8

Storage of organic peroxides

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Storage of Organic Peroxides

Ministerie van **Binnenlandse Zaken** *en* **Koninkrijksrelaties**

SZW

Ministerie van Verkeer en Waterstaat

Preface

Starting from June 1st 2004, the Advisory Council on Dangerous Substances (Adviesraad Gevaarlijke Stoffen - AGS) was installed by the Cabinet. At the same time the Committee for the Prevention of Disasters (Commissie voor de Preventie van Rampen - CPR) was abolished.

CPR issued several publications, the so-called CPR-guidelines (CPR-richtlijnen), that are often used in environmental permits, based on the Environmentap Protection Law, and in the fields of labouw safety, transport safety and fire safety.

The CPR-guidelines have been transformed into the Publicatioin Series on Dangerous Substances (Publicatiereeks Gevaarlijke Stoffen - PGS). The aim of these publications is generally the same as that of the CPR-guidelines. All CPR-guidelines have been reviewed, taking into account the following questions:
1. Is there still a reason for existence for the guideline or can the guideline be abolished;
2. Can the guideline be reintroduces without changes or does it need to be updated.

This 8th publication in the Series on Dangerous Substances (PGS 8E) is not different from the former publication CPR 3E, second edition 1997.

Also on behalf of my colleagues at the Ministries of Transport, Social Affairs and of the Interior, The State Secretary of Housing, Spatial Planning and the Environment (VROM).

Drs. P.L.B.A. van Geel

March 2006

Preamble

This directive, which has been realized under the auspices of the Committee for the Prevention of Disasters by Dangerous Substances (CPR), is published by order of:

- The Minister of Social Affairs and Employment
- The Minister for Housing, Spatial Planning and Environment
- The Minister of the Interior
- The Minister of State, Transport and Public Works

The regional Health Inspectors, charged with the supervision of environmental hygiene, will implement this directive in their advisory capacity, regarding requests for storage permits for organic peroxides.

The Labour Inspectorate will implement this directive in the same manner as in the instruction sheets issued by this Inspectorate.

The issue and circulation of these guidelines will be handled by the Directorate-General of Working Conditions.

The Hague, January 1997

THE DIRECTOR-GENERAL OF THE DIVISION OF WORKING CONDITIONS

Drs. R. Laterveer

Preface

Second issue 1997

After the publication of the first issue of the guidelines in 1982 various new developments made it necessary to publish a new issue. One of the developments is the introduction of the generic entry system for transport of organic peroxides which also involved new UN-Nos for the existing and the addition of many new formulations of organic peroxides. Also the introduction of tank transport and the subsequent tank storage made an update of the directive necessary. The same holds for the introduction of dosing vessels which were not taken into account in the first issue. While drafting this second issue due attention has been paid to the regulations drafted in other countries since the first issue was the first one ever published in Europe and North America. Especially the regulations from Germany and United Kingdom were used as basis for the new issue. Further the reference to standards and other regulations has been limited as much as possible and updated where necessary. With the release of this second issue, the first issue looses its validity.

The second issue of these directives is prepared by a sub-committee consisting of the following experts:

Ing.Th.M. Groothuizen (chairman)	– TNO Prins Maurits Laboratory *
A.B. van Balderen/B. Mulleman	– H & P Mixing
Ing. A.G. Bollen	– Akzo Nobel
Ir. P.A. Dekker	– Ministry of Home Interior Fire Services and Crisis Management
Ir. J.M.L. Devens	– Dutch State Mines (DSM)
Dr. J.J. de Groot (secretary)	– Akzo Nobel
Dr. A.H. Heemskerk	– TNO Prins Maurits Laboratory
Ir. W.H. van Houwelingen	– Polynorm
Mr.Ir. K.Posthuma	– Secretary Committee for the prevention of disasters, caused by dangerous substances
Ing. J. Schueler	– Dow Benelux N.V.
J.A.G. Verhoeff	– Association of the Dutch Chemical Industry
Ir. J.M. Zijderveld	– BPM

To all members of this sub-committee and to all others who co-operate in the realisation of this report the Committee for the Prevention of Disasters caused by Dangerous Substances (CPR) expresses their thanks.

The Hague, January 1997

THE CHAIRMAN OF THE COMMITTEE FOR THE PREVENTION OF DISASTERS CAUSED BY DANGEROUS SUBSTANCES,

Drs. H.C.M. Middelplaats

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Purpose and function of the CPR directives

In our increasingly complex society, a growing use is made of substances which in the event of misadventure can be dangerous to man or the environment. The risk presented by these substances is determined by the physical and chemical properties of the substances and the quantity involved, as well as by the way in which the substances are transported, transhipped, stored, or processed, and by the location at which these operations take place.
Critical and intensive guidance by the government and others with respect to the use of hazardous materials is indispensable, especially in this densely populated country. Within the government, the CPR has a coordinating and stimulating task in this field.
Its task is to advise the ministers concerned (Social Affairs and Employment, Housing, Spatial Planning and the Environment, Home Affairs, and Transport and Public Works) in matters concerning the technical and organizational measures required to prevent and limit the risks involved in the use of hazardous materials. The CPR does this by formulating directives covering the handling of hazardous materials, mostly after consulting experts from the industries involved. Following acceptance by the ministers concerned these directives are then published.

