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Organic peroxides: Storage
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Storage

Guideline for the labour-safe, environment-safe and fire-safe storage of organic peroxides

Hazardous Substances Publication Series 8:2011 version 1.0 (December 2011)
Foreword

The Publication Series provides assistance for companies who produce, transport, store or use hazardous substances and for authorities responsible for granting licences and monitoring these companies. The Publication series gives the current state of the art and where relevant gives references to regulations and guidelines. This Publication Series is the reference framework for implementing your own corporate responsibilities and could be used for granting licences, drawing up general rules and monitoring companies. The Publication Series focuses on an integral approach to occupational safety, environmental safety, transport safety and fire safety.

The guidelines are formulated such that should the case arise a company can choose other measures on an equivalence basis.

In 2005 the guideline relating to the storage of organic peroxides (CPR 3) was published unchanged as PGS 8. Both the Advisory Council on Hazardous Substances and other stakeholders realised that this guideline required updating, among other things because many of the state of the art included in the guidelines had meanwhile been adopted in national and international legislation and regulations. In this new PGS 8 the relevant legislation and regulations, and the norms, standards and codes of practice derived from them, have been fully updated. PGS 8 was drawn up by PGS team 8 including experts of the business community and the government. The members of this PGS team are listed in 0.

The contents of the publication were determined by the PGS Programme Council. This is formed of representatives from the authorities (the Association of Provincial Authorities (IPO), the Association of Dutch Municipalities (VNG), Labour Inspectorate, the Dutch Association for Fire Services and Crisis Management (NVBR) and the Ministry of Infrastructure and Environment (I&M)), the business community (VNO/NCW and the SME organisation, MKB Nederland) and employees (Federation of Professional and Managerial Staff).

The Publication Series is kept up-to-date by the PGS Management Organization under the direction of a Programme Council which is made up of all the stakeholder parties.

More information on the PGS and the most recent publications can be found on: www.publicatiereeksgevaarlijkestoffen.nl.

A summary of the work field of the Publication Series also giving a list of relevant legislation and regulations and the stakeholders is included in the note ‘Legal context of the Hazardous Substances Publication Series’. This can be downloaded from the website mentioned.

The chairman of the PGS Programme Council,

Gerrit J. van Tongeren

December 2011
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Summary

This publication gives the current state of the art for the labour-safe, environment-safe and fire-safe storage of organic peroxides. This summary is followed by the introduction, which discusses the purpose and scope of the guideline and the position in the field of action is described. The relation with other legislation and regulations is also discussed at length. Finally the introduction includes information on government bodies involved and a list of related legislation and regulations.

In this PGS publication the regulations are shown numbered in blue boxes (e.g. reg 4.2.1).

Clause 1 discusses the scope and the status of this guideline, including the equivalence principle. Clause 2 describes the properties and hazards of organic peroxides, while Clause 3 goes into the classification of organic peroxides. Clauses 4 and 5 deal respectively with the general requirements and specific facilities for the storage of organic peroxides, depending on the quantity. Clause 6 covers the storage of organic peroxides in storage tanks and in dosing vessels. Clause 7 then discusses the safety distances to be observed based on heat load. Clauses 8 and 9 cover aspects relating to the use of organic peroxides and the internal emergency plan. Finally Clause 10 describes the security aspects relating to the storage of organic peroxides.

In conclusion a series of Annexes are enclosed.
0 Introduction

0.1 Reason for the update

The Advisory Council on Hazardous Substances (AGS) stated in 2006 [1] that all the stakeholders subscribe to the fact that the Hazardous Substances Publication Series is out of date and that there is a general need for an update.

In addition to this general commitment to an update by the cabinet the representatives of industry also felt an update of PGS 8 was needed. The update is based on the following reasons among others:

- changes in the transport and labelling legislation and classification;
- requirements relating to the use of Ex equipment;
- to revisit the distance requirements relating to storage of organic peroxides from different storage groups in one room;
- texts relating to fire fighting require revision.

The update also incorporates the responses received by the InfoMil helpdesk and the PGS Project Bureau regarding errors, shortcomings and lack of clarity. The erratum to the previous PGS 8 is also incorporated in this version of PGS 8.

0.2 Relation with legislation and regulations

0.2.1 Introduction

Most of the requirements and regulations laid down for the use of hazardous substances are established in legislation, whether or not these are based on European Directives or follow directly from European regulations. The PGS publications aim to give the fullest possible description of the way in which companies can meet the requirements arising from legislation and regulations.

A summary is given divided in the following categories:

- general;
- management;
- technical integrity;
- requirement for environmental planning;
- transport.

For the most up-to-date legislation and regulations we advise you to consult the website wetten.nl.

In both transport and handling regulations organic peroxides are classified as a special group because of their specific (hazardous) properties.
0.2.2 General

0.2.2.1 General provisions for the Environment Act (Wabo)

The General Provisions for the environment Act (Wabo) came into force on 1 October 2010, together with the corresponding Environmental Licensing Act (Bor) and the Environmental Licensing Ministerial Regulation (Mor). Based on the Wabo (or Annex 1 of the Bor) more than 30,000 companies are obliged to have a permit to set up a new company or change of an existing company. This is defined in the All-in-one Permit for Physical Aspects, which replaces the Environmental Permit from 1 October 2010. When there are (or will be) activities in a company that fall within the scope of a PGS publication, the requirements of the PGS publication are the starting point for determining the regulations in the permit.

0.2.2.2 Activities Decree

General environmental regulations are given in the General Rules for Establishments (Environmental Management) (Activities Decree) for companies that do not need to apply for an environmental permit. Besides that the Activities Decree contains regulations, for certain activities that are applicable as well to companies that do need to apply for an environmental permit. For certain activities the Dutch Government refers to specific PGS requirements with Ministerial Regulations.

The Activities Decree distinguishes between three categories of companies: A, B or C. Type A and B companies are classified as falling under the general rules of the Activities Decree, whereas type A, because of their negligible impact on the environment, are under the light regime and do not need to submit an environmental management notification. Type C companies need an environmental permit, in which for certain activities the regulations of Clause 3 and other clauses of the Activities Decree apply directly, and do not need to be included in the permit.

According to Annex 1 of the Activities Decree the storage of organic peroxides by definition falls outside the scope of the Activities Decree unless:
- organic peroxides are stored in limited quantities (LQ packages) up to a maximum of 1,000 kg (category m, subclause 3).

0.2.2.3 Soil Protection Act (Wet Bodembescherming, Wbb)

The Soil Protection Act contains general rules for preventing soil contamination. The Act includes (mainly) three regulations, namely, a regulation for:
- protection of soil, including the obligation for the causers to clean everything they contaminated;
- the approach of other soil contamination on land;
- the approach of other soil contamination in the water bottom.

0.2.2.3.1 Dutch Guideline for Soil Protection (NRB)

The Dutch Guideline for Soil Protection (NRB) uses as starting point to create a negligible risk for soil contamination by combining measures and facilities.

0.2.2.4 ADR / UN GHS / EU-GHS (CLP)

The transport regulations are based on the UN Recommendations for the Transport of Dangerous Goods [2]. The transport classification of the UN Recommendations corresponds to the UN GHS criteria [3] and the EU-GHS (CLP) regulations [4]. In the UN Recommendations
Organic peroxides are assigned to class 5.2 and are assigned into seven types A to G according to the hazard of the organic peroxide based on a test series. The type determines the transport conditions, including the packing method. See also Clauses 2 and 3.

0.2.3 Management

0.2.3.1 Major Accidents Risks Decree (Brzo ‘99)

Major Accidents Risks Decree (Brzo ‘99) is a major part of the implementation of the Seveso-II Directive into Dutch legislation. It contains regulations for companies that are working with substantial quantities of hazardous substances. These requirements apply to the technical part of safety as well as the management aspects such as a safety policy, procedures and communication. A Brzo company shall have a coherent safety management system that guarantees a safe operational management. Specifications for a safety management system for risks of major accidents are given in NTA 8620. Larger Brzo companies shall also have a safety report that includes an identification of hazards and a description of risk control for the subjects internal safety, external safety, environmental safety and assistance on disaster. Besides, larger Brzo companies shall have an internal emergency plan. Moreover, the authorities for legislation and enforcement can demand a quantitative risk analysis.

Organic peroxides are on the basis of the Dangerous Substances and Dangerous Preparations Directives [5, 6] labelled as oxidizing and/or explosive. Based on these properties they shall be considered for their contribution to the threshold values of part 2 of Annex 1 of the Brzo ‘99. If the threshold is exceeded a direct reference to Brzo ‘99 will follow. If within a company several different, similar hazardous substances may be present, these shall be weighed together and added up. The application of the calculation rules in part 3 of Annex 1 of the Brzo ‘99 may then lead to an indirect Brzo ‘99 reference. During the (on-going) update of the Seveso Directive and the subsequent revision of Brzo ‘99 harmonisation with the CLP regulations will be carried out. A consequence of this will be that organic peroxides are no longer regarded as oxidizing substances but will be assigned to their own specific hazard category.

0.2.3.2 ARIE Regulation

Companies that have a certain quantity of hazardous substances in their installations or can be generated (regardless of any acts), shall perform an Supplementary Risk Inventory and Evaluation (ARIE) aimed at preventing major accidents and based on that take a set of measures.

0.2.3.3 Risk Inventory and Evaluation (RI&E)

Every company with employees shall (let someone) investigate if the work can cause a risk or can cause damage to the health of employees. This investigation is called a RI&E and shall be put down in paper.

0.2.4 Technical integrity

0.2.4.1 Legislation on explosive atmospheres (ATEX 95 and ATEX 137)

The ATEX 137 [7] Directive gives regulations on how to work safely in an environment where an explosive atmosphere may arise. ATEX 137 is implemented in Clause 3, Organization of Workplaces, of the Working Conditions Decree, where this decree again refers to NPR 7910-1 ‘Hazard zone classification (for electrical equipment) relating to gas explosion hazard’ [20].

Organic peroxides are chemically unstable substances. They therefore by definition do not fall under ATEX 137 and derived documents such as NPR 7910-1, NPR 7910-2 and the non-
binding guide belonging to the ATEX Directive. However, protection of employees against the hazards of organic peroxides, that is also against hazards of ignition of any explosive atmosphere, remain compulsory on the basis of PGS 8. As regards the hazards of a vapour or gas explosive atmosphere the following applies to organic peroxides:

- most organic peroxides have a flash point that cannot be measured because it is (far) above the self-accelerating decomposition temperature (SADT). A vapour-explosive atmosphere will not occur during storage and conditions of use;
- if liquid organic peroxides with a low flash point (below the SADT) are used (e.g. dosing installations) at a temperature that is higher than 5 °C to 15 °C below the flash point, the hazards are similar to those of combustible liquids;
- for solid organic peroxides that may give rise to the formation of a gas explosive atmosphere the same action should be taken as for other solid substances that may form a dust explosive atmosphere.

Because of the possibility that organic peroxides may decompose it is recommended that fixed electrical equipment installed in storage facilities, according to ATEX 95 and ATEX 137 [8, 7], comply with the requirements for equipment of group II, category 3 (EX IIB T3).

Note:

- Equipment of group II is equipment intended for above-ground use in places where as a result of an explosive environment a hazard may prevail (group I is for underground use, in mine-related activities).
- Category 3 includes equipment designed such that they can operate in accordance with the operating parameters laid down by the manufacturer and offer a normal protection level. The equipment in this category is intended for an environment in which it is unlikely that due to the presence of gas, vapour, mist, or dust/air mixtures an explosion hazard will prevail and in which such a hazard will in all probability only rarely occur and last for a short time. The equipment in this category guarantees during normal operation the required safety level aimed at preventing foreseeable ignition sources.
- EX IIB T3 indicates that the equipment is of explosion safe design for gases/substances from explosion group IIB (with an average minimum ignition energy) and temperature class T3 (an ignition temperature above 200 °C).

In the Netherlands ATEX 95 was implemented in the Commodities Act Decree on explosion safe equipment [9].

0.2.5 Occupation Health and Safety

The Dutch Occupational Health and Safety Act sets out the rights and obligations of both employer and employee in the area of working conditions. The Dutch Occupational Health and Safety Act applies wherever work is carried out. Not only in companies, but also in associations or foundations.

The Working Conditions Decree, a development of the Dutch Occupational Health and Safety Act, contains further rules which both employer and employee shall observe to counteract risks at work (target regulations). It also contains different and supplementary rules for a number of sectors and categories of employees.
0.2.6 Requirement for environmental planning

0.2.6.1 Introduction

Besides the technical integrity and management, environmental planning of installations is of importance in order to assess the hazards accompanying such an installation and to control any associated risks.

0.2.6.2 Building Decree

In the Building Decree general rules are given for the fire resistance, fire transfer and fire penetration. Guidelines for existing buildings are given to experimental determinations in standards NEN 6068 and NEN 6069. For newly built buildings is referred to methods for mathematical standards given in NEN 6071, NEN 6072 and NEN 6073. For determining the fire load the Building Decree refers to NEN 6090.

The aim of the Building Decree 2003 regarding the limitation of expansion of a fire (compartmentalization) is to control the fire. The Building Decree 2003 prescribes in principle (for newly built buildings) that industrial buildings shall be divided into fire compartments with a surface of not more than 1 000 m². For storage facilities with a surface of more than 1 000 m² equal safety shall be proven. This could be done using the report ‘Methode beheersbaarheid van brand’ (edition 2007).

0.2.6.3 External Safety (Establishments) Decree (Bevi)

The External Safety (Establishments) Decree (Bevi) – linked to the Environmental Management Act - imposes additional safety requirements on companies that constitute a risk for people outside the industrial site. The Bevi aims to diminish the risks that civilians are exposed to in their surroundings by activities with hazardous substances, to a fixed limit. Because of the Bevi the competent authority has been obliged since October 2004 to consider external safety (place-related and group-related risk) when granting environmental permits and with relevant environmental planning (especially zoning plans). Based on the Bevi the required distances are laid down in the External Safety (Establishments) Regulations (Revi) for certain branches of industry. For the companies, for example Brzo companies, the required distances shall be determined with a quantitative risk assessment (QRA) based on the mathematical rules mentioned in the Bevi. In this way, safety standards have been enforced indirectly to companies that by use, storage, transport or production of hazardous substances form a risk to people outside the industrial site.

The Bevi sketched in outlines:

− The Bevi regulates how municipalities and provinces shall take the risks for people outside the industrial site with hazardous substances into account
− The Bevi lays down the place-related risk. This could be used by municipalities and provinces to determine safety distances around risky companies.
− The Bevi lays down a justification duty for the group-related risk. This could be used by municipalities and provinces to determine safety distances around risky companies.
− If companies are too close to houses, additional safety measures are needed. In the utmost case municipalities and provinces could let houses being moved or demolished.

If a company falls under the Bevi, it is categorized as a type C establishment under the Activities Decree.

The storage of organic peroxides in itself does not fall under the Bevi. This may of course involve a Bevi establishment because of storage of organic peroxides in Brzo establishments or...
in PGS 15 stores of more than 10,000 kg per store or the storage of toxic peroxides in a containment system of more than 1,000 litres etc.

0.2.7 Fire Safety (Occupancy of Structures) Decree (Gebruiksbesluit)

Buildings shall be used fire-safe. As of 1 November 2008 national regulations came into force which are laid down in the Fire Safety (Occupancy of Structures) Decree. The industrial storage of organic peroxides does not fall under the Occupancy Decree but under the environmental regulations. For organic peroxide this involves industrial storage if more than 1 kg or 1 l is stored.

The storage of organic peroxides (ADR class 5.2), according to PGS 8, is therefore based on the above excluded from the Occupancy Decree. The supplementary regulations relating to the Building Decree are specified in this PGS 8 and shall be included in the environmental permit.

0.3 Government bodies involved

0.3.1 Municipality and province

For most companies the municipality (Municipal Executive) is the competent authority for the Environmental Management Act. The provinces (Provincial Executive) are the competent authority for most bigger and often more complex companies.

0.3.2 Fire service

In this respect the fire service may be involved from two levels, namely the regional fire service and the municipal fire service.

The regional fire service is involved in granting licences from its statutory advisory function in the situation involving a company that falls under the Bevi or Brzo.

The municipal fire service is not a statutory adviser, but may be consulted by the competent authority (Environmental Management Act) when determining requirements for fire prevention and suppression facilities, that may be included in environmental permits. In the latter case the municipal fire service forms part of the competent authority.

0.3.3 Labour Inspectorate

The Ministry of Social Affairs and Employment (SZW) is responsible for all regulations relating to working conditions. The Labour Inspectorate monitors compliance with these regulations. For the storage of organic peroxide this generally involves the Dutch Occupational Health and Safety Act and the Working Conditions Decree.

0.3.4 Department of Public Works and the district water boards

The Ministry of Transport and Public Works is the competent authority for the Water Act as regards national waters. These include among other things the coastal waters, the Waddenzee, Eems and Dollard, the IJsselmee, the Meuse, the Rhine, the IJssel and the Zeeland waters. In practice it is Department of Public Works that issues the Water Act permit on behalf of the Minister.

The local district water board is the competent authority for all other bodies of water not belonging to the national waters.
0.4 Relation with other PGS publications

0.4.1 PGS 15

The Hazardous Substances Publication Series 15 *Storage of packaged hazardous substances* gives the current state of the art for the fire-safe, environment-safe and labour-safe storage of packaged hazardous substances.

Clause 9 of PGS 15 includes guidelines for the storage of a limited quantity of organic peroxides. A maximum storage quantity of 1 000 kg of organic peroxides per establishment, under conditions indicated in PGS 15, is permitted. This exception only applies for organic peroxides packaged as ‘limited quantities’ (LQ) (ADR 3.2.1 and 3.4). This permission is also limited to the organic peroxides with UN number 3103 to UN number 3110 (types C to F without temperature control).

Note also that the maximum quantity of 1 000 kg organic peroxides per storage facility applies. If one wants to store more than 1 000 kg in a storage facility, the guidelines from this PGS 8 apply.

0.4.2 PGS 28, PGS 29 and PGS 30

PGS 28, PGS 29 and PGS 30 give regulations for the storage of liquid fuels in underground or above-ground installations. The general guidelines for structure, inspection and maintenance for storage in under- and above-ground tanks under these guidelines apply for the storage of organic peroxides where they do not conflict with the regulations under this PGS 8, see 6.2.
1 Application of the publication

1.1 General

Monitoring, enforcement and granting permits are regulated in the relevant legislation. Companies should comply with the described current state of the art, when a reference is made from a binding document to the PGS. A binding document is for example the Activities Decree or an environmental permit. For employee protection the current state of the art can be included in a Health & Safety catalogue, which is the point of reference for monitoring the relevant sector (or target group). Another possibility for PGS regulations is to be imposed on a company via a requirement for compliance by the Labour Inspectorate.

For the application of an updated PGS for granting licences within the framework of the Environmental Permitting (General Provisions) Act (Wabo) we can make a distinction between the following situations:

- new company to be set up;
- extension or change of an existing company;
- existing company.

For questions about the application of an updated PGS in existing situations or in case of an extension or change of an existing company please, refer to the ‘questions and answers’ on www.publicatiereeksgevaarlijkestoffen.nl.

1.2 Purpose

This PGS guideline gives the current state of the art for labour-safe, environment-safe and fire-safe storage of organic peroxides.

1.3 Scope

PGS 8 applies to the storage of organic peroxides. Figure 1.1 shows a schematic summary of applicable legislation for the storage of organic peroxides, including exception conditions to PGS 8 guideline.

Clause 9 of PGS 15 includes guidelines for the storage of a limited quantity of organic peroxides. A maximum storage quantity of 1 000 kg of organic peroxides per storage facility, under PGS 15 conditions, is permitted. This exception only applies for organic peroxides packaged as "limited quantities" (LQ) (ADR 3.2.1 and 3.4) and if the organic peroxides have a UN number from 3103 to 3110 (types C to F without temperature control). If you want to store more than 1 000 kg in a storage facility, the guidelines from this PGS 8 apply.

A number of peroxide formulations are exempted from the requirements of PGS 8. These are the organic peroxides assigned to storage group 5 (see also Table 3.3). However, if required, they may be stored together with other organic peroxides, see flow chart below. For further information on the classification of organic peroxides please refer to Clause 3. Organic peroxides that belong to type A (may detonate under normal conditions) are prohibited for transport and may not be stored under the conditions of PGS 8.
This guideline explicitly gives no regulations for the production and processing of organic peroxides in factories. Specific provisions and safety measures shall be taken into account that fall outside the framework of these guidelines.

