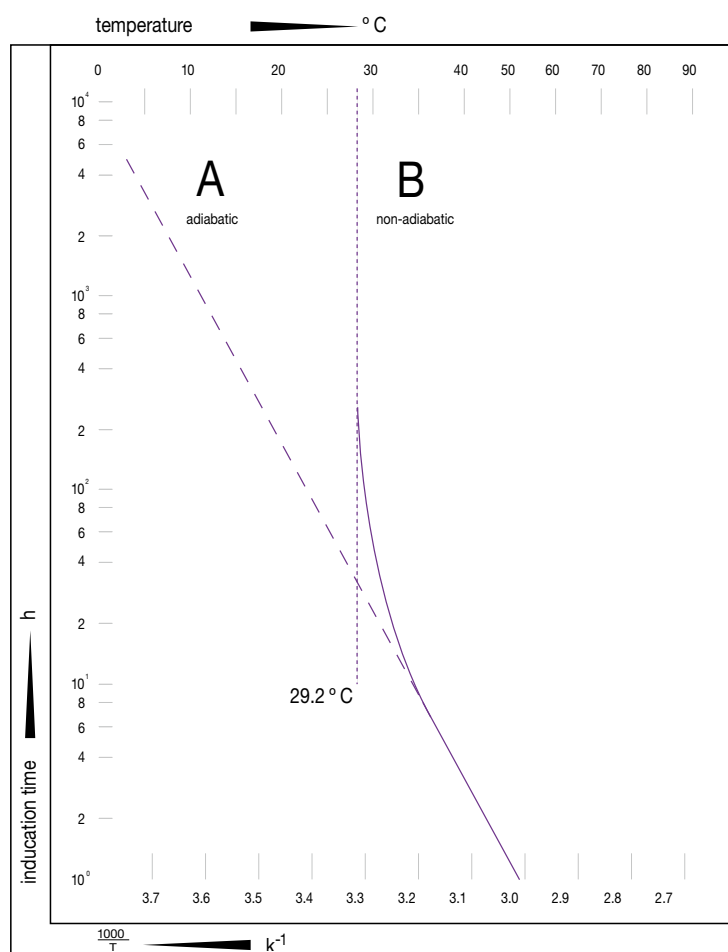
Cooling influences the SADT and induction times. The induction time becomes infinite at low temperature; the critical point being the SADT for the product in the tank.

At high temperatures the induction time decreases exponentially with temperature. Induction times are notably shorter than the corresponding half-lives of the product.

The induction time plot can be used to determine the time available for emergency actions.

One should restrict the duration of the operation at high temperatures to one fourth of the induction time.

Figure 3: Induction times of Trigonox 25-C25 in a 600 l vessel as a function of temperature



The graph is an example only and shown for reference. Specific charts can be made upon special request.

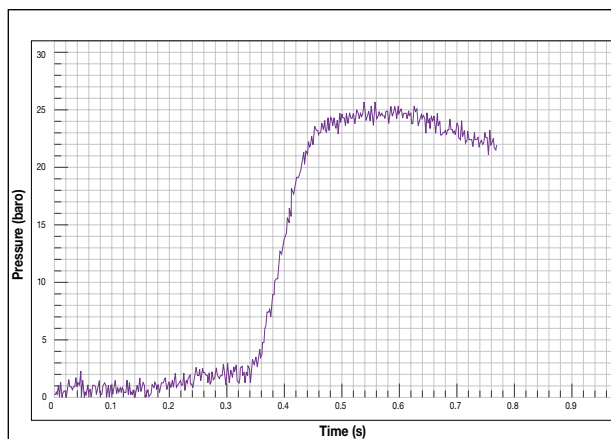
# Thermal explosion hazard

The thermal explosive decomposition of a peroxide is not the most common accident with peroxides; a fire.

Nevertheless, knowledge of the damaging effect caused by a violent decomposition is helpful for the preparation of a balanced set of precautions and is necessary for the design of appropriate means of protection. Peroxides are subjected to a number of safety tests to determine the effect of the decomposition under a variety of external circumstances. To obtain an impression of the thermal explosion hazard a brief description of the most important phenomena is given below.

peroxides showed violent or questionable effects. These peroxides are usually phlegmatized until a definite detonation is shown to be absent. Chemical substances which do not detonate can still be considered to have explosive properties, if the product shows violent decomposition effects or a rapid propagation of the decomposition.