Although observance of the directives guarantees that hazardous materials will be handled in as safe a manner as possible, an absolutely safe situation in the strict sense of the word is almost never attained. A certain residual risks remains, the extent of which depends in particular on the properties of the substance, the quantities involved, the manner of transport, transfer, storage and processing, and on the vulnerability of the environment, as well as on any outside influences. In making preparations for new activities that will involve hazardous materials, the primary aim should therefore be to investigate whether the application of the hazardous material(s) in question is indeed necessary and whether any safer alternatives can be found which may prevent or limit the application or use of the hazardous material(s).
If after careful consideration this proves to be impossible, the aim should be to limit the residual risk as much as possible at all times, e.g. by applying the smallest possible quantities of the substances in question and by taking suitable technical and organizational management measures. In doing so, it should be borne in mind that limiting the amount of the substance will usually entail an increase in supply frequency which in turn will increase the risk of disaster, albeit limited in scale.

The next thing to be considered in each separate case will be whether the residual risk can be tolerated in view of the importance to the community of the activity in question. In formulating the directives, the committee's objective is to provide as much security as possible against permanent damage to man, beast and the environment. For frequently occurring activities of similar nature, so far as these present no more than a limited risk, general directives may be formulated. For incidental cases and situations which present a potentially high risk, additional or more specific recommendations may be considered. Directives are generally based on the best practicable means[1)], or in specific situations involving high risk, the best technical means[2)].

[1)] Best practicable means: the techniques by which the greatest reduction in risk is obtained, taking into consideration the economic aspects, i.e. while still remaining acceptable to a normally enumerative enterprise from a cost viewpoint.
[2)] Best technical means: the techniques by which, at higher cost, a still greater reduction in risk is obtained and which have been applied at least once in practice.

In order to allow proper evaluation and arrive at a well-founded decision, the competent government authorities require proper insight into the risk aspects of the activity, particularly regarding the residual risk in the event of comprehensive application of the directives in a concrete situation. The responsibility for the consequences of the application of hazardous materials remains with the user, even if the relevant directives are fully observed.
Compliance with the directives constitutes no guarantee that the competent government authorities will agree to the proposed activity. It may however be expected that any additional requirements or deviations will be clearly motivated.
As a rule, the authorities advising the competent authorities issuing the licences or involved in the protection of employees, e.g. the regional Public Health Inspector charged with the supervision of environmental control, the District Head of the Labour Inspectorate and in certain cases the Fire Department Inspectorate, in carrying out their duties, will themselves be guided by the relevant directives, while still retaining their own responsibilities.

1. Properties and Hazards

Organic peroxides are organic chemicals which contain the unstable -O-O-peroxy linkage 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 liable to explosive decomposition,
- be flammable and burn rapidly,
- be sensitive to impact or friction,
- show hazardous reactions with other materials,
- show a toxicity or corrosivity.

In both transport and handling regulations organic peroxides are classified as a special group because of their specific (hazardous) properties. Regulations concerning the storage of packaged hazardous materials [1,2] are not valid for organic peroxides (excluded by name).

The transport regulations are based on the UN Recommendations on the Transport of Dangerous Goods [3]. In these UN Recommendations the organic peroxides are classified in Division 5.2, unless the active oxygen content is too low (max. 1.0% or 0.5% in presence of not more than 1.0% or 7.0% of hydrogen peroxide, respectively). In the UN Recommendations the Organic Peroxides are classified according to a series of tests in a flow chart. The outcome of the flowchart determines the hazard of the peroxide and provides maximum package sizes. The hazard classification of Organic Peroxides by the UN Recommendations is further discussed in Chapter 2.

In the European Community the safety in the chemical process industry is regulated by EC-directives. The regulations within the member countries, at least, must comply with EC-directives. In the Netherlands storage and handling of organic peroxides is, amongst other things, regulated within the "Wet Milieugevaarlijke Stoffen" and the "Besluiten 'Verplichtstelling Veiligheidsrapport', 'Verpakking en aanduiding milieugevaarlijke stoffen' and 'Risico's zware ongevallen'". The regulations comply with EU-directives such as 82/501/EEC (the Post-Seveso Directive) [4] and require information on the physico-chemical properties of materials, on possible major accident situations (emergency response plans, etc.) and on installations if the quantity of handled material may form a hazard. In such a case, depending on the site lay-out, the type of organic peroxide and the quantities in question the competent authorities may require the draft of an external safety report (EVR) or an operational safety report (AVR).