For the labour-, environment- and fire-safe use of organic peroxides please refer to the Safety Information Sheet (VIB) or the Material Safety Data Sheet (MSDS) of the manufacturer/supplier.

1.4 Equivalence principle

The equivalence principle applies for the use of PGS 8. This means that action can be taken other than that included in the regulations of this guideline. In practice this means that during the preliminary consultation, within the permit application, data shall be submitted showing that as a minimum equivalent protection of the environment, labour protection or fire safety can be achieved. The competent authority assesses, e.g. within the granting of permits, whether reporting ultimately or with the application of the other means and equivalent protection can be achieved.

The Labour Inspectorate reviews this upon inspections within the enforcement of the Working conditions legislation.
1.5 Use of standards and guidelines

Where reference is made to other standards and guidelines (e.g. NEN, ISO, BRL) the version that is in force at the time of publication of this PGS applies.
2 Properties and hazards

2.1 Introduction

This Clause discusses the following aspects of organic peroxides:

- temperature control;
- hazard of decomposition and/or explosion;
- fire hazard;
- hazard of toxicity and/or corrosivity;
- eco-toxicity or environmental hazard.

Organic peroxides are organic chemicals which contain the unstable -O-O-peroxy bond in their molecular structure. They are widely used as initiators for a variety of chemical reactions that require radicals.

Organic peroxides are highly reactive and thermally unstable substances which may show exothermic self-accelerating decomposition. In addition they may:

- be subject to explosive decomposition;
- be flammable and burn rapidly;
- shock or friction sensitive;
- enter into hazardous reactions with other substances;
- show toxicity or corrosion phenomena.

2.2 General aspects of temperature control

All organic peroxides are thermally unstable and may decompose more or less vigorously depending on the temperature. For this reason all organic peroxides shall be protected from direct sunlight and heat sources. This is generally indicated according to CLP regulations [4] with precautionary statement code P235 (keep cool) and P410 (protect from sunlight).

Some organic peroxides are even too unstable to be stored at ambient temperature and shall be temperature-controlled during transport and storage. This is indicated according to CLP regulations [4] with precautionary statement code P411 (store at temperatures not exceeding ...° C). The maximum transport and storage temperature is called the control temperature (Tc). Measures should be taken to keep the temperature of the peroxide below Tc during transport and storage. Should the temperature of an organic peroxide accidentally exceed the control temperature, emergency action shall be taken where an attempt is made to reduce the temperature of the organic peroxide.

An alarm shall be given if the temperature cannot be reduced when the temperature attains the emergency temperature (Te). All available means should be used to bring the temperature back under control and the emergency procedures should be started.

The control temperature and the emergency temperature are deduced from the self-accelerating decomposition temperature (SADT), i.e. the lowest ambient temperature at which
hazardous self-accelerating decomposition may occur for a substance in a packaged state. The SADT shall be determined in order to decide whether a substance shall be subjected to temperature control during storage. Instructions for determining the SADT are given in the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria [10], Chapter 28.

In the Table below the relationship is given between type of package, SADT, control temperature, emergency temperature and storage temperature.

Table 2.1 - Type of package, SADT, control, critical and storage temperature

<table>
<thead>
<tr>
<th>Type of package</th>
<th>Control temperature</th>
<th>Emergency temperature</th>
<th>Maximum storage temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple package and IBCs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 °C or less</td>
<td>20 °C below SADT</td>
<td>10 °C below SADT</td>
<td>Control temperature</td>
</tr>
<tr>
<td>35 °C or less and above 20 °C</td>
<td>15 °C below SADT</td>
<td>10 °C below SADT</td>
<td>Control temperature</td>
</tr>
<tr>
<td>Above 35 °C</td>
<td>10 °C below SADT</td>
<td>5 °C below SADT</td>
<td>Control temperature or 45 °C</td>
</tr>
<tr>
<td>Tanks</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 °C or less</td>
<td>10 °C below SADT</td>
<td>5 °C below SADT</td>
<td>Control temperature or 45 °C</td>
</tr>
<tr>
<td>above 50 °C **</td>
<td>N/A</td>
<td>N/A</td>
<td>45 °C</td>
</tr>
</tbody>
</table>

* for the substance as packaged
** organic peroxides with an SADT above 50 °C in tanks require no cooling

The following organic peroxides shall be subjected to temperature control during storage:

- organic peroxides types B and C with an SADT ≤ 50°C;
- organic peroxides type D that may show a moderate reaction on heating, with an SADT ≤ 50°C, or which show a slight or no reaction on heating in a confined space, with an SADT ≤ 45°C;
- organic peroxides types E and F with an SADT ≤ 45°C.

Note: Instructions for the determination of the consequences of heating in a confined state are given in “UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria” [10], Chapter 25.

Where applicable 0 includes a list of control and emergency temperatures. The actual temperature during storage may be below the control temperature, but shall be such that phase separation or solidification is avoided.

2.3 The hazard of decomposition and/or explosion

For organic peroxides, depending on the type of organic peroxide (see Table 3.1), slow to rapid runaway reactions (decomposition reactions) may occur that lead to a great deal of heat development. The effect of the runaway reaction is determined by two parameters, namely the rates at which the temperature and pressure rise. These rates depend on the decomposition behaviour and concentration. In concentrated form, however, for many organic peroxides a vigorous runaway reaction may take place. The effect of this runaway reaction may be reduced by diluting or mixing the organic peroxide with e.g. water, phthalates, isododecane or calcium carbonate.
No runaway reaction can occur as long as all the heat developed is removed from the organic peroxide (by natural or forced cooling) and there is no danger of rupture or fragmentation of the package if all the gaseous decomposition products can be removed.

To prevent a runaway reaction the heat balance (i.e. the nett result of heat development and heat removal) is controlled. This heat balance depends on the decomposition rate of the organic peroxide, the quantity stored, the storage temperature and the nature of the package.

The rate of decomposition, and thus, the heat production is increased considerably if the organic peroxide:

- is contaminated with incompatible materials, such as heavy metals, acids, bases, accelerators, etc. This is indicated with precautionary statement code P420 (store away from other materials);
- is used or stored at too high a temperature;
- is exposed to open flame.

Both a bigger packaging unit and a higher storage temperature lead to an increase in heat development and/or a reduction in heat transfer. Storage for a long period of time may accelerate decomposition by autocatalysis.

In addition to the organic peroxide type, the degree of containment also determines the effect of a runaway reaction. In a plastic package upon decomposition of the organic peroxide the wall of the package will be weakened by exposure to the high temperature. As a result the package will rupture at an early stage in the runaway reaction, at relatively low pressure. In the case of a metal storage container, if there is an insufficient relief vent facility a high pressure is reached. If the design pressure of the metal vessel is exceeded the vessel will explode violently. In all cases hot flammable vapours will be released which may ignite spontaneously. Furthermore the vapour cloud released may lead to a second (gas/vapour) explosion due to spontaneous combustion or contact with an external ignition source.

The occurrence of a runaway reaction is determined by the temperature of the organic peroxide. Apart from showing a runaway reaction a number of organic peroxides may deflagrate as well. Deflagration may already occur at a relatively low temperature. It is initiated by a heat source or by contamination of the organic peroxide. High local temperatures due to self-heating, exposure to hot surfaces, sparks, friction, impact etc. are often observed as heat sources for solid organic peroxides.

A number of organic peroxides are sensitive to ignition due to shock and to a lesser degree due to friction. Only a small number of organic peroxides may detonate. In practice the organic peroxides that may detonate are so inactivated that they no longer possess any detonation properties.

Virtually all organic peroxides are composed of aliphatic or aromatic hydrocarbon chains. Only a limited number of organic peroxides (e.g. di-4-chloro-benzoyl peroxide) contain elements, such as chlorine, which are closely linked with the formation of decomposition products with toxic properties. The decomposition products of organic peroxides are mostly saturated or partially oxidized hydrocarbons (CnHm) or carbon (COx) which may or may not be partly oxidized. This implies that the toxicity of the decomposition products of organic peroxides is generally similar to that of hydrocarbons with small chain lengths.

For more information on the toxicity and eco-toxicity of different organic peroxides please consult the Material Safety Data Sheets.
2.4 General aspects of fire hazard

Fire hazard is either a consequence of exposure to an external open flame or the flammability of the organic peroxide. Exposure to an external open flame is the same as exposure to hot surfaces (see Subclause 2.2). The flammability of organic peroxides varies: some of them ignite very easily, others are very difficult to ignite. The risk of flammability is indicated according to the CLP regulations [4] with hazard statements H241/H242 (Heating may cause a fire) and precautionary statement code P210 (Keep away from heat/sparks/open flames/hot surfaces – no smoking).

In most cases it is hardly possible to determine the flammability of an organic peroxide. The flash point of a liquid organic peroxide is e.g. decisive for its flammability. The flash point, however, is often considerably higher the temperature range in which the organic peroxide is sufficiently stable for handling and storage.

The flash point is therefore only relevant if its value coincides with the normal temperature range of storage and processing. Di-tert butyl peroxide is for instance a typical example of a peroxide that is stored at ambient temperature, whereas the flash point (6 °C) is lower.

Adequate ventilation of organic peroxide stores is recommended to limit the risk of ignition by dispersing the peroxide vapour and minimizing the vapour concentration. Ventilation is even required if the vapour concentration in the storage facility can exceed a level of 20 % of the lower flammability limit (LFL).

The gaseous products resulting from the decomposition of an organic peroxide can usually be ignited if they are mixed with air. Such a gaseous mixture may ignite spontaneously or by contact with an ignition source. For this reason the presence of potential ignition sources such as electrical equipment etc. can be avoided and the storage facility should be equipped with vent panels with sufficient capacity to avoid an excessive increase in pressure and to vent the gaseous products to a safe place in case of need.

A fire with liquid organic peroxides spreads rapidly as organic peroxide leaks and spreads from the rupturing peroxide package. This implies that measures shall be taken to contain the spread of organic peroxides. The intensity of a fire is very high compared with other combustible liquids. Special care should be taken with volatile organic peroxides where ignition of vapours is possible.

A fire with solid organic peroxides spreads differently. In this case a fire is less intense than in the case of liquid organic peroxides because of the smaller burning area. Adequate fire fighting systems can largely reduce the effects of a fire if they start operating at an early stage of the fire.

When fighting an organic peroxide fire it is of crucial importance to use fire extinguishing systems which provide efficient cooling (such as water). Extinguishing should also be continued after the flames have been extinguished since the still warm organic peroxide can ignite spontaneously again. In general non-cooling fire extinguishing agents are only suitable for fighting small fires.

2.5 Hazard of toxicity and/or corrosivity

Organic peroxides are in general moderately toxic. The degree of toxicity depends on the organic peroxide in question. Some are corrosive to the skin and mucous membranes and can cause severe damage to the eyes on direct contact. According to CLP regulations [4] this is indicated by hazard category P280 (wear protective gloves/protective clothing/eye protection/face protection). Inhaling the vapours of some organic peroxides may cause irritation of the
respiratory tract and lungs. Swallowing organic peroxides may cause burns to the mouth, throat, gullet and stomach.

Damage to the health of workers due to exposure to organic peroxides shall be avoided. To this end the regulations for toxic substances, as set forth in the Dutch Occupational Health and Safety Act (Arbeidsomstandighedenwet), shall be observed.

2.6 Eco-toxicity or environmental hazard

The eco-toxicity or hazard for the environment, i.e. the long-term impact on the environment of exposure to organic peroxides, depends on the stability of the organic peroxide. The eco-toxic effect (environmental hazard) of the decomposition product of organic peroxide from which the oxygen has been removed corresponds to that of its hydrocarbon counterpart.
3 Classification of organic peroxides

3.1 General

The hazards involved in individual organic peroxides vary considerably. These differences should be taken into account when storing the substances. Classification of organic peroxides into groups is therefore desirable. For support in the classification of organic peroxides please refer to the knowledge centres, see Annex H.

For this guideline the classification is based on that of the CLP regulations [4] combined with the burning rate.

The classification group and the quantity of product stored are used to determine the safety distances to be observed around the storage facility.

The hazards that have effects outside the storage facility and for which safety distances must therefore be observed are:

- explosive decomposition;
- heat radiation due to rapid combustion.

The other hazards indicated that may increase the risk of fire are:

- too high a temperature;
- sensitivity to shock and friction;
- reaction with other substances (contamination).

The hazards are covered in these guidelines by means of storage requirements, such as temperature control and handling instructions.

Finally some organic peroxides have additional hazards, such as corrosivity or toxicity. These hazards are marked on the package with labels for secondary risks, in addition to the labels for primary risks. Although the primary risks come before the secondary risks, it may be necessary to take additional safety measures.

The classification for the storage of organic peroxides is based on decomposition and combustion properties. The decomposition effects of organic peroxides are strongly influenced by the size and type of the package, in particular its mechanical strength. The CLP regulations take these aspects into account in the classification system for organic peroxides.

3.2 Change-over to CLP regulations

In the EU Directive 67/548/EEC concerning the classification, packaging and labelling of dangerous substances, organic peroxides are by definition regarded as oxidizing substances. In the CLP regulations [4], that replace this Directive, the classification as used in the transport regulations [2] is taken over in full. The classification and labelling according to EU Directive 67/548/EEC (including the use of R and S phrases) are superseded. The hazard is indicated depending on the organic peroxide type according to the CLP regulations [4] with hazard statements H240 (heating may cause an explosion), H241 (heating may cause a fire or
explosion) or H242 (heating may cause a fire). A list of relevant H and P phases is included in Annex E.

For pure substances the introduction of the CLP regulations is on 1 December 2010. The safety information sheet shall however give both the information according to Directive 67/548/EEC and according to the CLP regulations until 1 July 2015.

For mixtures the introduction date of the CLP regulations is 1 July 2015. After this introduction date for the CLP regulations for mixtures there is no requirement to also state the information required according to Directive 67/548/EEC in the safety information sheet.

3.3 Classification according to CLP regulations

The classification of organic peroxides is based on the CLP regulations [4]. The CLP regulations make a distinction between seven types of organic peroxides, namely types A to G. The hazard of the various organic peroxide types is described in Table 3.1.

As a supplement to the CLP regulations, the transport regulations specify the maximum dimension, type and material of the packaging permitted for each different organic peroxide type, see Table 3.2.

**Table 3.1 - Principles for classification according to CLP regulations**

<table>
<thead>
<tr>
<th>Type of organic peroxide</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Organic peroxides which, as packaged, can detonate or deflagrate rapidly</td>
</tr>
<tr>
<td>B</td>
<td>Organic peroxides possessing explosive properties and which, as packaged, neither detonate nor deflagrate rapidly, but are liable to undergo a thermal explosion in that package</td>
</tr>
<tr>
<td>C</td>
<td>Organic peroxides possessing explosive properties which, as packaged, cannot detonate or deflagrate rapidly or undergo a thermal explosion</td>
</tr>
</tbody>
</table>
| D | Organic peroxides which in laboratory testing:  
- detonate partially, do not deflagrate rapidly and show no violent effect when heated under confinement; or  
- do not detonate at all, deflagrate slowly and show no violent effect when heated under confinement; or  
- do not detonate or deflagrate at all and show a medium effect when heated under confinement |
| E | Organic peroxides which, in laboratory testing, neither detonate or deflagrate at all and show low or no effect when heated under confinement |
| F | Organic peroxides which, in laboratory testing, neither detonate in the cavitated state nor deflagrate at all and show only a low or no effect when heated under confinement as well as low or no explosive power |
| G | Organic peroxides which, in laboratory tests, neither detonate in the cavitated state nor deflagrate at all and show no effect when heated under confinement nor any explosive power, provided they are thermally stable (SADT of 60 °C or higher for a 50 kg package) (*) and, for liquid mixtures, a diluent having a boiling point of not less than 150 °C is used for desensitisation.  
If the organic peroxide is not thermally stable or a diluent having a boiling point of less than 150 °C is used for desensitisation, the organic peroxide shall be defined as organic peroxide type F.  

UN numbers are assigned to the organic peroxide types on the basis of their physical state (liquid/solid) and the temperature control requirement (no/yes). The so-called generic ranking used for the collective inclusion in the UN list of Dangerous Goods is applied. These UN numbers and the permitted maximum content of packages are set out in Table 3.2.

Table 3.2 - UN numbers and the permitted maximum content of packages

<table>
<thead>
<tr>
<th>Type of organic peroxide</th>
<th>UN number</th>
<th>Max. package capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Liquid</td>
<td>Solid</td>
</tr>
<tr>
<td>A</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>3101</td>
<td>3102</td>
</tr>
<tr>
<td>C</td>
<td>3103</td>
<td>3104</td>
</tr>
<tr>
<td>D</td>
<td>3105</td>
<td>3106</td>
</tr>
<tr>
<td>E</td>
<td>3107</td>
<td>3108</td>
</tr>
<tr>
<td>F</td>
<td>3109</td>
<td>3110</td>
</tr>
<tr>
<td>G</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1) Prohibited for transport
2) Exempted from category of organic peroxides
3) Depending on package used during the tests

3.4 Classification of storage

3.4.1 Organic peroxides

The classification of storage comprises five groups. The classification into a particular storage group is firstly based on the CLP regulations [4]. Secondly the burning rate is taken into account. The burning rate is largely decisive for the heat radiation from a peroxide fire. The term burning rate is defined as the amount of substance burned per minute for a 10 000 kg stack which is engulfed by fire. The stack shall consist of packages used for the transport and storage of organic peroxides. The classification can also be determined by means of representative burning tests with smaller quantities (see Annex F). Where the burning rate is not known, the highest classification for the type of organic peroxide should be used. Table 3.3 gives a breakdown of the classification group described above. Group 1 includes the most hazardous substances and group 5 the least hazardous.

The classification is based on the assumption that organic peroxides are only stored in the transport packaging permitted by law in the Netherlands. The risks indicated in Table 3.3 are described as:

- explosive/hazardous, which indicates that some containers may explode but no mass explosion will occur;
- burning, indicating that heat radiation from the fire will endanger the surroundings.
Table 3.3 - Classification for storage

<table>
<thead>
<tr>
<th>Storage group</th>
<th>Type of organic peroxide</th>
<th>Burning rate (kg/min)</th>
<th>* Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>B All</td>
<td>≥ 300</td>
<td>explosive or rapidly burning</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>≥ 60</td>
<td>very hazardous or rapidly burning</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>≥ 60</td>
<td>hazardous or burning comparable with solvents</td>
</tr>
<tr>
<td>2</td>
<td>C &lt; 300</td>
<td></td>
<td>not very hazardous and not or slowly burning</td>
</tr>
<tr>
<td></td>
<td>D ≥ 60</td>
<td></td>
<td>can be exempted</td>
</tr>
<tr>
<td></td>
<td>E ≥ 10 and &lt;60</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>F ≥ 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>D &lt; 60</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>E ≥ 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>F &lt; 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>E &lt; 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>F &lt; 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5**</td>
<td>G all</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* of 10 000 kg organic peroxides, corrected for radiation efficiency (see Annex F).
** including products that have a low active oxygen content, according to Subclause 3.7.

Based on this classification a list has been compiled of the organic peroxides used most in practice (see 0). Since new products regularly come onto the market or new tests are carried out with existing products, this list shall be updated from time to time. Requests for this shall be sent to the PGS management organization (see Annex H). Until the official classification has taken place, a product can be stored according to the requirements for storage group 1 or according to the requirements of another storage group if this is shown by the test data. A suitable test method for this is the laboratory test described in Annex F.

3.4.2 Mixtures of organic peroxides

When mixing organic peroxides it has been found that the effects of decomposition and fire are as a maximum equal to those of the organic peroxide with the highest classification. However, in a single case it appears that the thermal stability of the mixture (SADT) is below the SADT of the components. The transport legislation therefore states that for mixtures of organic peroxides the highest classification can be used. But the SADT shall still be determined. In line with this mixtures of organic peroxides may fall into the storage group of the organic peroxide with the highest classification.

3.5 Organic peroxides of type A

Organic peroxides of type A are prohibited for transport and are not included in a storage group because they may detonate under normal conditions and cannot therefore be stored under the conditions of PGS 8. The storage conditions for organic peroxides of type A shall be indicated by the competent authorities. In practice organic peroxides of type A are not stored except for Research & Development purposes and then in small quantities.