Figure 4:  
Fast pressure rise as  
a result of a thermal  
explosion  
 $P_{\max}$ : 25.3 bar  
 $dP/dt_{\max}$ : 250 bar/s



## The uncontrolled decomposition

A product heated to a temperature slightly above its SADT shows the following chain of events:



The temperature record of a peroxide decomposition is as shown in the graph on page 9. The asymptotic temperature increase can reach several hundred degrees centigrade. Recording the pressure of the explosive decomposition in a closed laboratory vessel is done on a routine basis at the AkzoNobel Safety Research Laboratory.

Figure 4 shows the pressure effect of a 5 g sample in a 200 ml vessel. The pressure reaches 35 bar in about 75 milliseconds. The shape of the pressure curve is similar to those of gas and dust explosions in closed containers. The maximum pressure of peroxide explosions is determined by the amount of peroxide in relation to the total volume of the container.

## Explosive properties

The most hazardous peroxides have been subjected to detonation tests. Detonation is a characteristic property of explosives. Some

## Hazard rating and labeling

Peroxides vary widely in contest. Lauroyl peroxide, tert-butyl cumyl peroxide, dicetyl peroxydicarbonate and others show minor hazardous effects. Dibenzoyl peroxide, diisopropyl peroxydicarbonate and in particular diacetone peroxide can be hazardous in the pure state or in case of inadequate phlegmatizing. Moreover, decompositions of dry dibenzoyl peroxide and dry acetone peroxide are easily initiated by friction. The combination of violence and high mechanical sensitivity attributed to organic peroxide molecules is widely feared for.

Our commercial peroxides have been selected so as to avoid such hazards. Mechanical sensitivity is essential for organic peroxide applications, therefore mechanical sensitive molecules are either not selected or made insensitive by appropriate formulation. Phlegmatization, dilution and formulation are frequently used to make a peroxide less hazardous. For example, the hazardous properties of the peroxide in aqueous suspensions and emulsions have been downgraded to such a low level that these products are regarded as non-hazardous.

All organic peroxides are labeled according to the international transport regulations (see section Transport regulations on page 13). In addition to the red and yellow Class 5, Division 5.2 label, the orange 'explosive' and/or white 'corrosive' subsidiary risk labels can be present.

The 'explosive' label is to be applied to those organic peroxides which show a violent decomposition or rapid deflagration in the package as used for transport.

The 'corrosive' label is mainly applicable to ketone peroxides and hydroperoxides.

In addition to the labeling according to international transport regulations, labels may be put on packages according to the Globally Harmonized System (GHS), national regulations valid in some geographical parts of the world (e.g. European Union, Malaysia, Canada). Since peroxides differ so widely in hazard, it is important to inquire about their properties before using them.



# Peroxide containers and their transport

Packing and mode of transport are important to the user, who must adapt his storage and handling systems accordingly. The container size has been selected on the criteria of safety. The basic point is that a number of small packing units is less hazardous than the same amount in a large container. Whereas in a large container the entire contents can decompose as a unit, it is impossible that all the small packing units decompose at the same time.





## Containers

Most of the pure and highly concentrated liquid peroxides are supplied in 30 l polyethylene containers.

Most solid peroxides are packaged in polyethylene bags inside a corrugated cardboard box. Others are available in fibre drums. The packing itself provides an optimum in safety: insulation (see chapter Thermal stability on page 8), rupture when necessary (see chapter The thermal explosion hazard on page 11).

The containers are stacked on pallets in two layers or four layers.

A few peroxides are packed in 200 l drums or larger containers. The peroxide and its container have to meet certain standards. The major safety criteria for the transport of the peroxide in a larger container are: no mechanical sensitivity, minor deflagration effects, low explosive power, low thermal explosion effect. The container must be adjusted to the peroxide hazards. Compatible construction material, mechanical strength, relief valves, bursting discs are some of the required provisions. The main objective is to prevent fragmentation of the tank in case of a decomposition.

AkzoNobel was the first organic peroxide producer to introduce intermediate bulk containers (IBC's). These IBC's offer a balance of economy and safety for the transportation, storage and handling of organic peroxides. In addition, IBC's have several advantages over smaller packages, such as: reduced worker exposure to organic peroxide vapors, elimination of packaging waste and reduced handling of organic peroxides and packaging.

The specifically designed 1250 l stainless steel IBC for diluted organic peroxides and peroxide emulsions has obtained approvals for the transport of organic peroxides by road and by sea. The spring-loaded clamping device, used as an emergency vent, is an AkzoNobel invention and has been patented. And we're continually looking for new ways to optimize safe transport, handling and storage of organic peroxides.

Most recently we've led the way with our unique composite IBC's for dilute type F organic peroxides. Due to their weight and dimensions, these IBC's offer benefits in safety and handling while giving all the advantages of our stainless steel containers. They also have a lower environmental impact. We provide recollection and recycling, showing our commitment to developing new products and packages which are more sustainable, without compromising on performance.

The AkzoNobel development of a cooled trailer with IBC's connected to a manifold eliminates the in-house handling and transport of IBC's. Organic peroxides can be directly pumped into storage tanks by a leak-free, dry-break connection. All unloading facilities are present on the trailer.

In diluted form (20 to 40% peroxide concentration) bulk transport is feasible for practically all peroxides in tanks of 10 to 20 m<sup>3</sup> capacity. Both the peroxide and the tank should be approved by the national governmental authorities. Since the polymer production and processing industries mostly use peroxides in diluents, the dilution does not constitute a problem. AkzoNobel has an increasing number of bulk carriers in operation.

The regulations divide substances into classes: flammable liquids, compressed gases, toxic substances, etc. Organic peroxides constitute a separate class, generally numbered 5.2 'Organic Peroxides'. Class 5.2 is a so-called restricted class: only those products listed in the regulations are allowed for transport.

Some of the items regulated are: transport temperature, packing type, maximum amount of product per packing, labelling, emergency temperature, etc.

Additional stipulations depend on the mode of transport, e.g. for sea transport the location of the load, storage, surveillance, emergency procedures, etc. We have a large fleet of sea containers, each of which is equipped with two independent refrigeration units, to safely transport our products.

## Transport regulations

Various transport regulations exist:

<b>Worldwide</b> transport recommendations sea transport air transport	United Nations IMDG code ICAO
<b>Europe</b> by road by rail	ADR RID
<b>United States</b> all modes	DOT
<b>Canada</b> all modes	TDG
<b>Mexico</b> all modes	SCT

Transfer of IBC to refrigerated peroxide storage room



# Storage

This chapter describes the storage of organic peroxides packed in the commercial container. For storage in tanks, see chapter 'The peroxide container and its transport' on page 12.

Due to their specific properties organic peroxides cannot simply be put in any chemical stock-room for chemicals.

Separate storage facilities are recommended. The separate storage and the requirements for such a storeroom have the same underlying principles.

## The essential items are:

1. peroxides should be kept below their recommended maximum temperatures allowed
2. peroxides burn vigorously
3. contamination should be prevented.

All detailed provisions are meant to cope with these essential items. Items 1 and 3 constitute precautions, whereas item 2 constitutes the main hazard.

The thermal explosion hazard has been reduced to a hazard of secondary importance due to the type of packing (small and fragile). This fact is supported by the accident record of peroxide storage rooms. Decomposition of peroxides in their containers mainly results in large amounts of fumes or a peroxide fire.

Peroxide fires and the subsequent consequences for storage rooms have been the subject of extensive investigations by the peroxide industry and the governmental authorities. The experiments performed with the Bundesanstalt für Materialprüfung (BAM) in Berlin were extended to tests involving 5,000 kg of liquid peroxide. These tests yielded the following characteristic data for highly concentrated liquid peroxides:

Typical values of a peroxide fire' burning rate	
• 10,000 kg	250 kg/min.
• heat of combustion	30,000 kJ/kg
• radiant heat fraction	approx. 25%

This results in a 8 kW/m<sup>2</sup> radiation at 25 metres, an intensity that just chars wood and that humans can endure only a short time (5 seconds).