3.6 New organic peroxides or formulations

Samples of new organic peroxides or new formulations of currently classified organic peroxides for which complete test data are not available may be assigned to storage group 2, provided the following conditions are met:
− the available data indicate that the sample is no more hazardous than a type B organic peroxide;
− the sample is packaged in a plastic package of maximum 0.5 l for liquids and maximum 0.5 kg for solids;
− the available data indicate that any control temperature is sufficiently low to prevent hazardous decomposition and sufficiently high to prevent any hazardous phase separation.

3.7 Organic peroxides from storage group 5

Organic substances may by dilution or otherwise contain only a small mass fraction of the bivalent -O-O-structure. Substances with a so-called low active oxygen content fall under storage group 5 if the formulation:

− contains no more than 1.0% active oxygen from the organic peroxides and contains no more than 1.0% hydrogen peroxide; or
− contains no more than 0.5% active oxygen from the organic peroxides and contains more than 1.0% but a maximum of 7.0% hydrogen peroxide.

The active oxygen content (%) of an organic peroxide formulation is calculated as follows:

\[ 16 \times \sum \left( n_i \times \frac{c_i}{M_i} \right) \]

where:

- \( n_i \) is the number of peroxide groups per molecule of organic peroxide \( i \);
- \( c_i \) is the concentration (mass percentage) of organic peroxide \( i \);
- \( M_i \) is the molecular mass (g/mol) of organic peroxide \( i \).

In addition to the above-mentioned substances, organic peroxide formulations of type G (see Table 3.1) are assigned to storage group 5 if:

− the formulation is stable (SADT \( \geq 60°C \) for a 50 kg package) and
− the boiling point of the diluents used for phlegmatising is not less than 150°C; in other cases they shall be regarded as peroxide storage group 3 or as storage group 4 peroxides.

These organic peroxide formulations are exempted from the requirements of PGS 8 but may be stored with other organic peroxides, see for this Figure 1.1.
4 General requirements for storage

4.1 Introduction

Safety guidelines for the storage of organic peroxides serve two purposes:

- the prevention of accidents;
- limiting the consequences if an accident occurs.

Action to prevent accidents and their consequences can be taken by special construction of the storage facilities, good management/good housekeeping and safe distances from the storage to other buildings. The extent to which safety measures shall be taken, depend on the quantity and hazard classification of the product stored as well as the purpose of the storage. The principles on which all these safety measures are based are nevertheless the same.

To prevent accidents Clause 5 includes specific regulations for each storage facility. These relate in particular to avoiding decomposition or fire by temperature control and the prevention of pollution. Should an accident still happen, it is necessary to limit the consequences as far as possible.

The regulations for each storage facility included in Clause 5:

- extinguishing to limit the fire and the decomposition of organic peroxides;
- detecting smoke, fire, and too high a temperature to discover the fire and/or decomposition at an early stage;
- pressure relief vent openings to limit damage to the structure of the storage building;
- prevention of environmental pollution;
- distances between the storage facilities for organic peroxides and the other buildings. The distance depends on the quantity of organic peroxide, the type of organic peroxide, safety measures and the nature of the premises at risk. The required distances are indicated in Clause 7.

4.2 The storage of organic peroxides

reg 4.2.1 Storage of organic peroxides is only permitted if the packaging bears labels according to the transport legislation, see Annex D.

reg 4.2.2 Organic peroxides shall, with the exception of the operational stock necessary, be stored in a dedicated storage facility. Except in the case of organic peroxides of storage group G, no chemicals, substances or materials may be stored here.

reg 4.2.3 Packages shall only be opened in storage facilities for analysis purposes.

Note:
This regulation does not apply to samples of organic peroxides.
4.3 Temperature control

In order to avoid self-accelerating decomposition each organic peroxide is bound to a maximum storage temperature. The specified maximum storage temperature is equal to the control temperature (Tc) indicated in 0 or 45 °C if no control temperature is indicated. Under the climatological conditions prevailing in the Netherlands the recommended cooling methods consist of:

- passive cooling if Tc ≥ 30 °C;
- active cooling if Tc < 30 °C.

If more than one product is stored in one room the lowest Tc and Te apply.

For actively cooled storage facilities the maximum temperature should be indicated on the outside of the storage facility.

The requirements for cooling, the restrictions for heating and the requirements for air circulation and ventilation for the storage of organic peroxides, partly based on the maximum storage temperature, are specified in Clause 5.

4.4 Emergency pressure relief vent

The decomposition or explosion of organic peroxide results in the release of vapours and subsequent pressure increase. To prevent destruction of the storage facility due to excess internal pressure this should be fitted with an emergency pressure relief vent.

4.5 Retention pit

To prevent the spread of the fire and soil pollution the extinguishing water and leaking organic peroxide shall be directed to a liquid retention pit. This pit may be located on or under the floor of the storage facility or in a safe place outside. Different storage facilities may be connected to an external retention pit.

As regards the retention pit soil protection provisions and action shall be taken that in combination lead to a negligible soil risk (A) according to the Dutch Protection Guidance for Industrial Activities [11]. There may not be any openings in the retention pit that are or can be directly connected to a sewer or to the surface water.

For the location of retention pits the safety distances indicated in Clause 7 shall be observed. If the storage facility connected to the pit is equipped with an automatic sprinkler or deluge installation it may be assumed that only a limited part of the quantity of peroxide stored will reach the pit. In that case the distance may be calculated and be applied according to the safety provision ‘LIMITED’ (see for this Table 7.1 of Clause 7.4).

Channels or gutters conducting the extinguishing water to the retention pit shall not endanger adjacent premises. Flooding of the retention pit or gutters during fire fighting shall be avoided, e.g. by pumping the (water) layer to a suitable sewer.
### 4.6 Fire fighting

#### 4.6.1 General

Fire safety is often regulated in the building regulations, among other things in the Building Decree and the Building Occupancy (Fire Safety) Decree (Occupancy Decree). A storage facility for hazardous substances is a structure that falls under the building regulations of the Building Decree, however the regulations in the Building Decree are not sufficient for the safe storage of hazardous substances. As a result supplementary requirements are necessary. Also the control, by the fire service, of incidents with hazardous substances is more dangerous so that a defensive approach will usually be chosen. This also increases the requirements for the structures. Because it is (in short) not legally possible under a building permit to deviate from the 2003 Building Decree these extra regulations (such as a regulation in an environmental permit or acting directly via an Administrative measure (AMvB) such as the Activities Decree) shall be specified. This PGS guideline includes the supplementary regulations.

If the action and provisions, as set out in this guideline (the size of the storage quantity in relation to the fire resistance of the structural parts, the fire fighting measures and the distances from surrounding premises), are carried out, it is assumed that in case of a fire a controllable situation will arise. It is also assumed that the burning time of organic peroxides will not exceed 30 minutes. When establishing the required resistance value of a fire wall the fact is taken into account that the wall will be loaded at temperature according to the course of the hydrocarbon curve. This course of a fire shows a higher temperature increase and a higher maximum value of the temperature.

#### 4.6.2 Fighting a small fire

For fighting small fires there must be at least one small portable fire extinguisher (CO₂, foam, powder) or hose reel present within a distance of 15 m from the entrance to a storage facility. Portable extinguishers and hose reels shall respectively comply with NEN 2559 and NEN-EN 671. Extinguishing foam may also be used e.g. in case of a starting fire or fire of a thin layer of organic peroxide. Cooling the remaining organic peroxide, after a fire has been extinguished, remains necessary to avoid re-ignition.

All mobile extinguishers, whose presence is specified on the basis of the Occupancy Decree, the environmental permit or the Activities Decree, shall on the basis of the Occupancy Decree be inspected and maintained at least once every two years.

#### 4.6.3 Fighting a large fire

In case of a fire involving organic peroxides the following should be taken into account [12]:

- organic peroxides shall be extinguished with a lot of water. The fire can also be extinguished with powder, but re-ignition is likely due to the high temperature;
- use of foam is not suitable;
- in some cases letting the organic peroxides burn out may also be considered (e.g. in case of a pool fire);
- burning is often accompanied by a lot of smoke development and decomposition is accompanied by the formation of a mist or fog that may be toxic and flammable.

In case of a fire in the vicinity of organic peroxides the following action should be taken:

- where necessary, call the manufacturer for advice;
- if the control temperature is exceeded restoration measures should be taken:
  - repair of the cooling;
− cooling with ice and sometimes water;
− transfer to another cold store.
− if the emergency temperature is reached sometimes cooling must be carried out with water, or the organic peroxide can be allowed to complete the reaction in a safe place;
− in case of both cooling with water and the apparent controlled decomposition, there is still a chance that the decomposition reaction will proceed rapidly.

4.6.4 Fire fighting

As regards fire fighting installation(s) a principles document (a so-called Programme of Requirements (PvE) or Inspection plan) shall be drawn up and assessed for every PGS 8 premises by a type A inspection body accredited by the Dutch Accreditation Council on the basis of NEN-EN-ISO/EC 17020. A storage facility may not be taken into use until a positive inspection report has been issued by an accredited inspection body.

The positive inspection report should be present within the establishment. As regards the capacity of the system (spray density) the values applicable are as mentioned in Clause 5 of PGS 8. If certification is given this will be based on these requirements for the capacity of the system. To ensure that the installation in the long term still provides the same performance as upon its delivery, the installation should be regularly tested, maintained and managed as set out in the principles document.
5 Storage facilities

5.1 Introduction

The storage facilities referred to in this Clause are facilities suitable for the long and short term storage of organic peroxides. Organic peroxides shall generally be stored in special facilities for this purpose. In most cases the facilities shall comprise a free standing store, while in some cases the use is permitted of facilities that form an integral part of a building, see Figure 5.1.

Key
1 Storage facility for quantities up to 30 kg
2 Storage facility for quantities up to 150 kg
3 Storage facility for quantities up to 1 000 kg
4 Storage facility for quantities greater than 1 000 kg
A Direction of emergency relief vent
B Safety distance based on heat load

Figure 5.1 - Example of possible locations for storage facilities

Note:
Freestanding: a building or external location used exclusively for storage of organic peroxides.

Integral: a part of a building or within a building separated from other activities by fire-resistant walls.
For long term storage a distinction is made between four different types of storage facilities, depending on the quantity of organic peroxide stored:

- storage of quantities up to 30 kg see 5.4
- storage of quantities up to 150 kg see 5.5
- storage of quantities up to 1 000 kg see 5.6
- storage of quantities greater than 1 000 kg see 5.7

For short term storage a daily stock storage unit shall be used, see 5.8.

The following subclauses set out the specific requirements for the different storage facilities. These specific requirements relate to the site of the storage facility, the structure of the building and materials used, emergency relief vent, temperature control, distance requirements, retention pit, fire fighting equipment and requirements for the electrical installations.

All safety provisions given in this Clause are based on the assumption that the organic peroxides are stored in packages permitted for transport.

5.2 General regulations for heating, air circulation and ventilation

In addition to the regulations that apply depending on the quantity of organic peroxides stored, the following regulations apply for the heating of a storage facility, air circulation and ventilation.

Heating
If a storage unit has to be heated, e.g. to prevent freezing or phase separation of the organic peroxides, the following regulations shall be observed:

reg 5.2.1 The temperature of the product and the package may, as a result of heating, not exceed the maximum storage temperature.

reg 5.2.2 The surface temperature of heating equipment in the storage facility shall remain below 60°C. The temperature of the air entering the storage facility shall also remain below 60 °C.

reg 5.2.3 The heating equipment shall be installed such that packages of organic peroxides cannot be placed against it, on it or immediately above it. A minimum distance of 0,5 m shall be kept between the packages of organic peroxide and the heating equipment.

reg 5.2.4 Storage facilities with a heating system shall be fitted with temperature sensors. It shall be possible to read the temperature from near to the storage facility. The temperature shall be checked at least weekly and this shall be noted. If more than 150 kg of organic peroxides are stored a warning system to a permanently manned station is required.

Air circulation
The circulation of air in the storage facility is very important to prevent self-heating of the organic peroxide.

To promote natural air circulation the following regulations shall be observed:
reg 5.2.5 In a storage facility for more than 1 000 kg the packages shall be placed at least 0.15 m from the wall.

reg 5.2.6 Between pallets or similar stacks a distance of at least 0.1 m shall be observed so that air can flow along at least two sides.

**Ventilation**

In a store for organic peroxides, packages shall only be opened in case of sampling for analysis purposes. The vapour pressure of organic peroxides is generally low. The main purpose of ventilation is therefore to remove (low concentrations) of troublesome vapours.

reg 5.2.7 If a regulation requires that a structure shall be designed with fire-resistance, doors, windows, ventilation openings, smoke vents and lead-throughs shall not adversely affect the required fire-resistance.

*Note:*

Ventilation openings are best positioned (diametrically) as far as possible from one another.

### 5.3 Safety signs

**reg 5.3.1** On the outside of a storage facility, near the entry door(s) warning notices should be placed in clearly visible places indicating the danger of the hazardous substances stored. The relevant hazard symbols should be affixed in suitable places:

- a notice with a peroxide label (for transport);
- a notice with safety goggles.

In addition in all storage facilities the prohibition notice ‘fire, open flame and smoking prohibited’ shall be affixed.

*Note:*

Annex D gives examples of the hazard symbols to be used for the safety signs.

### 5.4 Storage facility for quantities up to 30 kg

**Site**

**reg 5.4.1** For the storage of quantities up to 30 kg the following facilities can be used, see also Figure 5.1 (option 1):

- cabinet;
- refrigerator;
- freezer cabinet or box.

**reg 5.4.2** The storage facility for quantities up to 30 kg should be located in an easily accessible place equipped with a vent system for any decomposition vapours.

*Note:*

Not suitable are e.g. canteens, utility rooms, cellars, corridors and escape routes.
reg 5.4.3  **Quantities up to 30 kg may be stored in the inner packaging, in which they can be transported (that is without outer packaging)** [2].

**Emergency pressure relief vent**

reg 5.4.4  **The doors (of the cabinet, refrigerator of freezer box/cabinet) shall open automatically in case of decomposition of the organic peroxide (e.g. magnetic closures).**

**Temperature control**

**Passive cooling**

reg 5.4.5  **Organic peroxides with a \( T_c \geq 30°C \) do not have to have active cooling.**

reg 5.4.6  **The supply of heat shall be prevented.**

*Note:*

_For the storage of organic peroxides up to 30 kg the passive cooling may consist of a cabinet._

**Active cooling**

reg 5.4.7  **Organic peroxides with a \( T_c < 30°C \) shall be actively cooled. If the cooling fails, cooling shall be provided in an alternative way using e.g. ice or dry ice (solid CO\(_2\)).**

*Note:*

_For the storage of organic peroxides up to 30 kg the active cooling may consist of a refrigerator, freezer box or freezer cabinet._

reg 5.4.8  **For refrigerators or freezers, the lamp on the inside, if present, shall be removed.**

*Note:*

_The lamp shall be removed because this sometimes remains on when the door is closed. This is then a heat source that may cause decomposition of the organic peroxide._

**Distance requirements**

reg 5.4.9  **The places in front of the emergency pressure relief vent devices shall be kept free.**

reg 5.4.10  **Smoking and open flames are prohibited within a distance of 1 m from the device.**

*No other distances have to be observed.*

**Product collection**

reg 5.4.11  **Organic peroxides, preferably packed in plastic (e.g. polyethylene) shall be placed in a liquid-proof tray of a suitable material with a capacity as great as the total quantity of products.**

*Note:*

_For the collection of organic peroxides e.g. the following materials are suitable: polythene, SS._
Fire fighting

reg 5.4.12  A portable fire extinguisher or hose reel shall be positioned within 15 m of the storage facility.

5.5 Storage facility for quantities up to 150 kg

Site

reg 5.5.1  Organic peroxides up to a quantity of 150 kg from storage group 1 shall be stored in an outside facility, see Figure 5.1 (options 3 or 4). Organic peroxides from the other storage groups shall be stored in outside or inside vaults or fixed cabinets, see also Figure 5.1 (options 2, 3 or 4).

reg 5.5.2  A free standing storage facility (Figure 5.1, option 4) shall be located at a safe distance from other buildings.

Note: See Clause 7 for the minimum distances to be observed

Construction and materials

reg 5.5.3  Organic peroxides may not come into contact with substances and materials that adversely affect the thermal stability of the organic peroxide.

Note: Materials that adversely affect the thermal stability of the organic peroxide are e.g. heavy metals (copper), accelerators, acids and amines. Concrete may in theory cause a reaction but this occurs so slowly that it is not relevant. Concrete may therefore be used.

reg 5.5.4  The storage facility shall have a fire-resistance of at least 30 minutes, according to NEN 6069.

reg 5.5.5  The storage facility shall be able to withstand a positive static internal pressure that is higher than the opening pressure of the emergency pressure relief vent device.

Emergency pressure relief vent

reg 5.5.6  The storage facility shall be fitted with an opening (covered with a panel) of at least 0.25 m² that is connected directly to the outside air.

Note: The emergency pressure relief vent may consist of a door opening to the outside (not falling to), for example fitted with a magnetic or spring closure. A hatch or dome light can also be used as an emergency pressure relief vent.

Temperature control

Passive cooling

reg 5.5.7  Organic peroxides with a Tc ≥ 30 °C do not to be actively cooled.
The supply of heat shall be prevented.

Note:
For the storage of organic peroxides up to 150 kg the passive cooling may consist of a sunroof, a double roof, insulation walls, air ventilation, or a water sprinkler installation on the roof. What should above all be avoided is the input of heat by radiation of sunlight e.g. through the windows or plastic screens. Most forms of passive cooling can be achieved by proper structural measures.

Active cooling

Organic peroxides with a Tc < 30°C shall be actively cooled.

Note:
For the storage of organic peroxides up to 150 kg the active cooling may consist of:

- mechanical cooling unit(s);
- standby or emergency provisions in case of breakdowns of the cooling system e.g. coolants such as solid carbon dioxide, liquid nitrogen, ice. An ample standby cooling capacity should be provided.

The storage facility with active cooling shall be equipped with temperature sensors. It shall be possible to read the temperature from near to the storage unit. The temperature shall be checked at least weekly and this shall be noted.

Distance requirements

There should be no structure or obstacles such as trees, bushes etc. within 2 m of the emergency pressure relief vent. Apart from this no safety distances are required.

Retention pit

The storage facility shall be equipped with a retention pit/catch tray which can collect the entire contents of the products stored.

Fire fighting

A portable fire extinguisher or hose reel shall be present within 15 m of the storage facility.

Note:
For extinguishing a fire with organic peroxides this extinguishing equipment is of course not enough, but this is to extinguish small fires (starting) in the vicinity so that it does not spread to the storage facility.

Electrical equipment

The electrical equipment permanently installed within the storage facility shall meet the requirements for EX IIB T3 according to the Commodities Act Decree on explosion safe equipment.
### 5.6 Storage facility for quantities up to 1 000 kg

#### Site

<table>
<thead>
<tr>
<th>reg 5.6.1</th>
<th>Organic peroxides up to a quantity of 1 000 kg shall be stored in an integral or free standing storage facility (options 3 or 4 of Figure 5.1). Organic peroxides from storage group 1 shall be stored in a free standing facility (option 4 of Figure 5.1).</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>reg 5.6.2</th>
<th>An integral facility includes an outside wall equipped with an emergency pressure relief vent. If the storage facility is on the top floor the emergency pressure relief vent may also be fitted in the roof.</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>reg 5.6.3</th>
<th>The free standing facility shall be located at a safe distance from other buildings.</th>
</tr>
</thead>
</table>

**Note:**
See Clause 7 for the minimum distances to be observed.

#### Construction and materials

**General**

<table>
<thead>
<tr>
<th>reg 5.6.4</th>
<th>Organic peroxides shall be prevented from coming into contact with substances and materials that adversely affect the thermal stability of the organic peroxide.</th>
</tr>
</thead>
</table>

**Note:**
Materials that adversely affect the thermal stability of the organic peroxide are e.g. heavy metals (copper), accelerators, acids and amines. Concrete may in theory cause a reaction but this occurs so slowly that it is not relevant. Concrete may therefore be used.