The requirements for a peroxide storeroom can be derived from above mentioned items.

## Maximum temperature

Temperature control is only possible, if a thermometer is installed: Type TI for uncooled products and type TIC for cooled products. The temperature should preferably also be recorded outside at the door entrance, so that the personnel can check the inside temperature before entering. The proper storage temperature should be marked at the entrance. The thermometer can be used for fire alarm as well (TIA or TICA function).

In that case, two set-points are useful: low alarm to indicate an increase above the maximum storage temperature and high alarm to indicate decomposition or fire (see also section Fire protection on page 15). Close supervision should be given to any alarm situation. In order to avoid any temperature rise inside the peroxide as a result of self-heating (see chapter The safety parameters on page 6), it is necessary to have air circulation inside the building. Space between the pallets of peroxide and natural convective ventilation are sufficient to prevent selfheating at storage temperatures.

The design requirements to achieve a temperature inside the storage room, which is below the maximum storage temperature of the product, differ for the uncooled and the cooled peroxides.



### Uncooled products

In order to retain good quality of the peroxide for all uncooled products a maximum storage temperature of 40°C is strongly recommended. One should be aware of summertime conditions and hothouse effects. Adequate means are: walls and roof (non flammable or fire-retardant) of low heat transfer materials, no windows and sufficient air ventilation. Openings for ventilation should roughly constitute 0.5% of the floor area and be covered with gratings. Leave some space between wall and peroxide. In this way, sun radiation on the wall is not directly transferred to the product and air circulation removes the heat input from outside. In hot climates an extra sun-roof or water spray on the roof can be helpful to keep the temperature below 40°C. Wintertime can be a problem, as some products may solidify. If heating is applied, the temperature of the heater should not exceed 50°C nor act as an ignition source. Keep peroxides at a safe distance from the heater.

### Cooled products

Cooling/refrigerating will be necessary. Cooling agent: non-flammable and chemically non-reducing. The use of insulated walls, roof and door is evident. Special provisions are required to overcome a cooling unit failure. Firstly, a warning system is essential so that the failure is detected in an early stage. Secondly, a back-up refrigeration system that can be used in case of failure of the primary unit. Emergency cooling with ice or dry ice could be an action of last resort. Knowing the rate of temperature rise inside the storage building when the cooling units fail, will be helpful for planning the time schedule of emergency actions.

### Fire protection

Fire prevention and fire fighting are key issues in the safety strategy for peroxide storage buildings. Several countries have regulations on this point. Important items are briefly enumerated here:

- Construction of the building; walls and roof should be constructed of a highly fire resistant material (brick, concrete, foam glass, etc.) One part of the building (a sidewall, roof or doors) should be of a light construction.

The decomposition and fire of the peroxide produce large amounts of gases and smoke. These must be released before excessive pressure cracks the building.

Fire fighting equipment:

- a water deluge/spray system in combination with smoke detection or
- an automatic deluge/spray system actuated by temperature sensors or
- a sprinkler system that can be used in case of failure of the primary unit. A dry sprinkler system for refrigerated products or
- in the case of refrigerated products, a liquid nitrogen fire-protection system might be considered and
- a 10 kg sodium bicarbonate-based powder extinguisher for small fires, location outside near the door.

Fire control:

Burning material, liquid peroxide or solid peroxide floating on the fire-fighting water can spread in all directions if not contained by an adequate construction of the store.

Appropriate means for control are:

- basin type floor construction
- channels which direct the burning flow to an open pit. The common sewage system of the plant is not suitable for this purpose.
- safe distances: the fierce burning of peroxides can constitute a threat to the surroundings. Safe distances depend on sensitivity of neighbouring objects (hospitals, houses, roads, plants), amount and type of product stored, construction of store-room, etc. For a 7,200 kg store the distances can vary from 10 to 40 metres.