<table>
<thead>
<tr>
<th>reg 5.6.5</th>
<th>The storage facility shall be able to withstand a positive static internal pressure that is higher than the opening pressure of the emergency pressure relief vent.</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>reg 5.6.6</th>
<th>In case of an integral facility the walls shall in accordance with NEN 6069 be fire-resistant for at least 60 min within a distance from the emergency pressure relief vent of 2 m in a horizontal direction and 4 m in a vertical direction.</th>
</tr>
</thead>
</table>

**Integral facility**

<table>
<thead>
<tr>
<th>reg 5.6.7</th>
<th>For an integral facility the partition walls, internal doors and ceiling shall in accordance with NEN 6069 be fire-resistant for at least 60 min. The internal door(s) shall be self-closing and opening inwards.</th>
</tr>
</thead>
</table>

**Free standing facility**

<table>
<thead>
<tr>
<th>reg 5.6.8</th>
<th>The free standing storage facility should have a fire-resistance of at least 30 minutes, according to NEN 6069.</th>
</tr>
</thead>
</table>
Emergency pressure relief vent

**reg 5.6.9 Guide values for the dimensions of the emergency relief vent are**
- 1 m² for products from storage group 1;
- 0,5 m² for products from storage group 2;
- 0,25 m² for products from storage groups 3 and 4.

**Note:**
The emergency pressure relief vent may consist of a door that opens to the outside (not falling to), for example fitted with a magnetic or spring closure. A hatch or a dome light can also be used as an emergency pressure relief vent.

Temperature control

**Passive cooling**

**reg 5.6.10 Organic peroxides with a Tc ≥ 30°C, do not have to be actively cooled.**

**reg 5.6.11 The supply of heat shall be avoided.**

**Note:**
For the storage of organic peroxides up to 1 000 kg the passive cooling may consist of a sunroof, a double roof, insulation walls, air ventilation or a water sprinkler system on the roof. What should above all be avoided is the input of heat by radiation of sunlight, through e.g. the windows or plastic screens. Most forms of passive cooling can be achieved by proper structural measures.

**Active cooling**

**reg 5.6.12 Organic peroxides with a Tc < 30 °C shall be actively cooled.**

**Note:**
For the storage of organic peroxides up to 1 000 kg the active cooling may consist of:

- mechanical cooling unit(s);
- and standby or emergency provisions in case of breakdowns of the cooling system.

**reg 5.6.13 The storage facility with active cooling should be fitted with temperature sensors. It shall be possible to read the temperature from near to the storage unit. The temperature shall be checked at least weekly and this shall be noted.**

**reg 5.6.14 The temperature sensors in the storage facility with active cooling for the storage of organic peroxides with a Tc < 30 °C shall be fitted with a warning system to a permanently manned station.**

Distance requirements

**reg 5.6.15 Within a distance of 5 m from the emergency pressure relief vent (relief zone) there shall be no structures or obstacles such as trees, bushes etc. In this zone smoking and open flames are prohibited.**
For the distance requirements in front of the emergency pressure relief vent of an integral facility Clause 7 applies.

For the distance requirements for free standing storage facilities Clause 7 applies.

Retention pit

The minimum capacity of the retention pit is determined by the following requirements, where the biggest calculated value is decisive:

- 10% of the maximum quantity that may be present in the storage facility (or biggest storage compartment), plus 15 min water supply from the extinguishing system installed;
- for liquid organic peroxides, not belonging to storage groups 4 or 5, the value is determined by the volume of the maximum quantity of product present in the storage facility (or biggest storage compartment).

Fire fighting

The guidelines for determining a suitable extinguishing system are described in 4.6.4.

In integral facilities at least one of the following fire extinguishing systems shall be present.

1. **Automatic sprinkler**

   *Characteristics:*
   - fire detected by temperature or heat sensors (NEN 2535);
   - when activated only the area below the sprinkler head is covered;
   - the capacity of the system is at least equal to:
     - 10 l/min.m² for storage of peroxides from group 3;
     - 15 l/min.m² for storage of peroxides from group 2;
     - 20 l/min.m² for storage of peroxides from group 1.
   - the system complies with VAS 2004 or NFPA 13 [14, 15].

2. **Automatic deluge**

   *Characteristics:*
   - a fire shall as a minimum be detected by temperature or heat, where smoke detection may also be used (NEN 2535);
   - when activated the whole floor area of the storage facility is covered;
   - the capacity of the system is at least equal to:
     - 10 l/min.m² for storage of peroxides from group 3;
     - 15 l/min.m² for storage of peroxides from group 2;
     - 20 l/min.m² for storage of peroxides from group 1.
   - the system complies with NFPA 15 [16].

3. **(Local) fire service with dry deluge system.** The fire service shall be present within 6 minutes and have a water tender and sufficient crew (in the opinion of the fire service). The pump capacity and the water supply shall be matched to the capacity of extinguishing system to be supplied.
Characteristics:
- A fire shall, as a minimum, be detected by temperature or heat, where smoke detection may also be used (NEN 2535);
- When activated, the whole floor area is covered;
- The capacity of the system is at least equal to:
  - 10 l/min.m² for storage of peroxides from group 3;
  - 15 l/min.m² for storage of peroxides from group 2;
  - 20 l/min.m² for storage of peroxides from group 1.
- The system complies with NFPA 15 [16].

Note:
As regards fire fighting systems (in particular system 3) or alternative systems, the local fire service should be consulted regarding the alarm procedure and the call-out time of a local fire service.

Electrical equipment

Reg 5.6.20
The electrical equipment permanently installed within the storage facility shall meet the requirements for EX IIB T3 according to the Commodities Act Decree on explosion safe equipment.

5.7 Storage facility for quantities greater than 1 000 kg

Site

Reg 5.7.1
Quantities of organic peroxides of more than 1 000 kg shall be stored in free standing facilities (option 4 in Figure 5.1).

Note:
The storage facility may consist of a number of smaller units or compartments that each have an outside door.

Reg 5.7.2
The free standing facility shall be located at a safe distance from the other buildings.

Note:
An exception to these regulations is the possibility of reducing the distance to 0 m as described in 7.4.

Construction and materials

Reg 5.7.3
The storage facility shall be able to withstand a positive static internal pressure that is higher than the opening pressure of the emergency pressure relief vent.

Reg 5.7.4
Organic peroxides shall be prevented from coming into contact with substances and materials that adversely affect the thermal stability of the organic peroxide.

Note:
Materials that adversely affect the thermal stability of the organic peroxide are e.g. heavy metals (copper), accelerators, acids and amines. Concrete may in theory cause a reaction but this occurs so slowly that it is not relevant. Concrete may therefore be used.

Reg 5.7.5
A free standing storage facility shall have a fire-resistance of at least 30 min according to NEN 6069.
Emergency pressure relief vent

**reg 5.7.6** For free standing storage facilities the following guide values apply for the emergency pressure relief vent:
- 1 m² / 1 000 kg for products from storage group 1;
- 0,5 m² / 1 000 kg for products from storage group 2;
- 0,25 m² / 1 000 kg for products from storage groups 3 and 4.

**Note:**
The emergency pressure relief vent may consist of a door opening to the outside (not to be locked), e.g. fitted with a magnetic or spring closure. A hatch or dome light may also be used as an emergency pressure relief vent.

Temperature control

**General**

**reg 5.7.7** The storage facilities for quantities more than 1 000 kg in which organic peroxides with a specified Tc are stored shall be fitted with one or two independent temperature sensors with temperature alarm going to a permanently manned station that are actuated when the Te is exceeded.

**Note:**
One of the sensors may be replaced by a smoke or gas detector connected to a warning system. If more than one product is stored in one room the lowest Tc and Te apply.

**Passive cooling**

**reg 5.7.8** Organic peroxides with a Tc ≥ 30 °C do not have to be actively cooled.

**reg 5.7.9** The supply of heat shall be avoided.

**Note:**
For the storage of organic peroxides greater than 1 000 kg the passive cooling may consist of a sunroof, a double roof, insulation walls, air ventilation or a water sprinkler system on the roof. What should be avoided above all is the input of heat by radiation of sunlight, through e.g. the windows or plastic screens. Most forms of passive cooling can be achieved by proper structural measures.

**Active cooling**

**reg 5.7.10** Organic peroxides with a Tc < 30 °C shall be actively cooled.

**Note:**
For the storage of organic peroxides more than 1 000 kg the active cooling may consist of:
- mechanical cooling unit(s);
- and standby or emergency provisions in case of breakdown of the cooling system.

**reg 5.7.11** The storage facility with active cooling shall also be fitted with temperature sensors. It shall be possible to read the temperature from near to the storage unit. The temperature shall be checked at least weekly and this shall be noted.
**ORGANIC PEROXIDES: STORAGE**

**Distance requirements**

**reg 5.7.12** The temperature sensors in the storage facility with active cooling for the storage of organic peroxides with a $T_c < 30 \, ^\circ\text{C}$ shall be fitted with a warning system to a permanently manned station.

**Distance requirements**

**reg 5.7.13** In free standing storage facilities for more than 1 000 kg of organic peroxides Clause 7 applies for the distance requirements.

**Distance requirements**

**reg 5.7.14** In cases where the facility is subdivided into compartments the requirements relating to safety distances and emergency relief vent may be applied to each compartment provided:
- the partition walls have a fire-resistance of at least 60 min, in accordance with NEN 6069;
- the walls adjacent to the wall or roof with the emergency pressure relief vent continue for 0.5 m.

**Distance requirements**

**reg 5.7.15** The free standing storage facilities shall (in consultation with the local fire service) be accessible to the fire service.

**Distance requirements**

**reg 5.7.16** In storage facilities with more than 1 000 kg of organic peroxides stored the emergency pressure relief vent shall be kept clear of the storage by at least 0.5 m

**Distance requirements**

**reg 5.7.17** Within a distance of 5 m from the emergency pressure relief vent (relief zone) there shall be no structures or obstacles such as trees, bushes etc. In this zone smoking and open flames are prohibited.

**Retention pit**

**reg 5.7.18** The minimum capacity of the retention pit is determined by the following requirements, where the biggest calculated value is decisive:
- 10% of the maximum quantity that may be present in the storage facility (or biggest storage compartment), plus 40 min water supply from the extinguishing system installed;
- for liquid organic peroxides, not belonging to storage groups 4 or 5, the value is determined by the volume of the maximum quantity of product present in the storage facility (or biggest storage compartment).

**Note:**
*Containment of peroxides in pipes and pits shall be avoided. The depth of the layer of organic peroxide in a retention pit may therefore not be more than 0.5 m.*

**Fire fighting in relation to effect or safety distances**
The safety distances to be observed for type A and B premises are set out in Table 7.1 of Clause 7.4. These distances depend on the safety provisions. The required effect or safety distances (based on heat load) that shall be observed may be limited if one of the following fire fighting systems are installed.
1. Automatic sprinkler

*Characteristics:*

- fire detected by temperature or heat sensors (NEN 2535);
- when activated only the area below the sprinkler head is covered;
- the capacity of the system is at least equal to:
  - 10 l/min.m² for storage of peroxides from group 3;
  - 15 l/min.m² for storage of peroxides from group 2;
  - 20 l/min.m² for storage of peroxides from group 1.
- the system complies with VAS 2004 of NFPA 13 [14, 15].

2. Automatic deluge

*Characteristics:*

- a fire shall as a minimum be detected by temperature or heat, where smoke detection may also be used (NEN 2535);
- when activated the whole floor area of the storage facility is covered;
- the capacity of the system is at least equal to:
  - 10 l/min.m² for storage of peroxides from group 3;
  - 15 l/min.m² for storage of peroxides from group 2;
  - 20 l/min.m² for storage of peroxides from group 1.
- the system complies with NFPA 15 [16].

3. (Local) fire service with dry deluge system. The fire service shall be present within 6 minutes and have a water tender and sufficient crew (in the opinion of the fire service). The pump capacity and water supply shall be matched to the capacity of the extinguishing system to be supplied.

*Characteristics:*

- a fire shall as a minimum be detected by temperature or heat, where smoke detection may also be used (NEN 2535);
- when activated the whole floor area is covered;
- the capacity of the system is at least equal to:
  - 10 l/min.m² for storage of peroxides from group 3;
  - 15 l/min.m² for storage of peroxides from group 2;
  - 20 l/min.m² for storage of peroxides from group 1.
- the system complies with NFPA 15 [16].

*Note:*

Relating to fire fighting systems (in particular system 3) or alternative systems the local fire service shall be consulted about the alarm procedure and the call-out time of a local fire service.

**Electrical equipment**

reg 5.7.19  The electrical equipment permanently installed within the storage facility shall meet the requirements for EX IIB T3 according to the Commodities Act Decree on explosion safe equipment.

**Lightning strike**

reg 5.7.20  The free standing facilities shall be earthed.
Note:
To determine the risk of lightning strike in the storage of organic peroxides a risk assessment according to part 2 of the standard NEN-EN-IEC 62305 is necessary. This will show whether a lightning conductor is required on the free standing facility. It may also be necessary to fit a lightning conductor for other reasons, e.g. fire prevention from indirect ignition or protection of the cooling system and emergency provisions.

5.8 Operational stock and daily stock storage unit

reg 5.8.1 Operational stock is the quantity organic peroxide that is necessary on the production room/ work room or near a process installation.

- The operational stock shall be strictly necessary;
- At the most one opened container is allowed for each hazardous substance;
- The operational stock is not allowed in the driving route or forklift trucks or other vehicles;
- The operational stock shall not block the escape;
- Organic peroxides that are present as operation stock in a production room or work room shall be stored in a sound container, that is resistant to the relevant hazardous substance;
- If the operational stock exists of a quantity more than 25 l than the container shall be placed above a liquid tight tray or similar facility;

This can be deviated from if (the relevant part of) the floor of the relevant production room/ work room is at least a fluid-tight floor. However, for combustible liquids a liquid prove tray or similar facility is always required.

The competent authority may require additional measures regarding the safe use of the operational stock, in order to avoid the exposure to organic peroxides, or avoid the risk of fire and explosion.

Note:
The operational stock shall be as such that production can be performed normally. Nevertheless, it shall not be that large that several unopened containers are unnecessarily present in the operational stock for days or even for weeks. That should mean there is an ‘ulterior stock’. These containers should be stored in a storage room or a daily stock storage unit. The border between daily stock and operational stock is difficult to establish. It is up to the company to make plausible that the organic peroxides will be used in the production process within a reasonable timeframe (several days or at the most several weeks).

The operational stock does not have to be transferred to a stock at the end of the day (and vice versa at the start of the working day): the risks of transport are then bigger than with a stationary operational stock. With batch production or with round-the-clock companies the operational stock partly has a flow through character and each case must be judged on its own merits for good proceedings.

The reason for the requirement of a liquid tight tray for a quantity more than 25 l for combustible liquids is to diminish the evaporation surface in case of a leak.

To have a spare stock close to the process or for tapping activities, a daily stock storage unit could be established. In regulations 5.8.2 to 5.8.17 the requirements for such a stock unit are given.
Daily stock storage unit

**reg 5.8.2** A daily stock storage unit is a facility for the temporarily (maximum 72 hours) storage of organic peroxides as well as a tapping room for the purpose of the production process.

**Site**

**reg 5.8.3** A daily stock storage unit may take the form of an integral facility and/or free standing facility, see also Figure 5.1 (options 2, 3, 4 or 5).

**reg 5.8.4** The daily stock storage unit forming part of a production building shall be located at an outside wall or the roof.

**Construction and materials**

**reg 5.8.5** The walls, roof and floor of the daily stock storage unit shall in accordance with NEN 6069 be fire-resistant for at least 60 min for quantities of organic peroxides of less than 1 000 kg and 90 min for quantities above 1 000 kg.

**reg 5.8.6** The daily stock storage unit shall have a mechanical strength that is higher than the emergency pressure relief vent. The internal doors shall be self-closing and fire-resistant for at least 60 min. For quantities of more than 1 000 kg the door opening shall be closed with a fire door that is fire-resistant for at least 90 minutes.

**reg 5.8.7** The daily stock storage unit shall be able to withstand a positive static internal pressure that is higher than the opening pressure of the emergency pressure relief vent.

**Emergency pressure relief vent**

**reg 5.8.8** The walls within a distance from the emergency pressure relief vent of 2 m in a horizontal direction and 4 m in a vertical direction shall in accordance with NEN 6069 be fire-resistant for at least 60 min.

**reg 5.8.9** Guide values for the dimensions of the emergency relief vent are:
- 1 m² for products from storage group 1;
- 0,5 m² for products from storage group 2;
- 0,25 m² for products from storage groups 3 and 4.

**Note:**
The emergency pressure relief vent may consist of a door opening outwards (not falling to), for example fitted with a magnetic or spring closure. A hatch or dome light may also be used as an emergency pressure relief vent.

**Temperature control**

**Passive cooling**

**reg 5.8.10** Organic peroxides with a $T_c \geq 30 \, ^\circ\text{C}$ do not have to be actively cooled.
The supply of heat shall be avoided.

Note:
For the storage of organic peroxides the passive cooling may consist of a sunroof, a double roof, insulation walls, air ventilation or a water sprinkler system on the roof. What should be avoided above all is the input of heat by radiation of sunlight, through e.g. the windows or plastic screens. Most forms of passive cooling can be achieved by proper structural measures.

Active cooling

Organic peroxides with a Tc < 30 °C shall be actively cooled.

Note:
For the storage of organic peroxides the active cooling may consist of:

- mechanical cooling unit(s);
- and standby or emergency provisions in case of breakdown of the cooling system.

The storage facility with active cooling shall also be fitted with temperature sensors. It shall be possible to read the temperature from near to the storage facility. The temperature shall be checked at least weekly and this shall be noted.

There shall not be any obstacles in the vent zone of the emergency pressure relief vent. Smoking and open flames are prohibited in the vent zone. The distances to be observed are:

- 2 m for peroxide quantities of less than 150 kg;
- 5 m for peroxide quantities of less than 1 000 kg;
- 10 m for peroxide quantities of more than 1 000 kg.

The minimum capacity of the retention pit is determined by the following requirements, where the biggest calculated value is decisive:

- 10 % of the maximum quantity that may be present in the storage facility (or biggest storage compartment), plus 15 min water supply from the extinguishing system installed;
- for liquid organic peroxides, not belonging to storage groups 4 or 5, the value is determined by the volume of the maximum quantity of product present in the storage facility (or biggest storage compartment).

Note:
Containment of organic peroxides in pipes and pits shall be avoided. The depth of the layer of organic peroxide in a retention pit may not therefore be more than 0.5 m.

Fire fighting
The guidelines for determining a suitable extinguishing system are described in 4.6.4.

At least one of the following fire extinguishing systems shall be present in the daily stock storage unit.
1. Automatic sprinkler

*Characteristics:*

- fire detected by temperature or heat sensors (NEN 2535);
- when activated only the area below the sprinkler head is covered;
- the capacity of the system is at least equal to:
  - 10 l/min.m² for storage of peroxides from group 3;
  - 15 l/min.m² for storage of peroxides from group 2;
  - 20 l/min.m² for storage of peroxides from group 1.
- the system complies with VAS 2004 of NFPA 13 [14, 15].

2. Automatic deluge

*Characteristics:*

- a fire shall as a minimum be detected by temperature or heat, where smoke detection may also be used (NEN 2535);
- when activated the whole floor area of the storage facility is covered;
- the capacity of the system is at least equal to:
  - 10 l/min.m² for storage of peroxides from group 3;
  - 15 l/min.m² for storage of peroxides from group 2;
  - 20 l/min.m² for storage of peroxides from group 1.
- the system complies with NFPA 15 [16].

3. (Local) fire service with dry deluge system. The fire service shall be present within 6 minutes and have a water tender and sufficient crew (in the opinion of the fire service). The pump capacity and the water supply shall be matched to the capacity of the extinguishing system to be supplied.

*Characteristics:*

- a fire shall as a minimum be detected by temperature or heat, where smoke detection may also be used (NEN 2535);
- when activated the whole floor area is covered;
- the capacity of the system is at least equal to:
  - 10 l/min.m² for storage of peroxides from group 3;
  - 15 l/min.m² for storage of peroxides from group 2;
  - 20 l/min.m² for storage of peroxides from group 1.
- the system complies with NFPA 15 [16].

*Note:*

As regards fire fighting systems (in particular system 3) or alternative systems the local fire service should be consulted about the alarm procedure and the call-out time of a local fire service.

**Electrical equipment**

*reg 5.8.17 The electrical equipment permanently installed within the storage facility shall meet the requirements for EX IIB T3 according to the Commodities Act Decree on explosion safe equipment.*
6 Storage in tanks and dosing vessels

6.1 General

To simplify the safe storage and handling of liquid organic peroxides organic peroxides may be stored in tanks or metering systems such as dosing vessels. This type of storage facility shall be constructed and operated with great care, since the decomposition of organic peroxide in metal tanks can cause violent explosions, where the tank may rupture. The hazard of explosions may be prevented by restricting the size of the tanks and fitting the tanks with the necessary emergency relief vent devices.