### Contamination

One of the main reasons for a separate peroxide store is to prevent contamination, which can seriously reduce the thermal stability of peroxides. Thus, maximum storage temperatures would become unreliable safeguards. In the peroxide store itself leakage and spillage are another type of contamination hazard. Spilled peroxide on the ground gets contaminated with dirt which is a reputed source of ignition. Remove spillage with vermiculite, perlite or sand. Proper 'housekeeping' will suffice.

### General storage recommendations

The recommended maximum capacity of a peroxide store unit depends on the available safety distance. When large quantities are to be stored, the storage building can be divided into several units by means of fire resistant walls. The entrance should be clearly marked with the international organic peroxide shield and the required storage temperature. Other common provisions to be applied are: lightning protection and flame proof electrical equipment inside the store.

Observe the good practical rules with respect to the stored product:

- use the oldest material first (first in/first out principle)
- do not store for longer than half a year.

### Small quantities

Small quantities of organic peroxides do not need a separate building. A separate room, chest or, for cooled products, a refrigerator/freezer will suffice. Basically, the same principles as those outlined in the previous chapters are applicable. Particularly the following items should be observed:

- doors or lids open easily to release any pressure build up inside (no locks, etc.)
- the organic peroxide may auto-ignite
- maximum storage temperature of the product.

### Final remarks

The construction of a peroxide storage building appears to be as complicated as for many other chemicals (LPG, HCl, etc.). This can be overcome, if some general aspects are taken into account right from the start, such as:

- national laws, local regulations, codes of practice, etc.
- plant lay-out, local circumstances, amount of peroxide to be stored
- insurers opinion
- advice of a knowledgeable peroxide supplier.

AkzoNobel can provide you with detailed instructions and examples of storage rooms.

# Cleaning and disposal

The disposal of organic peroxides should also be carried out properly. The destruction of peroxides and cleaning of peroxide equipment, e.g. containers is not complicated but should be done with accuracy and care.







Safety dump pit  
with fire wall

### Cleaning

First verify that the container or equipment is empty. Then flush or rinse equipment with a mineral oil; heptane, dodecane, etc. will do. Do not use acetone as a start, especially not with ketone peroxides and hydroperoxides, because the hazardous solid acetone peroxide might be formed and precipitate.

Subsequently, apply copious amounts of water. Finally, proceed with the regular cleaning or disposal procedure.

In order to avoid confusion, remove or cross out the organic peroxide labels. Never reuse the polyethylene container for food and drinks.

Equipment that will be reused for peroxides after some time, or any new equipment should be passivated before use (ask your supplier for the passivation procedure).

Please keep in mind that any clothing wetted with peroxide should be placed in water immediately and not worn again until laundered. Spills of liquid organic peroxides can be absorbed with large amounts of vermiculite. Add water to saturate the vermiculite.

### Disposal

The most effective way of peroxide elimination is burning. An alternative is chemical destruction. You can, of course, contract the waste treatment out to an officially recognized disposal company.

### Burning

Organic peroxides burn very well. However, technically pure peroxides burn too violently for direct incineration.

As a result of the dilution the hazardous peroxide properties have been reduced to a minimum. Acceptable diluents are mostly the common hydrocarbons and fuel oil.

On handling the diluted waste peroxide, two possible hazards should be taken into account:

- the peroxide waste may give rise to gas evolution
- heating of the peroxide waste when contained in closed metal vessels or pipe segments will result in substantial pressure build up.

These hazards can easily be controlled by appropriate venting devices. Small quantities of organic peroxides can be burned without dilution, if necessary and allowed by the relevant authorities.

Preferably, the burning is carried out as a pool fire in a shallow basin. In emergency situations the peroxide in the commercial container can be burned as a whole. The best way is to cover the container with wood chips or other similar material and sprinkle it slightly with gasoline. In all cases the ignition should be done from a safe distance, e.g. by means of a burning rag fastened to a pole. This type of burning, if permitted, must be done in the open at some distance (minimum 15 metres) from buildings.

Furthermore, it will be clear that such a job should be carried out by experienced fire-brigade personnel.