Note:
Transport packages, whether or not connected to a process (e.g. spraying equipment) are not regarded as dosing vessels.

An IBC is regarded as a package and as regards the storage of organic peroxides the regulations of the Clauses 1 to 5 therefore apply.

reg 6.1.1 The general regulations regarding the storage of organic peroxides as set out in Clauses 5.1 to 5.3 apply in full for storage in tanks and dosing vessels.

6.2 Storage tanks

Storage in tanks is permitted for organic peroxides of type F, listed in 0. The safety of the organic peroxide in the tank shall be demonstrated. Dilutions of concentrated organic peroxides made by users themselves are not on the list in 0. These may also be stored in tanks provided it is shown that they have properties that are comparable with peroxides of type F. Any change in classification shall be based on tests, like the peroxides appearing in the list.

Further data on this can be provided by the supplier of the organic peroxide or by specialist institutes (see Annex H).

Emergency situations that shall be taken into account are the self-accelerating decomposition of the organic peroxide and the situation where the tank is surrounded by fire (heat load as laid down in the transport regulations for transport of organic peroxides in tanks 4.2.1.13 of ref. [17]).

General regulations for storage in tanks

reg 6.2.1 The general guidelines for the construction, inspection and maintenance for storage in tanks for liquid fuels, set out in the PGS 29 and 30 [18, 19] shall be followed, where in case of conflicting requirements those of PGS 8 take precedence.

reg 6.2.2 Tanks may not be filled to more than 90 % of their capacity.
Site

reg 6.2.3 A storage tank for the storage of organic peroxides shall preferably be located outdoors. However, if the tank is located indoors, the emergency relief vent shall be connected to the outside air.

Construction of tank and materials

reg 6.2.4 The materials of construction of the tank shall be demonstrably compatible with the organic peroxides that come into contact with the tank.

Note:
A tank of stainless steel (SS) or HDPE (High Density Polyethylene) is demonstrably compatible with organic peroxides.

reg 6.2.5 The capacity of the tank may not be more than 100 m³.

reg 6.2.6 The tank shall be fully insulated:
- if the SADT of the organic peroxide in the tank is 55 °C or less, or,
- if the tank is made of aluminium.

The insulation material shall be non-flammable, determined in accordance with NEN 6064.

Note:
The SADT and therefore the Tc and Te of organic peroxides that are stored in tanks differ from that of the same organic peroxides in (smaller) packages.

(Emergency) pressure relief vent

reg 6.2.7 The tank shall be able to withstand a positive static internal pressure that is higher than the opening pressure of the emergency pressure relief vent. The emergency pressure relief vent shall meet the transport regulations for the transport of organic peroxides as set out in 4.2.1.13 of ref [17].

Note:
The emergency relief device(s) may be of the springloaded or frangible types designed to relief all the decomposition products and vapours evolved during an emergency.

Temperature control

General

reg 6.2.8 The temperature of the tank contents shall be representatively monitored (for the volume and shape of the tank) by at least three thermometers, of which:
- two independent thermometers shall be placed in the liquid phase. The alarm value may not be set higher than the critical storage temperature, Te;
- at least one thermometer shall be placed in the vapour phase with a value set at 50 °C or less.

The message that the alarm values have been exceeded shall be sent to a permanently manned station.
Passive cooling

reg 6.2.9 Organic peroxides with a Tc ≥ 30 °C do not have to be actively cooled if the outside of the storage tank is made of white or clear metal.

reg 6.2.10 The supply of heat shall be avoided.

Active cooling

reg 6.2.11 Organic peroxides with a Tc < 30 °C shall be actively cooled.

Note:
For the storage of organic peroxides in storage tanks the active cooling may be provided by means of:

- spiral cooling or;
- jacket cooling or;
- cooling via circulation systems;
- and standby or emergency provisions in case of breakdowns of the cooling system.

Distance requirements

reg 6.2.12 For determining distances according to 7.4 organic peroxides stored in tanks (based on the volume) shall be considered as storage group 2.

reg 6.2.13 The distance from one peroxide tank (peroxide of type F) to another may be reduced to half the diameter of the tank measured from wall to wall if:

- the tanks are insulated with a material that in accordance with NEN 6069 is fire-resistant for at least 60 min, or;
- is located outside the tank deluge systems to protect the tanks from external fire and to provide extra cooling.

Retention pit

reg 6.2.14 Each tank shall be connected to a retention pit. Several tanks may be connected to one pit. The capacity of the pit shall be 150 % of the capacity of the biggest tank connected.

Fire fighting

If organic peroxides are stored in a tank, the tank shall be regarded as one package, where the tank itself cannot burn. In other words in case of fire, compared with the storage of packages in a storage facility, there is no risk that due to the fire other packages will be affected, the fire will get bigger and the risk will arise that the fire will spread if it is not extinguished (see also reg 6.2.12).

Based on this fact it is also recommended that in case of fire of organic peroxides from a tank, the fire service will allow the controlled burning of the organic peroxides. One should of course also prevent the fire from spreading to other premises within the establishment.

Note:
The internal emergency plan, see also Clause 9, should also clearly state that in case of fire of the tank no extinguishing activities shall be undertaken, other than to prevent the fire spreading.
Electrical equipment

reg 6.2.15 The electrical equipment permanently installed within and directly around the storage tank shall meet the requirements for EX IIB T3 according to the Commodities Act Decree on explosion safe equipment.

Lightning strike

reg 6.2.16 The storage tank for organic peroxide shall be earthed.

Note: To determine the risk of lightning strike in the storage of organic peroxides a risk assessment according to part 2 of standard NEN-EN-IEC 62305 is necessary. This will show whether a lightning conductor is required on the free standing facility. It may also be necessary to fit a lightning conductor for other reasons, e.g. fire prevention from indirect ignition or protection of the cooling system and emergency provisions.

6.3 Dosing vessels

Metering vessels, day storage tanks, IBCs and so on that are used as a dosing vessel are covered in this PGS guideline by the term dosing vessels. They serve for the storage of daily stocks for organic peroxides.

Organic peroxide in the original transport package (30 litre drums and/or jerry cans whether or not with a pump) that is used on the shop floor, are not covered by the term dosing vessels.

Note: Using the above-mentioned original transport package on the shop floor is regarded as use and not storage. This also falls outside the scope of this PGS guideline, but comes under occupational safety. The use of these packages shall be regulated in a Risk Assessment. If this small package is connected to a mobile installation it is preferable for this installation to be placed in a fixed place at the end of the day. In this way, in case of an emergency outside working hours, it is clear for the fire service among others where the organic peroxides are located. For a stationary installation on the other hand it is immediately clear where the organic peroxides are located.

Site

reg 6.3.1 Dosing vessels may be located both indoors and outdoors.

reg 6.3.2 Dosing vessels with a capacity of more than:

- 30 l for organic peroxides of type C or
- 60 l for organic peroxides of type D or
- 225 l for organic peroxides of type E

shall be placed in

- a separate building, where the distances given in Clause 7 shall be observed. The guidelines for storage facilities for quantities greater than 1 000 kg apply, see Subclause 5.7 or a separate room, where the requirements for a daily stock storage unit are met, see 5.8. The maximum permitted total quantity per room is 5 000 l, with a maximum of five containers.
Construction of dosing vessel and materials

reg 6.3.3 The materials from which the dosing vessel is composed shall be demonstrably compatible with the organic peroxides that come into contact with the tank.

Note:
A dosing vessel of stainless steel (SS) or HDPE (High Density Polyethylene) is demonstrably compatible with organic peroxides.

reg 6.3.4 The size of the dosing vessel is a maximum of:
- 100 l for organic peroxide of type C;
- 200 l for organic peroxide of type D;
- 1 500 l for organic peroxide of type E;
- 5 000 l for organic peroxide of type F.

If the organic peroxides belong to storage group 4 the dosing vessel is a maximum of 10 000 l.

Note:
In case of larger quantities explosions cannot be excluded.

Emergency pressure relief vent

reg 6.3.5 The dosing vessel shall be able to withstand a positive static internal pressure that is higher than the opening pressure of the emergency pressure relief vent.

Note:
For the emergency relief vent e.g. a hinged lid on the whole of the top of the vessel can be used.

Temperature control

Passive cooling

reg 6.3.6 Organic peroxides with a $T_c \geq 30 \, ^\circ\text{C}$ do not have to be actively cooled.

reg 6.3.7 The supply of heat shall be avoided.

Note:
For the storage of organic peroxides in dosing vessels the passive cooling may consist of a sun shield or insulation. Direct radiation by sunlight should be avoided above all. Most forms of passive cooling can be achieved by proper construction measures.

Active cooling

reg 6.3.8 Organic peroxides with a $T_c < 30 \, ^\circ\text{C}$ shall be actively cooled.

Note:
For the storage of organic peroxides in dosing vessels the active cooling may be carried out by means of:
− spiral cooling; or
− jacket cooling; or
− cooling via circulation systems;
− and standby or emergency provisions in case of breakdowns of the cooling system.

reg 6.3.9 The temperature of the organic peroxide in the vessel shall be monitored:

- for organic peroxides with a $T_c \leq 20^\circ C$ at least two temperature sensors shall be used;
- for organic peroxides with a $T_c > 20^\circ C$ at least one temperature sensor shall be used.

reg 6.3.10 The alarm value may not be set higher than the emergency temperature. Higher temperatures are permitted if extra safety provisions are applied.

Note:
The higher temperatures are required to bring the organic peroxides closer to the process temperature. The extra safety provisions are therefore cooling facilities to remove the extra heat.

Distance requirements

reg 6.3.11 Depending on the volume of the dosing vessels as included in the regulation reg 6.3.2 the distance requirements from 5.7 and 5.8 apply.

Retention pit

reg 6.3.12 Each dosing vessel shall be connected to a retention pit. Several dosing vessels may be connected to one pit. The capacity of the pit shall be 150 % of the capacity of the biggest dosing vessel connected.

Fire fighting
For storage of organic peroxides in a dosing vessel, the dosing vessel shall be seen as one package; where the dosing vessel itself cannot burn, the fire will be of short duration in view of the limited quantity of organic peroxides and the storage facility where the dosing vessel is located consists of fire-resistant material. In other words: in case of a fire, compared with the storage of packages in a storage facility, there is no risk that other packages will be affected by the fire, the fire will become bigger and the risk arise that the fire will spread if it is not extinguished.

Because of this fact it is therefore recommended that in case of fire of organic peroxides from a dosing vessel, the fire service allows controlled burning of the organic peroxides. In addition the fire shall of course be prevented from spreading to other premises within the organization1.

Note:
The internal emergency plan, see also Clause 9, shall clearly state that in case of fire of the dosing vessel no extinguishing activities shall be undertaken, other than to prevent the fire spreading.

1 This procedure will often be chosen in those cases where one dosing vessel is present in a room. If several dosing vessels are installed in a room the choice to extinguish the fire will often be made so as to prevent it spreading to other dosing vessels. Check for each room what the required method is in case of fire.
Electrical equipment

reg 6.3.13 The electrical equipment permanently installed within and directly around the dosing vessel shall meet the requirements for EX IIB T3 according to the Commodities Act Decree on explosion safe equipment.

Lightning strike

reg 6.3.14 The dosing vessel for organic peroxide shall be earthed.

Note: To determine the risk of lightning strike in the storage of organic peroxides a risk assessment according to part 2 of the standard NEN-EN-IEC 62305 is necessary. This will show whether a lightning conductor is required on the free standing facility. In addition it may be necessary to fit a lightning conductor for other reasons, e.g. fire prevention from indirect ignition or protection of the cooling system and emergency provisions.

6.4 Construction of auxiliary equipment

reg 6.4.1 Specific construction rules for auxiliary equipment (such as funnels, pump etc.) fall outside the framework of this PGS guideline. To obtain the best practical and technical auxiliary equipment experts shall be consulted.

For the construction of auxiliary equipment the following general regulations are stated to apply.

reg 6.4.2 The self decomposition of organic peroxide shall be prevented when using the auxiliary equipment by temperature control and preventing contamination of the organic peroxides.

reg 6.4.3 Sufficient safety provisions shall be used to prevent uncontrolled decomposition of the organic peroxide in the auxiliary equipment.

Note: Examples of the safety provisions referred to are relief valves and rupture disks

reg 6.4.4 The residence times of the organic peroxides in the auxiliary equipment shall be limited. To remove any remaining substances (organic peroxides) in the auxiliary equipment the equipment shall be rinsed with suitable solvent.

Note: Containment of organic peroxide between two valves should e.g. be avoided to prevent explosion of the equipment as a consequence of a decomposition reaction.
7 Distances to be observed to premises based on heat load

7.1 Introduction

The application of a safety distance between storage facilities for organic peroxides within the establishment is necessary to offer protection against the effects of a fierce fire in the storage facility. In addition a store shall be protected from an external fire, since such a fire may lead to decomposition and/or ignition of the organic peroxide.

External safety distances based on the place-related risk between stores for organic peroxides and vulnerable premises outside the establishment are not necessary because the specified distance to the property boundary (based on the heat radiation) is so big that for the heat radiation the person-related risk of $10^{-6}$ by definition lies within the property boundary. Based on the current standards set in the Netherlands for the place-related risk there is therefore no zoning outside the property boundary.

For organic peroxides from group 1 in addition to fire explosions of the different packages may also occur. However due to the use of weak packages the effect of explosions is less than the heat radiation. The safety distances for PGS 8 are therefore fixed based on heat radiation instead of pressure effects (by analogy of German legislation and regulations). The following scenarios are important for determining the distances for stores for organic peroxides:

a) Fire in the peroxide store
   Determines the distances relative to surrounding premises based on the possible consequences of burning organic peroxides for these premises.

b) Fire in premises in the vicinity of the peroxide store
   As a result fire may occur in the organic peroxide store. As a rule the distances to be observed to prevent this effect will be smaller than those mentioned under (a).

c) As under (b) but assuming that as a result of the heat radiation from the burning premises to the peroxide store decomposition or explosion of the organic peroxide may be caused. Note that explosions are only expected for organic peroxides from group 1 that have a secondary ‘explosion risk’ transport label (see Annex D).

When determining the distances between stores for organic peroxides and other premises the heat radiation from a peroxide fire shall be taken into account. The technical data in references [21] to [24] are used as a basis for information on peroxide fires. The acceptable heat radiation values for premises within the property boundary were taken from the limit values issued by the Ministry of the Interior for heat load.

7.2 Limit values for heat load

The required safety distance, based on heat load between storage facilities for organic peroxides and other premises, depends on:

- the storage group of the organic peroxide;
- the quantity of organic peroxide stored;
− safety measures for the storage facility;
− nature and safety provisions of the exposed premises;
− permitted limit values for exposed premises.

The damage distances due to heat radiation in case of fire are based on:

− 3 kW/m² for damage to physical health;
− 10 kW/m² for fatal injury.

For information:

The Ministry of the Interior, Fire Services and Crisis Management Directorate, uses the following limit values with respect to radiation intensity:

− person, long term exposure 1 kW/m²;
− person, fleeing (10 seconds) 3 kW/m²;
− person, 5 seconds exposure 10 kW/m²;
− equipment, including tanks 10 kW/m²;
− fire damage to timber 10 kW/m².

7.3 Types of premises exposed

Type A premises
Type A includes facilities within the property boundary where people are present, such as workshops, offices and control rooms on the factory site. The permitted heat radiation for premises of type A is 3 kW/m².

Type B premises
Type B includes facilities within the property boundary where in general no people are at work, such as:

− other storage facilities;
− buildings and production rooms in which people are not permanently present.

The property boundary itself is also regarded as type B premises.

The permitted heat radiation for Type B premises is 10 kW/m².

7.4 Safety distances based on heat load

The safety distances are calculated based on heat load and depend on the storage group and the total quantity of organic peroxides stored from storage groups 1, 2 and 3. The quantity from storage groups 4 and 5 does not have to be included here, in view the low hazard level. The safety distances apply for storage facilities or compartments of storage facilities as described in Clause 5. The distances shall be measured from the emergency relief vent.

Table 7.1 gives the distances required for stored quantities greater than 150 kg. This Table gives the distance as a function of the floor area, assuming that 500 kg of product is stored on 1 m² floor area.

The safety distance is calculated according to the formula

\[
D = \frac{c}{8} \times m^{1/3}
\]
with \( A = \frac{m}{500} \) this gives the following calculation formula

\[
D = c \times A^{1/3}
\]

where:

- \( A \) is the floor area [m\(^2\)]
- \( m \) is the total mass [kg]
- \( D \) is the safety distance [m]
- \( c \) is the constant value according to Table 7.1

The safety distance shall be determined based both on the floor area and the total quantity of product stored. The greatest distance in these two calculations applies. For products from storage group 3 fixed distances are given in Table 7.1, irrespective of the mass and floor area. For storage groups 1 and 2 the distance may never be less than the fixed distance of storage group 3.

If organic peroxides from different storage groups are stored in one room, to determine the safety distances the organic peroxides with the lowest storage group shall be taken (or the biggest safety distances). If the quantity for the storage group with the biggest safety distance is less than or equal to 10% of the whole quantity stored an exception may be made to this rule.

The safety distances apply for storage facilities or compartments of storage facilities as described in Clause 5. The distances shall be measured from the emergency relief vent.

The safety distances for storage facilities for organic peroxides from storage group 1 are based on a burning rate (BR) of 1200 kg/min (see Annex F). Since many organic peroxides burn less fiercely, for organic peroxides of type C from storage group 1 the distance according to the following formula can be used:

\[
d = c \times A^{1/3} \times \sqrt[3]{\frac{BR_c}{1200}}
\]

\( BR_c \) can be obtained from the results of burning tests in packages as explained in Annex F.
Table 7.1 - Safety distances (in metres) from storage facilities to other premises (based on heat load), assuming a storage of 500 kg of product per m² floor area

<table>
<thead>
<tr>
<th>Safety provision</th>
<th>Storage group 1 (c \times A^{1/3})</th>
<th>Storage group 2 (c \times A^{1/3})</th>
<th>Storage group 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type A premises</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NONE</td>
<td>24 ( \times A^{1/3} )</td>
<td>11 ( \times A^{1/3} )</td>
<td>16</td>
</tr>
<tr>
<td>LIMITED</td>
<td>16 ( \times A^{1/3} )</td>
<td>7 ( \times A^{1/3} )</td>
<td>10</td>
</tr>
<tr>
<td>EXTENSIVE</td>
<td>11 ( \times A^{1/3} )</td>
<td>4.5 ( \times A^{1/3} )</td>
<td>5</td>
</tr>
<tr>
<td>Type B premises</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>16 ( \times A^{1/3} )</td>
<td>7 ( \times A^{1/3} )</td>
<td>10</td>
</tr>
<tr>
<td>LIMITED</td>
<td>11 ( \times A^{1/3} )</td>
<td>4.5 ( \times A^{1/3} )</td>
<td>5</td>
</tr>
<tr>
<td>EXTENSIVE</td>
<td>7 ( \times A^{1/3} )</td>
<td>3 ( \times A^{1/3} )</td>
<td>0</td>
</tr>
</tbody>
</table>

* The minimum distance for storage groups 1 and 2 is always the same as the fixed distances of storage group 3

The safety provisions indicated in Table 7.1 are as follows:

NONE: the storage facility has no provisions other than the minimum required;

- a fluid-tight floor/pit.

LIMITED: the storage facility is fitted with a limited number of safety measures:

- a fluid-tight floor/pit and;
- one of the fire fighting methods described in 5.6, 5.7 or 5.8.

EXTENSIVE (not in the direction of the discharge opening): the storage facility is fitted with extensive safety measures, namely:

- a fluid-tight floor/pit and;
- one of the fire fighting methods described in 5.6, 5.7 or 5.8 and;
- walls that in accordance with NEN 6069 are fire-resistant for at least 60 min, except for the emergency relief vent and;
- an emergency relief vent that in accordance with NEN 6069 is fire-resistant for at least 30 min;
- the storage facility shall be able to withstand a positive static internal pressure that is higher than the opening pressure of the emergency relief vent.

EXTENSIVE (in the direction of the discharge opening):

- the storage facility is fitted with extensive safety measures as listed above for ‘EXTENSIVE’ and;
- the walls of the premises that are exposed to danger facing the emergency relief vent, within the safety distances are fire-resistant for at least 60 min, in accordance with NEN 6069.

The distances indicated in Table 7.1 are given in Figure 7.3 and Figure 7.4 as a function of floor area or quantity of product stored. An example of the application of these rules is given in Figure 7.1.
Figure 7.1 - Safety distances (based on heat load) to Type A premises for 10 000 kg of organic peroxides from storage group 2 in a storage facility with extensive safety provisions, where the doors serve as an emergency relief vent

In some cases the safety distances may be reduced to zero e.g. if a fire-resistant wall can protect the premises sufficiently and the premises meet certain requirements. The required facilities are:

– the fire-resistant wall between the storage facility and the premises exposed to danger shall be fire-resistant for 120 min, 90 min and 60 min in accordance with NEN 6069 for organic peroxides from respectively storage group 1, storage group 2 and storage group 3. The fire-resistant part of the wall shall extend vertically to the roof of the highest building and horizontally over a distance equal to the width of the premises exposed to danger, but a bigger distance than according to
Table 7.1 designation ‘EXTENSIVE’ is not required, and:

− the action taken for the storage facility meets the criteria for ‘EXTENSIVE’, provided an automatic fire fighting system is installed;
− the roof of the endangered premises within the safety zone is fire-resistant for at least 30 minutes, and;
− for Type A premises the emergency relief vent shall be fitted in the opposite direction of the endangered premises;
− for Type B premises the emergency relief vent may not face the endangered premises.

Note:
It is difficult to give precise guidelines for reduction to 0 m, as additional safety provisions shall be geared to the local situation in consultation between the company, the competent authority and any experts. Instead of a fire-resistant wall it is also possible to make the premises of material that meets the same requirements. An example of this is given in Figure 7.2.

Key
A  Safety zone
B  Fire-retaining wall
C  Distance as required in “EXTENSIVE”
D  Direction of emergency relief vent

Figure 7.2 - Example for reduction to 0 m
Figure 7.3 - Safety distances for peroxides of storage group 1
## Key to Figure 7.3

<table>
<thead>
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<th>Safety device</th>
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<th>Limited</th>
<th>Extensive</th>
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<td>Line A</td>
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<td>PREMISES A</td>
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</tr>
<tr>
<td>Line C</td>
<td>PREMISES B</td>
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</tr>
<tr>
<td>Line D</td>
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</table>
Figure 7.4 - Safety distances for peroxides of storage group 2
Key to Figure 7.4

<table>
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<th>Limited</th>
<th>Extensive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line A</td>
<td>PREMISES A</td>
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<tr>
<td>Line B</td>
<td>PREMISES B</td>
<td>PREMISES A</td>
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<tr>
<td>Line C</td>
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<td>PREMISES B</td>
<td>PREMISES A</td>
</tr>
<tr>
<td>Line D</td>
<td></td>
<td></td>
<td>PREMISES B</td>
</tr>
</tbody>
</table>
8 Use of organic peroxides

8.1 Logistics

8.1.1 Monitoring stores

reg 8.1.1 For the management and monitoring of stores for organic peroxides only well trained personnel are appointed. Each store has a supervisor.

8.1.2 Escape routes

reg 8.1.2 When storing organic peroxides escape routes may not be blocked.

8.1.3 Stock

reg 8.1.3 A consignment of organic peroxides shall be unloaded as soon as possible after arrival and stored in the right way.

reg 8.1.4 Before unloading the organic peroxides in refrigerated vehicles first the temperature in the space in which the material has been transported shall be checked. This temperature shall be recorded in the stock records together with the name of the organic peroxides, the lot number, the date of receipt, and the name of the supplier.

reg 8.1.5 If the temperature measured is above the emergency temperature, the consignment may not be unloaded and the responsible management of the supplier shall be informed. The truck with which the freight has been transported shall then be taken to a pre-determined place that is deemed to be safe, while awaiting the decision of the responsible management. The responsible management will in consultation with the supplier decide on the ultimate destination of the organic peroxide lot (see also 9.1).

reg 8.1.6 If the temperature in the refrigerated truck is between the control and the emergency temperature, the organic peroxide may be unloaded, on condition that the lot continues to be monitored until the control temperature is reached. Refrigerated organic peroxides shall always be unloaded such that their heating by contact with the ambient air and/or another heat source remains limited to a minimum (e.g. to less than 30 min).

reg 8.1.7 Damaged packages that leak, or run a great risk of doing so, may not be stored in the store. The contents of such packages shall be transferred to a package or catch tray and used immediately. Spilled material shall be destroyed. See 8.1.4.
To prevent deterioration in quality in case of storage of organic peroxides it is recommended that the first in – first out principle (FIFO) is used.

8.1.4 Disposal

The disposal of waste (and therefore also of organic peroxides) is regulated in the Environmental Management Act. An establishment may not process or destroy waste itself unless it has been granted a waste permit for this. No supplementary regulations are therefore included for this.

Note:
The user may in consultation with the supplier of the organic peroxides destroy the organic peroxides himself by dilution or chemical destruction.

Empty organic peroxide packages shall be treated as hazardous waste until they have been cleaned. They shall be stored in a suitable place for this on the site.

8.1.5 Stock records

If more than 2 500 kg of hazardous substances are stored in an establishment, an up-to-date log book of the storage of hazardous substances present in the establishment shall be kept.

The log book shall be dated.

The log book shall be available for inspection in the establishment in a place that is directly accessible for the emergency services.

The log book shall include at least the following parts:
- the correct transport name, supplemented, where applicable, with the technical name (see 3.1.2 ADR/IMDG code) and the class of the substance as indicated in the ADR or the IMDG code;
- the quantity of the substance;
- the packaging group (if assigned);
- the UN number of the substance as well as the model numbers of the hazard label(s) according to Article 5.2 of ADR;
- CMR substances shall be entered in the log book with their chemical name and the indication CMR.

The log book shall also include a current drawing indicating the following:
- the structure of the establishment;
- the location of the buildings and the activities to be distinguished;
- the location where the hazardous substances are stored;
- a north-pointing arrow.
The log book shall contain instructions with the names and telephone numbers of people whom the emergency services can contact in case of an emergency.

Note:
The purpose of the log book is in case of an emergency to give the emergency services an idea of the type, quantity and location of hazardous substances stored. The above-mentioned regulations are an example (e.g. for the transport sector) of the way in which the log book obligation can be included in a permit. If e.g. in an establishment more than 2 500 kg of hazardous substances are present, but these are only stored in cabinets, it is not sensible to demand the data mentioned in the regulations in the log book for each cabinet.

The following points for attention can be mentioned for formulating the log book obligation:
- if tank containers are present in the establishment this shall also be indicated in the log book;
- if several storage facilities each with a capacity of more than 10 tonnes are present within the establishment, for each storage facility the hazard classes present in each storage facility should be indicated;
- in consultation with the local fire service or the Competent authority for Wabo (Environmental Permitting (General Provisions) Act) another form of the log book may be chosen;
- establishments that fall under Brzo 1999 and have a safety report (SR) obligation, are already obliged to keep a list of substances; the advice is to refer to this in the environmental permit and not to demand a separate log book;
- the obligation to keep a log book applies above a quantity of 2 500 kg of hazardous substances per establishment; it may however be desirable also to specify a log book for smaller storage quantities, e.g. where very toxic substances are stored or the establishment is in the vicinity of vulnerable zones or surface water;
- by recording the model numbers of a hazard label according to Clause 5.2 of ADR in the log book all the relevant hazards of a substance are known (e.g. a class 3 with additional hazard 6.1, 3 + 6.1 shall then be indicated);
- if ADR class, UN number, packaging group and quantity of the hazardous substances stored do not change frequently (not a transport-related establishment) a one-off list of the maximum storage (e.g. the hazardous substance list from the environmental permit application), the type of hazardous substance and the storage location (e.g. a drawing) may possibly be enough. If in a storage facility substances change drastically daily as regards type and quantity, the log book shall be updated daily;
- if an up-to-date internal emergency plan is present and available for the emergency services, it is not necessary to include a drawing and personal data in the log book.

8.1.6 Spillage, leakage and destruction

Packages that contain organic peroxides shall be inspected at least once a week. Leaking, bulging packages shall be removed or rendered harmless as soon as possible.

Note:
‘Harmless’ means: dilution or neutralisation and then disposal as waste. Incineration is only an option if the establishment has a waste permit for this, see Subclause 8.1.4.

A stock of non-flammable material such as vermiculite, kiezelguhr or sand shall always be ready on site to absorb any spillages, which shall immediately be cleared up. Everything shall be done to prevent spillages from contaminating drainage or other water discharge systems. Materials such as old rags, sawdust or paper may not be used.
reg 8.1.18 Spilled organic peroxide and materials soaked with organic peroxide shall be removed without delay and shall be disposed of for destruction in a package suitably and correctly labelled for this purpose. Where necessary, contaminated premises shall be cleaned with water. If the quantity needed is less than the contents of the supply package, the remainder shall be prevented from coming into contact with incompatible materials and combustible substances.

reg 8.1.19 When transferring liquid organic peroxides any spillage shall be collected. Any organic peroxide remaining shall be returned to the stores for this purpose.

8.2 Hygiene and good housekeeping

8.2.1 General

reg 8.2.1 The employer lays down rules and procedures for handling organic peroxides, cleaning the workplace and personal hygiene which employees shall comply with. The employer shall ensure compliance with these procedures and rules.

reg 8.2.2 The employer sets up facilities and provides equipment (work clothing) to employees for optimum hygiene in places where hazardous substances are present.

reg 8.2.3 If organic peroxides are present in the workplace, the greatest possible care and tidiness should be observed and there shall be good-housekeeping.

reg 8.2.4 Work and storage facilities are kept as clean as possible. In work and storage facilities smoking, eating and drinking is prohibited and no food shall be stored.

8.2.2 Instrumentation and inspections

reg 8.2.5 All instruments used for normal operation and for emergencies shall be inspected at regular intervals. These inspections are recorded in a log book. Items for inspections include:

- temperature meters;
- alarm set points;
- cooling system;
- fire extinguishing systems.

For the inspections and maintenance schedules the suppliers’ recommendations shall be followed.
8.2.3 Maintenance and repair

**reg 8.2.6** Before maintenance and repair work may be carried out in a room where organic peroxides are located, a work permit shall be issued for this by a competent person in which the order, working conditions and the required safety measures are specified.

**reg 8.2.7** The person competent for this shall only sign the permit when he has inspected the working conditions for safety. The maintenance personnel shall receive instructions regarding the required safety aspects.

**Note:**
*The supervisor of the store (see reg 8.1.1) is authorised after inspection to sign and to issue the work permit referred to.*
9 Internal emergency plan

9.1 Internal emergency plan

reg 9.1.1 If more than 10 000 kg of unrefrigerated organic peroxides are stored in the establishment, an up-to-date internal emergency plan shall be present in the establishment, in which the organisational and technical action to deal with any reasonably expected accident or incident are described. The emergency plan shall among other things include a list of telephone numbers for use in case of incidents.

reg 9.1.2 At least once every three years the internal emergency plan shall be assessed, checked and if necessary amended. The assessment shall take into account changes that have occurred in the establishment, and new knowledge and understanding.

Note: If an internal emergency plan as referred to in Article 22 of Brzo '99 is drawn up or an emergency plan according to the supplementary risk assessment (ARIE), the regulations reg 9.1.1 and reg 9.1.2 are met. The frequency for assessment and checking is in accordance with the Brzo '99.

reg 9.1.3 An internal emergency plan shall be drawn up that is activated when the cooling system fails.

Note: In this action plan e.g. the following points may be specified:

− the employees who must be informed in case of an alarm;
− the temperature rise per unit time that can be expected in the store after failure of the cooling equipment;
− where and how assistance can be obtained for the repair of the cooling unit;
− where dry ice can be obtained to keep the temperature below a certain level if the cooling unit is out of action for long;
− whether water can be used as an emergency coolant (e.g. for an a emergency storage temperature > 15°C);
− whether it is possible in case of power failure to switch over to an emergency power supply and how this shall be handled;
− whether it is possible to transfer organic peroxides to another cold room, and where this facility is located;
− the procedure for access to the storage facility after rectification of the situation (e.g. with a view to increased flammability, oxygen shortage, or toxicity in the storage facility).

See also the note on reg 9.2.2.
9.2 Fire fighting

**reg 9.2.1** Fire fighting equipment shall be present in all places where organic peroxides are stored or processed. This equipment shall be within reach to fight a fire at the earliest stage.

**reg 9.2.2** All employees involved in the storage of organic peroxides shall be trained in the use of small fire extinguishers.

*Note:* A very small peroxide fire can be extinguished with CO₂, on the other hand foam, powder and water are also suitable for this purpose. Because of its cooling effect for bigger fires only water is suitable.

The decomposition of organic peroxides takes place without oxygen. Keeping out oxygen in case of a fire with organic peroxides therefore has no effect.

A big peroxide fire can best be fought with water with which extinguishing is carried out from a safe distance. In addition use of a water mist, when possible, is very effective.

See 5.6, 5.7 and 5.8 for recommended fire extinguishing systems.

The following aspects relating to fire and fire fighting may form part of the internal emergency plan, see 9.1:

- If a fire occurs in the vicinity of a stock of organic peroxides that cannot be removed, this shall be constantly dampened with water because of the cooling effect.
- In case of a large scale peroxide fire the fire service personnel shall be protected from potential thermal explosions and sudden ejection of burning peroxide. Personnel and fire fighting equipment shall be stationed at a safe distance from the fire.
- After extinguishing the fire copious quantities of water shall be used to ensure the remains of the fire are cooled to prevent the unburned organic peroxides from reigniting.

9.3 First Aid

Organic peroxides are corrosive to the skin and mucous membranes, and may seriously damage the eyes in case of direct contact (see 2.5).

**reg 9.3.1** In places where organic peroxides are stored or processed, facilities shall be present to thoroughly clean the skin and eyes.

Unless otherwise indicated, in case of an accident the following actions may be carried out by anyone, whether or not trained in first aid:

**Skin:**

- rinse with copious quantities of cold water;
- in case of burns on the skin, rinse continuously for 15 min with cold water;
- immediately remove items of contaminated clothing; avoid contact with the skin (immerse items of clothing in water to prevent spontaneous combustion);
- cover burned skin with sterile gauze;
- consult a doctor.
Eyes:
- rinse immediately with tepid, slowly running water. Keep the eyes open while doing this. Do this continuously for at least 15 min;
- cover severe eye injuries with sterile material;
- immediately consult an eye doctor.

If swallowed:
- rinse out the mouth cavity well;
- give copious quantities of water to drink (do not induce vomiting);
- consult a doctor.

Inhalation:
- in case of symptoms of irritation of the respiratory tract and the lungs (coughing, shortness of breath), allow the patient to rest in a semi-upright position;
- give 8 l to 10 l oxygen per min (only by trained personnel!);
- consult a doctor.
10 Security aspects for the storage of organic peroxides

10.1 People

reg 10.1.1 People involved in the storage of organic peroxides shall be aware of aspects relating to security. This means in any case:

- that no product is supplied to customers whose name and address is not known;
- that suspect transactions, that is situations where abnormalities are found in purchase, sale, transfer, storage or disposal, are reported to the local police.

10.2 Storage

reg 10.2.1 The site, on which the organic peroxides stores are located, or the organic peroxide stores themselves shall be adequately secured against entry by unauthorised people. This requirement is met if the site as a whole is adequately protected by walls (buildings), fences, ditches of sufficient width and so on. If this is not the case the (part of the) site (intended for storage) shall be protected by at least 1.8 m high fencing or netting of a durable material.

reg 10.2.2 Entry doors to the storage facilities and any entry gate shall be locked after business hours.

10.3 Organization

reg 10.3.1 After closing time the site may not be freely accessible.

reg 10.3.2 Unusual and suspect transactions or incidents shall be recorded in a log book.

reg 10.3.3 Unmanned buildings where organic peroxides are stored shall be regularly inspected for damage by burglary, with a minimum frequency of once a week. This regular inspection shall be recorded in a log book.

reg 10.3.4 In case of theft of product this shall be reported to the police.
Annexes
Annex A Terms and definitions

A.1 Abbreviations

ARIE
Aanvullende Risico Inventarisatie & Evaluatie (Supplementary Risk Assessment)

Bevi
Besluit externe veiligheid inrichtingen (External Safety (Establishments) Decree)

Brzo '99
Besluit risico's zware ongevallen 1999 (Major Accidents Risks Decree 1999)

FIFO
First in first out, see ‘Stock rotation’

IBC
Intermediate Bulk Container

OP
Organic peroxide

SADT
Self-accelerating decomposition temperature

Tc
Control temperature, see also A.2 for the definition

Te
Emergency temperature, see also A.2 for the definition

Wabo
Wet algemene bepalingen omgevingsrecht (General provisions for the Environment Act)

A.2 Definitions

Active oxygen content
The relative number of peroxy groups in the molecule as defined in 3.7

Air (circulation of)
Internal air flow without supply of outside air (see 5.2)

Air (ventilation of)
Constant air supply and disposal in store (see 5.2)

Burning area
Total area available for leaking organic peroxide (= floor area) (see 2.4)

Retention pit
Retention pit for organic peroxides and extinguishing water, to prevent spreading of the fire and environmental pollution
Cavitation
Occurrence of in particular small air bubbles in a liquid that may arise during transport (shaking) or during processing (stirring, pumping). Such small air bubbles may make the liquid more sensitive. A cavitated liquid may under the effect of an impact or shock explode sooner than a non-cavitated liquid.

Cooling plant
Installation that removes heat from a room or process equipment.

Control temperature (Tc)
The maximum, controlled temperature at which an organic peroxide may be stored. This temperature is derived from the SADT (see ref [17] Subclause 7.1.5.3.1.2).

Daily stock storage unit
See 5.8

Decomposition
Reaction in which a molecule is split into two or more smaller molecules.

Deflagration
Heterogeneous decomposition of a reactive material, propagated by a reaction front and where the speed of the reaction front is lower than that of sound in the material. No oxygen is needed for the decomposition of a peroxide. The driving force of the reaction front is heat transfer.

Detonation
Heterogeneous decomposition of a reactive material, propagated by a reaction front and where the speed of the reaction front is generally higher than that of sound in the material. No oxygen is needed for this decomposition. The driving force of the reaction front is a shock wave.

Dosing vessel
Vessel that is used for addition of organic peroxide to the reaction vessel or the processing equipment (see 6.3). An IBC may also be used as a dosing vessel. Organic peroxide in the original transport package (30 l drums and/or jerry cans, whether or not with a pump) that are used on the shop floor, do not fall under the term dosing vessels.

Effect distance = Safety distance
The distance that is required between the storage facility and surrounding premises, see Subclause 7.4.

Emergency temperature (Te)
Temperature at which emergency procedures shall be activated. This temperature is derived from the SADT (see ref [17] 7.1.5.3.1.2).

Exothermic reaction
Reaction that generates heat during conversion (see 2.2)

Fire-resistant
Resistance to fire of a structural part of a building, determined in accordance with NEN 6069.

Flash point
Lowest temperature at which a vapour that is in equilibrium with a liquid can be ignited by means of an external ignition source (spark, flame).