### Chemical destruction

Chemical destruction is possible, but requires a chemical process installation: reaction vessel equipped with jacket for cooling and heating, stirrer and a scrubber. The chemical reduction of peroxides should not be carried out without a proper process description. Most processes are based on hydrolysis of the peroxide in a 25% caustic solution with a surfactant and a protic solvent, followed by or combined with an aqueous sodium sulfite treatment.

The peroxide must be added slowly; the total amount per batch should not be more than 30% of the total aqueous solution. The active oxygen concentration needs to be checked after the phase separation. The batch time is several hours. In case chemical destruction is considered, please consult your supplier for an appropriate process description.

# Contact us

**For further information on the use and the safe handling and storage of our products, please contact your AkzoNobel account manager or regional AkzoNobel sales office.**

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### Additional information

Product Data Sheets (PDS) and Material Safety Data Sheets (MSDS) for our organic peroxides are available at [www.akzonobel.com/polymer](http://www.akzonobel.com/polymer)  
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# Leading the way in safety

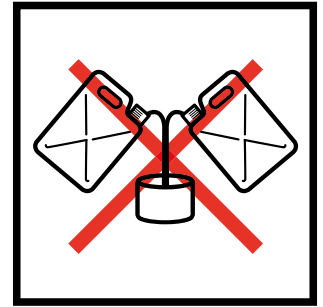
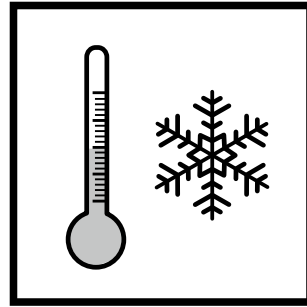
AkzoNobel is recognized as the global leader in organic peroxide safety. We always place safety as our top priority.

Sharing our experience in safety is one of the most important resources we offer. Classroom reviews of safety and handling of organic peroxides, consultation on storage and peroxide dosing equipment as well as demonstrations and publications on the safe use and handling of organic peroxides are just some of the services we offer.

[www.akzonobel.com/polymer](http://www.akzonobel.com/polymer)

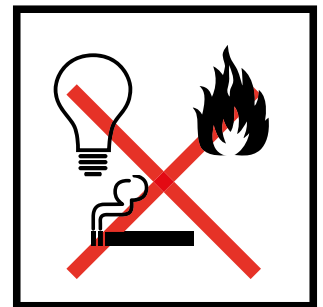


## How to store peroxides



- Store in a cool room away from direct sunlight.
- Observe maximum and minimum storage temperature as printed on the packaging and MSDS.
- Leave in the original packaging.
- Close packaging after use.
- Return packaging to peroxide store after use.
- Do not store together with accelerators or other chemicals.
- Do not mix peroxides with accelerators.
- Avoid any contact with dust, metal or other chemicals.

## How to handle peroxides



- Wear safety goggles.
- Wear appropriate protective gloves and clothing.
- Remove spillages immediately.
- Only use compatible materials when handling.
- Do not smoke.
- Avoid heat sources.
- Avoid open fire.
- Never heat peroxides.

## How to act in case of:

### Fire

Alert fire department.

Fight small fire with powder or carbon dioxide and apply water.

### Spillage

Liquids: absorb with inert material and add water.

Solids/pastes: take up with compatible aids and add water.

Move to safe place and arrange disposal as soon as possible.

### Skin contact

Wash with water and soap.

### Eye contact

First rinse with water for at least 15 minutes.

Always seek medical attention.

### Ingestion

Drink large amounts of water and consult doctor immediately thereafter. Do not induce vomiting.

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AkzoNobel is the largest global paints and coatings company and a major producer of specialty chemicals. We supply industries and consumers worldwide with innovative products and are passionate about developing sustainable answers for our customers. Our portfolio includes well known brands such as Butanox, Perkadox, Trigonox, Dulux and Sikkens. Headquartered in Amsterdam, the Netherlands, we are a Global Fortune 500 company and are consistently ranked as one of the leaders on the Dow Jones Sustainability Indexes. With operations in more than 80 countries, our 55,000 people around the world are committed to excellence and delivering Tomorrow's Answers Today™.

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