Freezer cabinet
Storage facility within which the temperature is kept below 0°C.
Hazard
Chemical or physical state that may cause damage to people, goods and the environment

Hazard statement
Phrases that indicate the nature of the hazard, see Annex E

H phrases
See “Hazard statement”

Intermediate Bulk Container (IBC)
An IBC is regarded as a package and with regard to the storage of organic peroxides, Clauses 1 to 5 of this PGS publication therefore apply to it. In specific situations mentioned an IBC may also be used as a dosing vessel, see for this 6.3

Lower flammability or explosion limit (LFL of LEL)
Lowest concentration of a gas or vapour in air where the vapour/air mixture may be ignited with the help of an ignition source (spark, flame)

Non-flammable
Non-flammable material determined in accordance with NEN 6064

Operational stock
See 5.8

Organic peroxide
Organic substance with a molecular structure characterised by an O-O-peroxy bond

P phrases
Phrases that indicate the nature of the precautionary measures to be taken, see Annex E

Precautionary measures
P phrases from CLP regulations

Risk
The degree of economic and personal damage measured by the chance and extent of this damage

Risk phrase (R phrase)
A specification of the potential hazard of the chemical in question

Runaway reaction
Reaction that accelerates uncontrollably and may lead to a big increase in temperature and pressure. In the confined state (e.g. in a reactor or tank with insufficient emergency relief capacity) a runaway reaction may lead to a physical explosion where fragments are ejected

Safety distance = Effect distance
Distance that is required between the storage facility and surrounding premises, see Subclause 7.4

Safety phrase (S phrase)
Phrase that gives advice on the way to handle chemicals to prevent accidents

Self-accelerating decomposition
Decomposition that accelerates as a function of temperature and/or decomposition conversion
**Self-accelerating decomposition temperature (SADT)**
Lowest temperature at which the organic peroxide as packaged may start self-accelerating decomposition

**Spontaneous ignition temperature**
Lowest ambient temperature at which a solid, liquid or gas spontaneously ignites, that is without an external ignition source

**Stock rotation**
Putting into stock and removal from stock according to the FIFO principle

**Storage group**
Division of organic peroxides into five groups with a view to the hazard during storage (see 3.4)

**Upper flammability or explosion limit (UFL of UEL)**
Highest concentration of a gas or vapour in air where the vapour/air mixture may be ignited with the help of an ignition source (spark, flame)

**(Emergency) vent opening**
Part of a building e.g. door or panel, that provides for the discharge of excessive quantities of gases and/or liquids, with sufficient capacity to keep the pressure sufficiently low
Annex B Standards

i. NEN-EN 671, Vaste brandblusinstallaties – Brandslangsystemen (Fixed fire fighting systems – Hose systems) (part 1 to 3)


iii. NEN 2559, Onderhoud van draagbare blustoestellen (Maintenance of portable fire extinguishers) (including 2001/A3:2009)

iv. NEN 6064, Bepaling van de onbrandbaarheid van bouwmaterialen (Determination of the non-combustibility of building materials) (including 1991/A2:2001)

v. NEN 6068, Bepaling van de weerstand tegen branddoorslag en brandoverslag tussen ruimten (Determination of the resistance to fire movement between spaces)

vi. NEN 6069, Experimentele bepaling van de brandwerendheid van bouwdelen en bouwproducten en het classificeren daarvan (Experimental determination of the fire-resistance of building parts and building products and their classification) (including 2005/A1:2005)

vii. NEN 6071, TGB standard, Rekenkundige bepaling van de brandwerendheid van bouwdelen – Betonconstructies (Determination by calculation of the fire resistance of building elements – Concrete structure), withdrawn

viii. NEN 6072, TGB standard, Rekenkundige bepaling van de brandwerendheid van bouwdelen – Staalconstructies (Determination by calculation of the fire resistance of building elements – Steel structures), withdrawn

ix. NEN 6073, TGB standard, Rekenkundige bepaling van de brandwerendheid van bouwdelen – Houtconstructies (Determination by calculation of the fire resistance of building elements – Timber structures), withdrawn

x. NEN-EN-IEC 62305, Bliksembeveiliging (Protection against lightning) (2006)

## Annex C  List of relevant organic peroxides

**Key to Table C.1:**

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage group</td>
<td>The group in which the peroxide is classed according to 3.4</td>
</tr>
<tr>
<td>Organic peroxide</td>
<td>The chemical name of the peroxide</td>
</tr>
<tr>
<td>Concentration</td>
<td>The minimum and/or maximum concentration of the peroxide</td>
</tr>
<tr>
<td>Diluent type A</td>
<td>The concentration of the diluent as defined in the transport legislation:</td>
</tr>
<tr>
<td></td>
<td>organic liquid that is inert with respect to the peroxide and has a boiling</td>
</tr>
<tr>
<td></td>
<td>point of at least 150°C. Diluents of type A may be used for desensitisation</td>
</tr>
<tr>
<td></td>
<td>of all organic peroxides</td>
</tr>
<tr>
<td>Diluent type B</td>
<td>The concentration of the diluent as defined in the transport legislation:</td>
</tr>
<tr>
<td></td>
<td>organic liquid that is inert with respect to the peroxide and has a boiling</td>
</tr>
<tr>
<td></td>
<td>point below 150°C but not below 60°C and has a flash point of at least 5°C</td>
</tr>
<tr>
<td>Inert solid</td>
<td>Organic or inorganic solid that is used for the desensitisation of</td>
</tr>
<tr>
<td></td>
<td>organic peroxides on condition that it is inert</td>
</tr>
<tr>
<td>Water</td>
<td>The water concentration</td>
</tr>
<tr>
<td>Packing method</td>
<td>Maximum size of the package as defined in the transport legislation</td>
</tr>
<tr>
<td>Control temperature</td>
<td>Maximum storage temperature</td>
</tr>
<tr>
<td>Emergency temperature</td>
<td>Maximum temperature at which the alarm is actuated</td>
</tr>
<tr>
<td>Number – Generic Entry</td>
<td>Number indicated in the transport legislation that specifies:</td>
</tr>
<tr>
<td></td>
<td>• type of organic peroxide (B to F)</td>
</tr>
<tr>
<td></td>
<td>• physical state (liquid/solid)</td>
</tr>
<tr>
<td></td>
<td>• temperature control (if applicable)</td>
</tr>
<tr>
<td>Remarks</td>
<td>Supplementary requirements and secondary risks which apply</td>
</tr>
<tr>
<td></td>
<td>for the relevant product.</td>
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<tr>
<td>Storage group/opslaggroep</td>
<td>ORGANIC PEROXIDE</td>
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<td>------------------------------------------------------------</td>
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<tr>
<td>2</td>
<td>ACETYL ACETONE PEROXIDE</td>
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<tr>
<td>3</td>
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<tr>
<td>1</td>
<td>ACETYL CYCLOHEXANESULPHONYL PEROXIDE</td>
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<tr>
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<td>tert-AMYL HYDROPEROXIDE</td>
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<td>tert-AMYL PEROXYBENZOATE</td>
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<tr>
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</tr>
<tr>
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<td>tert-BUTYL CUMYL PEROXIDE</td>
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<td>2</td>
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<td>tert-BUTYL-4,4-DI-(tert-BUTYLPEROXY)VALERATE</td>
</tr>
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<td>tert-BUTYL HYDROPEROXIDE</td>
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<tr>
<td>Storage group/opslaggroep</td>
<td>ORGANIC PEROXIDE</td>
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<td>3</td>
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<tr>
<td>Storage group/opslaggroep</td>
<td>ORGANIC PEROXIDE</td>
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<td>tert-BUTYL PEROXY-2-ETHYLHEXANOATE + 2, 2-Di-(tert-BUTYLPEROXY)BUTANE</td>
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<td>([3R-{3R,5aS,6S,8aS,9R,10R,12S,12aR**}] - Decahydro-10-methoxy-3,6,9-trimethyl-3,12-epoxy-12H-pyrano[4,3-j]-1,2-benzodioxepin)</td>
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**Emergency temperature (°C)**

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<td>≤ 35</td>
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**Control temperature (°C)**

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<td>≤ 52</td>
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**Water (%)**

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**Inert solid (%)**

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**Diluent type A (%)**

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**Diluent type B (%)**

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**Packing Method**

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**Number (Generic entry)**

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**Storage group/ opslaggroep**

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<td>Diluent type A (%)</td>
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<td>≤ 72</td>
<td>&gt; 42 - 52</td>
<td>≥ 48</td>
<td>≥ 13</td>
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<td>DI-(2-ETHYLHEXYL) PEROXYDICARBONATE</td>
<td>&gt; 77 - 100</td>
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<td>OP5</td>
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<td>2</td>
<td>*</td>
<td>≤ 77</td>
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</tr>
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<td>3</td>
<td>*</td>
<td>≤ 62 as a stable dispersion in water</td>
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<td>OP8</td>
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<td>*</td>
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<td>Diluent type B 1 (%)</td>
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<td>Water (%)</td>
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<td>≤ 32</td>
<td>≥ 68</td>
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<td>≤ 52</td>
<td>≥ 48</td>
<td></td>
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<tr>
<td>2</td>
<td></td>
<td>*</td>
<td>≤ 32</td>
<td>≥ 68</td>
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<td>DILAUROYL PEROXIDE</td>
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<td>4</td>
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<td>≤ 42 as a stable dispersion in water</td>
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<td>≥ 48</td>
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<td>≤ 20 + ≤ 18 + ≤ 4</td>
<td>≥ 58</td>
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<td>Water (%)</td>
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<td></td>
<td></td>
<td>≥ 18</td>
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<td></td>
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<td>3</td>
<td>&quot;</td>
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<td>≥ 48</td>
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<td>≤ 47 as a paste</td>
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<td>≥ 14</td>
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<td>Diluent type B (%)</td>
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<td>Water (%)</td>
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<td>4</td>
<td></td>
<td>≤ 42 as a stable dispersion in water</td>
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<td>≥ 48</td>
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<td>DI-n-NONANOYL PEROXIDE</td>
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<td>≤ 85</td>
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<td>DI-(3,5,5-TRIMETHYLHEXANOYL) PEROXIDE</td>
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<td>&gt; 52-82</td>
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<td></td>
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<td>≤ 38</td>
<td>≥ 62</td>
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<td>≤ 67</td>
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<td>Concentration (%)</td>
<td>Diluent type A (%)</td>
<td>Diluent type B (%)</td>
<td>Inert solid (%)</td>
<td>Water (%)</td>
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<td>2</td>
<td>*</td>
<td>≤ 77</td>
<td>≥ 23</td>
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<tr>
<td>2</td>
<td>*</td>
<td>≤ 52</td>
<td>≥ 48</td>
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<td>≥ 45</td>
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<td>≥ 23</td>
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<tr>
<td>2</td>
<td>*</td>
<td>≤ 52</td>
<td>≥ 48</td>
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<td>4</td>
<td>*</td>
<td>≤ 52 as a stable dispersion in water</td>
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<td>ISOPROPYL sec-BUTYL PEROXYDICARBONATE + Di-sec-BUTYL PEROXYDICARBONATE + Di-ISOPROPYL PEROXYDICARBONATE</td>
<td>≤ 32 + ≤ 15 - 18 ≤ 12 - 15</td>
<td>≥ 38</td>
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<tr>
<td>1</td>
<td>*</td>
<td>≤ 52 + ≤ 28 + ≤ 22</td>
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<td>ISOPROPYLCUMYL HYDROPEROXIDE</td>
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<tr>
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<td>*</td>
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<td>≥ 28</td>
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<td>METHYLCYCLOHEXANONE PEROXIDE(S)</td>
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<td>Concentration (%)</td>
<td>Diluent type A (%)</td>
<td>Diluent type B (1) (%)</td>
<td>Inert solid (%)</td>
<td>Water (%)</td>
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<td>*</td>
<td></td>
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<td>≥ 55</td>
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<td>*</td>
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<td>METHYL ISOPROPYL KETONE PEROXIDE(S)</td>
<td>See remark 31)</td>
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<td>PEROXYLAURIC ACID</td>
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<td>*</td>
<td>≤ 56</td>
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<td>≥ 44</td>
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<td>POLYETHER POLY-tert-BUTYLPEROXYCARBONATE</td>
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<td>≥ 48</td>
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<td>1,1,3,3-TETRAMETHYLBUTYL HYDROPEROXIDE</td>
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<td>Concentration (%)</td>
<td>Diluent type A (%)</td>
<td>Diluent type B 1 (%)</td>
<td>Inert solid (%)</td>
<td>Water (%)</td>
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<td>≤ 72</td>
<td>≥ 28</td>
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<td>3</td>
<td>*</td>
<td>≤ 52 as a stable dispersion in water</td>
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<td>2</td>
<td>1,1,3,3-TETRAMETHYLBUTYL PEROXYPIVALATE</td>
<td>≤ 77</td>
<td>≥ 23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3,6,9-TRIETHYL-3,6,9-TRIMETHYL-1,4,7 TRIPEROXONANE</td>
<td>≤ 42</td>
<td>≥ 58</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>*</td>
<td>≤17</td>
<td>≥ 18</td>
<td>≥65</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) Diluent type B may always be replaced by type A. The boiling point of diluent type B shall be at least 60 °C higher than the SADT of the organic peroxide.
2) Active oxygen content ≤ 4,7 %
3) Requires the additional risk label EXPLOSIVE (model no. 1; see 5.2.2.2.2).
4) Diluent may be replaced by di-tert-butyl peroxide.
5) Active oxygen content ≤ 9 %
6) With ≤ 9 % hydrogen peroxide; active oxygen content ≤ 10 %
7) Only non-metal packages permitted.
8) Active oxygen content > 10 % and ≤ 10,7 %, with or without water.
9) Active oxygen content ≤ 10 %, with or without water.
10) Active oxygen content ≤ 8,2 %, with or without water.
11) See 2.5.3.2.5.1
12) Up to 2 000 kg per tank classed as ORGANIC PEROXIDE TYPE F based on large scale tests.
13) Requires the label with the statement CORROSIVE (model no. 8; see 5.2.2.2.2).
14) Peroxyacetic acid formulations that meet the criteria of 2.5.3.3.2 (d)
15) Peroxyacetic acid formulations that meet the criteria of 2.5.3.3.2 (e)
16) Peroxyacetic acid formulations that meet the criteria of 2.5.3.3.2 (f)
17) Addition of water to this organic peroxide will reduce the thermal stability
18) For concentrations below 80 % a label with the statement CORROSIVE is not required
19) Mixtures with hydrogen peroxide, water and acid(s)
20) With diluent A, with or without water
21) With ≥25 wt % diluent type A in addition to ethyl benzene
22) With ≥19 wt % diluent type A in addition to methyl isobutyl ketone
23) With < 6% di-tert-butyl peroxide
24) With ≤8 % 1-isopropylhydroxyperoxi-4-isopropyl hydroxyl benzene
25) Diluent type B with a boiling point > 110 °C
26) Hydroperoxide content < 0.5 %
27) With CORROSIVE label if the concentration > 56% (model no. 8; see 5.2.2.2.2)
28) Active oxygen content ≤7.6% in diluent type A with a boiling point between 200 – 260 °C
29) Not subject to the requirements of the Regulation for class 5.2
30) Diluent type B with a boiling point > 130 °C
31) Active oxygen content ≤6.7 %
Table C.2 - Organic peroxides allowed for storage in tanks

<table>
<thead>
<tr>
<th>UN No</th>
<th>Substance</th>
<th>Control temperature [°C]</th>
<th>Emergency temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3109</td>
<td>Tert-Butyl hydroperoxide, not more than 72% with water&lt;sup&gt;2&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cumyl hydroperoxide, not more than 90% in diluent type A</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Di-tert-butyl peroxide, not more that 32% in diluent type A</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Isopropyl cumyl hydroperoxide, not more than 72% in diluent type A</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>p-Menthy hydroperoxide, not more than 56% in diluent type A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3110</td>
<td>Dicumylperoxide&lt;sup&gt;3&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3119</td>
<td>Tert-Amyl peroxyneodecanoate, not more than 47% in diluent type A</td>
<td>-10</td>
<td>-5</td>
</tr>
<tr>
<td></td>
<td>Tert-Butyl peroxyacetate, not more than 32% in diluent type B</td>
<td>+30</td>
<td>+35</td>
</tr>
<tr>
<td></td>
<td>Tert-Butyl peroxy-2-ethylhexanoate, not more than 32% in diluent type B</td>
<td>+15</td>
<td>+20</td>
</tr>
<tr>
<td></td>
<td>Tert-Butyl peroxypropionate, not more than 27% in diluent type B</td>
<td>+5</td>
<td>+10</td>
</tr>
<tr>
<td></td>
<td>Tert-Butyl peroxy-3,5,5-trimethyl-hexanoate, not more than 38% in diluent type A or type B</td>
<td>+35</td>
<td>+40</td>
</tr>
<tr>
<td></td>
<td>Di-(3,5,5-trimethyl hexanoyl) peroxyde, not more than 38% in diluent type A or type B</td>
<td>0</td>
<td>+5</td>
</tr>
<tr>
<td>3120</td>
<td>No peroxides listed yet</td>
<td>+30</td>
<td>+35</td>
</tr>
</tbody>
</table>

2 Provided that steps have been taken to achieve the safety equivalence of 65% tert-Butyl hydroperoxide and 35 % water.
3 Maximum quantity per portable tank 2 000 kg.
4 Formulations derived from distillation of peroxyacetic acid originating from peroxyacetic acid in concentration of not more than 41 % with water, total active oxygen (peroxyacetic acid + H₂O₂) ≤ 9,5 % which fulfils the criteria of 2.5.3.3.2 (f) of ref. [17].
<table>
<thead>
<tr>
<th>UN No</th>
<th>Substance</th>
<th>Type of IBC&lt;sup&gt;5&lt;/sup&gt;</th>
<th>Max. quantity [l]</th>
<th>Control temperature [°C]</th>
<th>Emergency temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3109</td>
<td>Ter-Butyl hydroperoxide, not more than 72% with water</td>
<td>31A</td>
<td>1250</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ter-Butyl peroxyacetate, not more than 325 in diluent type A</td>
<td>31A</td>
<td>1250</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>31HA1</td>
<td>1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ter-Butyl peroxybenzoate, not more than 32% in diluent type A</td>
<td>31A</td>
<td>1250</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ter-Butyl peroxy-3,5,5-trimethylhexanoate, not more than 37% in diluent type A</td>
<td>31A</td>
<td>1250</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>31HA1</td>
<td>1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cumyl hydroperoxide, not more than 90% in diluent type A</td>
<td>31HA1</td>
<td>1250</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dibenzoyl peroxide, not more than 42% as a stable dispersion</td>
<td>31H1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Di-tert-butyl peroxide, not more than 52% in diluent type A</td>
<td>31A</td>
<td>1250</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>31HA1</td>
<td>1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,1-Di-(tert-butylperoxy)cyclohexane, not more than 37% in diluent type A</td>
<td>31A</td>
<td>1250</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,1-Di-(tert-butylperoxy)cyclohexane, not more than 42% in diluent type A</td>
<td>31H1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Diarouylperoxide, not more than 42% as stable dispersion in water</td>
<td>31HA1</td>
<td>1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Isopropylocumyl hydroperoxide, not more than 72% in diluent type A</td>
<td>31HA1</td>
<td>1250</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>p-Menthyl hydroperoxide, not more than 72% in diluent type A</td>
<td>31HA1</td>
<td>1250</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Peroxyacetic acid, stabilized, not more than 17%</td>
<td>31H1</td>
<td>1500</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>31H2</td>
<td>1500</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>31HA1</td>
<td>1500</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>31A</td>
<td>1500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3110</td>
<td>Dicumyl peroxide</td>
<td>31A</td>
<td>2000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>31H</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>31HA1</td>
<td>2000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3119</td>
<td>Ter-Amyl peroxy-pivalate, not more than 32% in diluent type A</td>
<td>31A</td>
<td>1250</td>
<td>+10</td>
<td>+15</td>
</tr>
<tr>
<td></td>
<td>Ter-Butyl peroxy-2-ethylhexanoate, not more than 32% in diluent type B</td>
<td>31HA1</td>
<td>1000</td>
<td>+30</td>
<td>+35</td>
</tr>
<tr>
<td></td>
<td>Ter-Butyl peroxyneodecanoate, not more than 32% in diluent type A</td>
<td>31A</td>
<td>1250</td>
<td>+30</td>
<td>+35</td>
</tr>
</tbody>
</table>

<sup>5</sup> 31A – metal; 31HA1 – composite IBC with plastic inner receptacle, 31H1 – rigid plastic with structural equipment; 31H2 – rigid plastic, free standing
<table>
<thead>
<tr>
<th>UN No</th>
<th>Substance</th>
<th>Type of IBC</th>
<th>Max. quantity [l]</th>
<th>Control temperature [°C]</th>
<th>Emergency temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Tert-Butyl peroxyneodecanoate, not more than 42% stable dispersion in water</td>
<td>31A</td>
<td>1250</td>
<td>-5</td>
<td>+5</td>
</tr>
<tr>
<td>5</td>
<td>Tert-Butyl peroxyneodecanoate, not more than 52% stable dispersion in water</td>
<td>31A</td>
<td>1250</td>
<td>-5</td>
<td>+5</td>
</tr>
<tr>
<td></td>
<td>Tert-Butyl peroxypivalate, not more than 27% in diluent type B</td>
<td>31HA1</td>
<td>1000</td>
<td>+10</td>
<td>+15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31A</td>
<td>1250</td>
<td>+10</td>
<td>+15</td>
</tr>
<tr>
<td></td>
<td>Di-(2-neodecanoylperoxyisopropyl)benzene, not more than 42% stable dispersion in water</td>
<td>31A</td>
<td>1250</td>
<td>-15</td>
<td>-5</td>
</tr>
<tr>
<td></td>
<td>3-Hydroxy-1,1-dimethylbutyl peroxyneodecanoate, not more than 52% stable dispersion in water</td>
<td>31A</td>
<td>1250</td>
<td>-15</td>
<td>-5</td>
</tr>
<tr>
<td></td>
<td>Cumyl peroxyneodecanoate, not more than 52% stable dispersion in water</td>
<td>31A</td>
<td>1250</td>
<td>-15</td>
<td>-5</td>
</tr>
<tr>
<td></td>
<td>Di-(4-tert-butylcyclohexyl) peroxydicarbonate, not more than 42% stable dispersion in water</td>
<td>31HA1</td>
<td>1000</td>
<td>+30</td>
<td>+35</td>
</tr>
<tr>
<td></td>
<td>Dicetyl peroxydicarbonate, not more than 42% stable dispersion in water</td>
<td>31HA1</td>
<td>1000</td>
<td>+30</td>
<td>+35</td>
</tr>
<tr>
<td></td>
<td>Dicyclohexylperoxydicarbonate, not more than 42% stable dispersion in water</td>
<td>31A</td>
<td>1250</td>
<td>+10</td>
<td>+15</td>
</tr>
<tr>
<td></td>
<td>Di-(2-ethylhexyl) peroxydicarbonate, not more than 62% stable dispersion in water</td>
<td>31A</td>
<td>1250</td>
<td>-20</td>
<td>-10</td>
</tr>
<tr>
<td></td>
<td>Dimyristyl peroxydicarbonate, not more than 42% stable dispersion in water</td>
<td>31HA1</td>
<td>1000</td>
<td>+15</td>
<td>+20</td>
</tr>
<tr>
<td></td>
<td>Di-(3,5,5-trimethylhexanoyl) peroxydecanoate, not more than 38% in diluent type A</td>
<td>31HA1</td>
<td>1000</td>
<td>+10</td>
<td>+15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31A</td>
<td>1250</td>
<td>+10</td>
<td>+15</td>
</tr>
<tr>
<td></td>
<td>Di-(3,5,5-trimethylhexanoyl) peroxydecanoate, not more than 52% stable dispersion in water</td>
<td>31A</td>
<td>1250</td>
<td>+10</td>
<td>+15</td>
</tr>
<tr>
<td></td>
<td>1,1,3,3-Tetramethylbutyl peroxyneodecanoate, not more than 52% stable dispersion in water</td>
<td>31A</td>
<td>1250</td>
<td>-5</td>
<td>+5</td>
</tr>
<tr>
<td>3120</td>
<td>No peroxides listed yet</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Annex D  Labels

A – Transport labels

Transport labels - Class 5.2

Class 5.2 labels - both labels are permitted for organic peroxide formulations assigned to class 5.2

Transport labels - secondary risks

a - label for secondary explosiveness risk   b - label for secondary corrosivity risk

Transport label – marine pollutant
B - Use labels as required for GHS

a - Toxic
b - Toxic for the aquatic environment
c - Hazardous for public health
d - Corrosive
e - Explosive
f - Highly inflammable
g – Irritant or harmful if swallowed, inhaled, upon skin contact or contact with the eye
Annex E  List of H and P phrases

Organic peroxides shall be classified and labelled according to CLP regulations [4]. In addition to the hazard pictograms and the signal words the H phrases (hazard statement) and no more than six P phrases (precautionary measures), unless more are necessary to indicate the nature of the hazards, shall be included on the label.

<table>
<thead>
<tr>
<th>H phrases: hazard statement</th>
</tr>
</thead>
<tbody>
<tr>
<td>H240 Heating may cause an explosion hazard</td>
</tr>
<tr>
<td>H241 Heating may cause a fire or explosion</td>
</tr>
<tr>
<td>H242 Heating may cause a fire</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P phrases: precautionary measures prevention</th>
</tr>
</thead>
<tbody>
<tr>
<td>P210 Keep away from heat/sparks/open flame/hot surfaces – no smoking</td>
</tr>
<tr>
<td>P220 Keep store away from clothing / … / combustible materials</td>
</tr>
<tr>
<td>P234 Keep only in original package</td>
</tr>
<tr>
<td>P280 Wear protective gloves/protective clothing/eye protection/face protection.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P phrases: precautionary measures storage</th>
</tr>
</thead>
<tbody>
<tr>
<td>P411+P235 Store at temperatures not exceeding … °C. Keep cool</td>
</tr>
<tr>
<td>P410 Protect from sunlight</td>
</tr>
<tr>
<td>P420 Store away from other materials</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P phrases: disposal precautionary measures disposal</th>
</tr>
</thead>
<tbody>
<tr>
<td>P501 Dispose of contents/packages to …</td>
</tr>
</tbody>
</table>
Annex F  Burning rate test

Test for the classification into storage groups

The test methods to be used to determine the burning rate of 10 000 kg of product are described in the following subclauses. Subclause F1 describes the ‘large scale’ tests. These are used to determine the burning rate of all peroxide formulations. Subclause F2 describes a ‘small scale’ test for liquid peroxide. With the exception of boundary cases based on the small scale test the burning rate on a scale of 10 000 kg can be reasonably well approximated. Each of the two tests can be used as the basis for assignment to storage groups. The large scale test is decisive in case of doubt. However, if a burning rate below 1200 kg/min is used to calculate safety distances, for ‘type C’ peroxides from storage group 1 only the large scale test is used (25).

F1 Determination of burning rate by means of large scale testing

Test method

Introduction
The burning rate referred to in Clause 2 is defined as the burning rate of a mass of 10 000 kg. In practice this burning rate is determined using a stack of packages with a total mass of around 500 kg. Organic peroxide and the organic peroxide in a package shall be further referred to respectively as ‘the organic peroxide’ and ‘the package’.

The test may only be performed if the organic peroxide can neither detonate in the package nor in a stack of packages. The test is carried out to determine:

- the way in which the packages react in a fire;
- the effect of the total quantity of organic peroxide available on the burning rate of the packages;
- the degree of hazard for the immediate environment.

The test shall be performed such that the most unfavourable results are obtained. Tests shall be performed individually:

- on 1, 6 and 10 packages, with a maximum total weight of 500 kg and a maximum individual weight of 25 kg;
- 1, 3 and 6 packages, with a maximum total weight of 500 kg and packages varying in weight from 25 to 50 kg;
- or more packages, up to a maximum weight of 500 kg, with packages of more than 50 kg each.

The number of tests and, where necessary, the total test mass, shall be increased if the results and the corresponding risks cannot be properly determined.

Test description
The packages shall stand on wooden, level pallets, according to DIN 15146. The pallets shall stand in a catch tray (or two, if necessary). A catch tray shall provide at least enough room for one full pallet plus a clearance of 10 cm around the pallet.

In addition the volume of the tray shall be sufficient to contain the whole organic peroxide content.
On three sides of the seat of the fire a 1,6 m high wind screen shall be set up. Flammable material shall be placed under and around the packages such that the organic peroxide ignites as rapidly and as well as possible. The quantity and type of material shall be selected such that the:

- organic peroxide tested also actually ignites;
- the process of burning of the organic peroxide tested hardly intensifies\(^6\).

The radiation heat shall be measured during the test using the equipment intended for this in at least three places, each at a different distance from the seat of the fire. The distances shall:

- on the one hand be sufficiently large;
- on the other hand not be so great that the measurement equipment cannot pick up signals in all cases.

Equipment suitable for measuring the radiation includes e.g. thermo columns that determine absolute signals and that:

- have a linear sensitivity of 0,5 mm to 0,9 mm and within this measure with high precision;
- have radiation properties that closely correspond with those of a ‘black body’;
- have an active area of at least 0,25 cm\(^2\);
- have an angle of incidence that makes possible complete capture of the flame size of the organic peroxide tested at the detection distance;
- have a high heat insensitivity; that is they are compensated in such a way that the signal level is not affected by changes in the ambient temperature;
- have a detection range of radiation levels between 100 W/m\(^2\) and 300 W/m\(^2\), or a sensitivity of at least 1 V/W;
- have a good response time, or a response time of less than 100 ms (time-to-63,2 % level of the final signal value).

The signals shall be continuously recorded. The time at which the organic peroxide tested begins to react measurably is defined as the starting point of ignition. The end of the fire is read off from the radiation curves recorded. This point is characterised by a reduction in the radiation level \(I\) (as caused by the fire) to less than 5% of the maximum value \(I_{\text{max}}\) recorded.

Neither the effect of the remains nor that of the burning flammable materials, if present, are taken into account in the assessment.

The burning time \(\pi\) is the time between the starting point and the end point of the fire.

The burning rate \(BR\) (kg/min) shall be calculated for each lot tested \(m\) (kg) and the corresponding burning time \(\pi\) (min) according to the formula:

\[
BR = \frac{m}{\Pi}
\]

The percentage average radiation efficiency \(h\) at a distance from the seat of the fire shall be determined based on the radiation levels measured and the theoretical maximum energy.

\(^6\) A quantity of around 10 kg of dry wood wool is usually sufficient for 200 kg of highly flammable organic peroxide. For non-flammable organic peroxides thin wooden lathes can be used whether or not soaked in a liquid mixture of light heating oil (90 %) and light petroleum (10 %). The packages can also be sprinkled with flammable liquid.
The theoretical maximum energy is calculated by multiplying the individual mass of the organic peroxide tested (kg) by the combustion heat (kJ/kg). The quantity of energy that in practice appears to be transferred, is determined by integration of the area under the radiation curve, measured after this has where necessary been smoothed and corrected.

The average form factor \( f \) which shall be taken into account during the maximum fire intensity can be calculated with the formula:

\[
f = \frac{I_{\text{relevant}}}{I_{\text{calculated}}}
\]

For this a graph is plotted that shows the radiation level \((\text{kW/m}^2)\) as a function of time \( t \) (min).

The total radiation quantity is calculated by integration of the smoothed and corrected curve to 1-5% of the maximum radiation heat.

\( I_{\text{relevant}} \) is obtained from the maximum of the curve. \( I_{\text{calculated}} \) is calculated as an average radiation value by converting the integrated area into a rectangle that remains the same size over the same period of time.

**Test report**

The test report shall contain the following data:

- the formulation of the organic peroxide tested;
- the quantities of organic peroxide used for each test;
- the type and construction of each package;
- the test set up and, in particular, the type, quantities of ignition and starter materials, as well as the ignition products used;
- the test history, in particular the period up to the first reaction of the organic peroxide observed (incubation time), the duration and the burning behaviour of the reactions themselves (main burning stage and the complete burning time of the organic peroxide), as well as the complete conversion process;
- the effect of the reaction on the environment;
- the various burning rates \( BR \) and the corresponding quantities of organic peroxide \( m \), including a graphic representation;
- the weather conditions during testing;
- the radiation levels as measured at the different distances;
- the percentage average radiation efficiency \( h \) and the form factor \( f \).

The test report shall contain further illustrations of a package and of the stack of packages tested, as well as copies of the reports of the measured data. These reports shall also include the data that are important for the interpretation of the curves measured (the separating capacity of the instrument, calibration factors etc.).

**Assignment to a storage group**

In general the organic peroxide shall be assigned to the storage group that corresponds to the effects measured in the tests with the organic peroxide in packages. Experiences with other tests or even accidents may however also be taken into account.

Organic peroxide in packages cannot be assigned to a storage group if during the burning period the contents of the different packages explode at virtually the same time (in which case these are presumably organic peroxides of type A).
If, during the test, the packages do not explode at virtually the same time in the sense described in the previous paragraph, but on the other hand only individual explosions take place of which the frequency may increase over a long burning period, and if the surroundings are endangered by fragments and flames ejected in all directions, the organic peroxide shall then be assigned in its standard package to storage group 1 with a $BR_c$ value of 1200 kg/min.

The organic peroxide in packages may be assigned to storage groups 2, 3, 4 or 5 if the packages neither explode at virtually the same time, nor during the fire show individual explosion behaviour as described in the previous paragraphs, but on the other hand only burn more or less intensively, where separate parts of the package may be ejected from the hearth of the fire and end up elsewhere in the vicinity.

The assignment to storage groups 2, 3, 4 or 5 is carried out by burning rate. The criterion used for this is burning rate $BR_c$ of a quantity of 10 tonnes of organic peroxide. The burning rate $BR_c$ is calculated as follows: the burning rates $BR$ measured are plotted in a graph as a logarithmic function of the organic peroxide mass $m$ (In $BR$ against In $m$). The test results observed are extrapolated using this graph to an uncorrected burning rate $BR_{10t}$ for a mass of 10 000 kg, by applying the formula:

$$BR \propto m^{2/3}$$

The extrapolation can generally best be performed on the basis of the biggest test quantities. The value $BR_{10t}$ shall be corrected to the pure burning rate for a mass of 10 tonnes of organic peroxide ($BR_c$) using the formula:

$$BR_c = BR_{10t} \times \frac{H_v}{33500} \times \frac{h}{0.25} \times \frac{f}{2.78}$$

where:

$H_v$ is the heat of combustion of the organic peroxide (kJ/kg) (that is the reaction enthalpy of the combustion reaction);

$BR_c$ is the burning rate as specified in 3.4;

$BR_c$ is used for the assignment to storage groups as indicated in Table 3.3. The assignment must be approved by the competent body based on the test results and can ultimately be indicated in the Annex to PGS 8. In the Netherlands the Ministry of Social Affairs and Employment is the competent authority.

**F2 Small scale laboratory test**

**Test method**

**Introduction**

The rate at which a liquid peroxide burns is tested on a laboratory scale. The burning rate is determined by measuring the weight loss of the burning peroxide sample as a function of time. During measurement the surface area that burns remains the same. The quotient of the quantity of product that burns per minute and the size of the burning area is defined as the burning rate (kg/m$^2$ min). To simulate the burning of a stack of peroxide packages, the burning area of the test sample shall be divided into small segments.

**Test description**

The burning rate test is performed in a shallow glass Pyrex or Duran glass beaker.
The test beaker is around 54 mm high, has an internal diameter of 90 +/- 2 mm and is thermally insulated. The insulating action is obtained by positioning the test beaker concentrically in a second beaker that is 65 mm high and has a cross-section of 115 mm. The space of 1 cm between the bottoms and cylindrical walls of the two beakers is filled with rock wool. 14 upright Pyrex glass tubes of an outside diameter of 20 mm, a height of 29 mm and a wall thickness of 2 mm just fit side the inner test beaker. The tubes, which are open at both ends, divide the contents of the test beaker into a number of segments (in total 19) such that the space between the tubes is not more than 1 mm (see Figure below).

An electronic balance is used to measure the weight loss of the sample during the test. The balance is connected to a chart recorder with zero point suppression, so that the weight loss can be recorded at a safe distance from the test set up.

The balance has the following technical specifications:

- standard deviation 0.1 g;
- linearity 0.15 g;
- max. range 1 000 g.

An aluminium plate of around 22 mm x 36 mm and around 1.5 mm thick is placed on the balance to protect this instrument from fire damage. Most peroxides are difficult to ignite and the prolonged use of a gas flame would disturb the temperature of the sample. For this reason a simple ignition cord is used.

The cord, that is around 6 cm long and 1 mm thick, consists of 4 glass wool threads. When soaked in peroxide, the cord can be ignited with a match.

The test shall be performed in a room that:

- is free of fire, to prevent the fire spreading;
− is shatter-proof to protect people in the unlikely case that the glass beakers explode during the test;
− is at least 2 m high, 0,5 m wide and 0,5 m deep;
− is fitted with an extraction fan for vapour mists and smoke.

The test beaker is filled with 100 gram peroxide. The temperature of the sample in the beaker shall be Tc + 10°C (see 0) with a maximum of 25°C.

The test beaker is placed on an aluminium plate that rests on the balance. The balance and the measuring instrument are set. Then one end of the ignition cord is partly immersed in the sample and lit at the other end with a match. The fire then spreads over the whole surface area of the test beaker. The weight loss of the burning sample is recorded. The test is carried out in duplicate.

Except at the start and end of the fire, the weight loss of the sample will be virtually linear. The time elapsing between 20% and 80% weight loss is called the burning time. The test is assessed on the basis of the shortest burning time.

The burning rate (BR) is calculated from the equation:

$$BR = \frac{0.6 \times m}{t \times A}$$

where:

- $m$ is weight loss during the burning test in kg;
- $A$ is the area = 0,00636 m²;
- $t$ is the burning time = x min.

Test report
The test report contains at least the following data:

− a description of the test and a specification of the chemical formulation;
− the test temperature;
− the recorded ignition time;
− the calculated burning rate.

A copy of the printout from the measurement instrument shall be attached to the test report in order to be able to judge whether the burning rate responsible for the weight loss between 20% and 80%, is representative of the material tested.

Assignment to a storage group

Organic peroxides of types D, E and F are assigned to storage group 3 if the burning rate is below 0,9 kg/(min.m²).

Organic peroxides of types of C, D and E are assigned to storage group 2 if the burning rate is not higher than 9,0 kg/(min.m²).

Organic peroxides of type B are assigned to storage group 1.
Annex G  Literature


2. ADR, Accord Européen relatif au transport international des marchandises dangereuses par route (European Agreement concerning the Carriage of Dangerous Goods by Road)

3. Globally Harmonised System of Classification and Labelling of Chemicals (GHS), United Nations, Geneva


7. ATEX 137, European Directive on minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres (1999/92/EEC)


11. Nederlandse Richtlijn Bodembescherming bedrijfsmatige activiteiten (Dutch Soil Protection Guidance for Business Activities)


13. Handreiking Certificatie Brandbeveiligingssystemen (Guide on Certification of Fire Protection Systems)


18. PGS 29, Richtlijn voor bovengrondse opslag van brandbare vloeistoffen in verticale cilindrische tanks (Guideline for above-ground storage of combustible liquids in vertical cylindrical tanks), version 7 October 2008

19. PGS 30, Vloeibare brandstoffen – bovengrondse installaties (Liquid fuels – above-ground installations)

20. NPR 7910-1, Gevarenzone-indeling met betrekking tot ontploffingsgevaar – Deel 1: Gasontploffingsgevaar (Hazard zone classification relating to explosion hazard - Part 1: Hazard of gas explosion), based on NEN-EN-IEC 60079-10


22. CPR 14E, Methods for the calculation of the physical effects of the release of hazardous materials

23. Brandproeven met peroxyazijnzuur (40%) (Burning tests with peroxyacetic acid (40%)), TNO Prins Maurits Laboratory, Report M9434, 21 November 1979


25. Sprengstofflager-Richtlinie: SprengLR Nrn. 1.-2.1.2 AII8a’ (Explosive Store Directive)
Annex H  Knowledge centres involved

TNO

TNO is among other things:

− a knowledge centre and research laboratory for safety tests on organic peroxides;
− a knowledge centre in the area of GHS;
− appointed by the Ministry of Infrastructure and Environment as competent authority for the classification of organic peroxides for road and rail transport (ADR/VLG and RID/VS).

Contact info:

TNO
Procesveiligheid en Gevaarlijke Stoffen (Process Safety and Hazardous Substances)
PO Box 45
2280 AA  Rijswijk
Telephone number +31 (0)88 866 1265
www.tno.nl/prosafe

InfoMil

InfoMil runs the helpdesk for:

− (technical) content questions about a PGS guideline, or on practical application

Contact info:

InfoMil
PO Box 93144
2509 AC Den Haag
www.infomil.nl/helpdesk

PGS Management Organization

You can contact the PGS Management Organisation for:

− request to extend 0 with new organic peroxides or to revise them based on new test results for existing organic peroxides
− suggestions and ideas on a PGS guideline
− a question on the PGS management organization
− a question on the process of the creation of a PGS guideline

Contact info:

PGS Management Organization
PO Box 5059
2600 GB  Delft
Telephone number +31 (0)15 2690 120
www.publicatiereeksgevaarlijkestoffen.nl
Annex I  Composition of PGS team 8

Members of PGS team 8

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</tr>
</thead>
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<tr>
<td>Mr P. Schuurman</td>
<td>AkzoNobel</td>
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<tr>
<td>Mr H. Hilljesdam</td>
<td>IPO / Province of Overijssel</td>
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<tr>
<td>Mr L. Jansen</td>
<td>VNG / Regional Environmental Service West-Brabant</td>
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<td>Mr M.G.G.M. Faber (chair)</td>
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