The "Wet Milieugevaarlijke Stoffen" regulates the classification, packaging and labelling of dangerous substances as well in compliance with the Directive 67/548/EEC [5] and its regular amendments. In the regulations peroxides are only characterized by the occurrence of the -O-O-peroxy linkage in the structural formula (i.e. concentrations are not taken into account). Flammability, auto-flammability and explosivity of peroxides must be investigated as well by test methods as specified in EC-Directive

92/69/EEC on the notification of new chemicals [6].
The hazard classification is based on the product properties and is reflected by showing relevant symbols, and Risk and Safety phrases.
These hazard identifications work complementary: symbols primarily draw attention to the inherent hazard of a chemical, the risk phrases specify the hazards involved and safety phrases advice on handling issues to avoid the occurrence of incidents.
A list of symbols and common phrases for peroxides is shown in Annex 3 and Annex 4.

The group of organic peroxides is in principle labelled as O (oxidizing agent). This symbol can be omitted if the active available oxygen (i.e. the -O-O-) concentration is extremely low. Other symbols are provided as well for instance if the peroxide shows corrosive (C) or extreme flammable (F+) or explosive (E) properties. Typical applications of risk and safety phrases are elucidated in the remainder of chapter 1.
The following aspects of organic peroxides are further briefly discussed in this chapter:
- temperature control
- the hazard of decomposition and/or explosion,
- the hazard of fire,
- the hazard of toxicity and/or corrosivity.

1.1 Temperature control

All organic peroxides are thermally unstable and may more or less vigorously decompose as a function of temperature. Therefore, all peroxides shall be protected from direct sunlight and sources of heat. This is generally indicated by using the safety sentence S3 (keep in a cool place).
Some organic peroxides are even too unstable to be stored at ambient conditions and shall be temperature-controlled upon transport and storage. This is indicated by using the safety sentence S47 (keep at temperatures not exceeding ...ºC). The recommended maximum transport and storage temperature is called the control temperature (TC). Provisions shall be made to keep the temperature of the peroxide during transport and storage lower than TC. If the temperature of an organic peroxide inadvertently exceeds the control temperature actions shall be taken to reduce the temperature of the peroxide.
An alarm shall be given if the temperature attains the emergency temperature (TE). All available means shall be used to bring the temperature under control and the emergency procedures shall be started.

The control and the emergency temperature are derived from the Self-Accelerating Decomposition Temperature (SADT), which is defined as the lowest ambient temperature at which hazardous self-accelerating decomposition may occur with a substance in the packaging. The SADT shall be determined in order to decide whether a substance shall be subjected to temperature control during storage. Provisions for the determination of the SADT are given in Appendix A.1, marginal 3105 of ADR (7). The correlation between SADT, control temperature, emergency temperature and storage temperature are given in the next table.

Sadt	**Control temperature**	**Emergency temperature**	**Maximum storage temperature**
20°C or less	20°C below SADT	10°C below SADT	control temperature
over 20°C to 35°	15°C below SADT	10°C below SADT	control temperature
over 35 °C	10°C below SADT	5°C below SADT	control temperature or 45°C

The following organic peroxides (for a description of the types of organic peroxides see 2.2, table 1) shall be subjected to temperature control during storage:
- organic peroxides types B and C with an SADT ≤ 50°C;
- organic peroxides types D with an SADT ≤ 50ºC showing a medium effect when heated under confinement or with an SADT ≤ 45ºC showing a low or no effect when heated under confinement,
- organic peroxides types E and F with an SADT ≤ 45ºC.

Note: Provisions for the determination of the effects of heating under confinement are given in Appendix A.1, marginal 3105 of ADR [7].

Where applicable, control and emergency temperatures are listed in Annex 2. The actual temperature during storage may be lower than the control temperature, but shall be selected so as to avoid dangerous separation of phases.

1.2 The hazard of decomposition and/or explosion

Organic peroxides show fast decomposition reactions during which a large amount of heat is generated. The rate of decomposition depends on temperature and on concentration. The hazard of a runaway reaction is reduced by diluting or inactivating the peroxide with materials such as water, phthalates, isododecane and calcium carbonate. This type of hazard is reflected by the use of risk sentence R2 (risk of explosion).

In concentrated form, however, many organic peroxides can show severe decomposition. This is reflected by the use of risk sentence R3 (extreme risk of explosion), which is used for certain undiluted organic peroxides. The hazard of the runaway reaction is determined by two parameters, viz. the rates of temperature and pressure rise.
No self accelerating decomposition reaction can occur as long as all heat generated is removed from the peroxide (either by natural or by forced convection) and no hazard of vessel fragmentation exists if any gaseous decomposition products can be either relieved from or contained in the vessel.
In practice, complete containment of gaseous decomposition products is hardly possible if larger quantities of peroxides are stored. Therefore, the heat balance (i.e. the net result of heat generation and heat transfer) is to be controlled.
This heat balance depends on the decomposition rate of the peroxide, on the stored quantity and the storage temperature, and on the type of packaging. The rate of decomposition, and thus, the heat production is increased strongly if the organic peroxide:
a.is contaminated by incompatible materials such as heavy metals, acids and bases, rust, accelerators, etc. (use of S14: keep away from ..., or S50: do not mix with ...),
b.is used or stored at unduly high temperatures,
c.is exposed to fire.

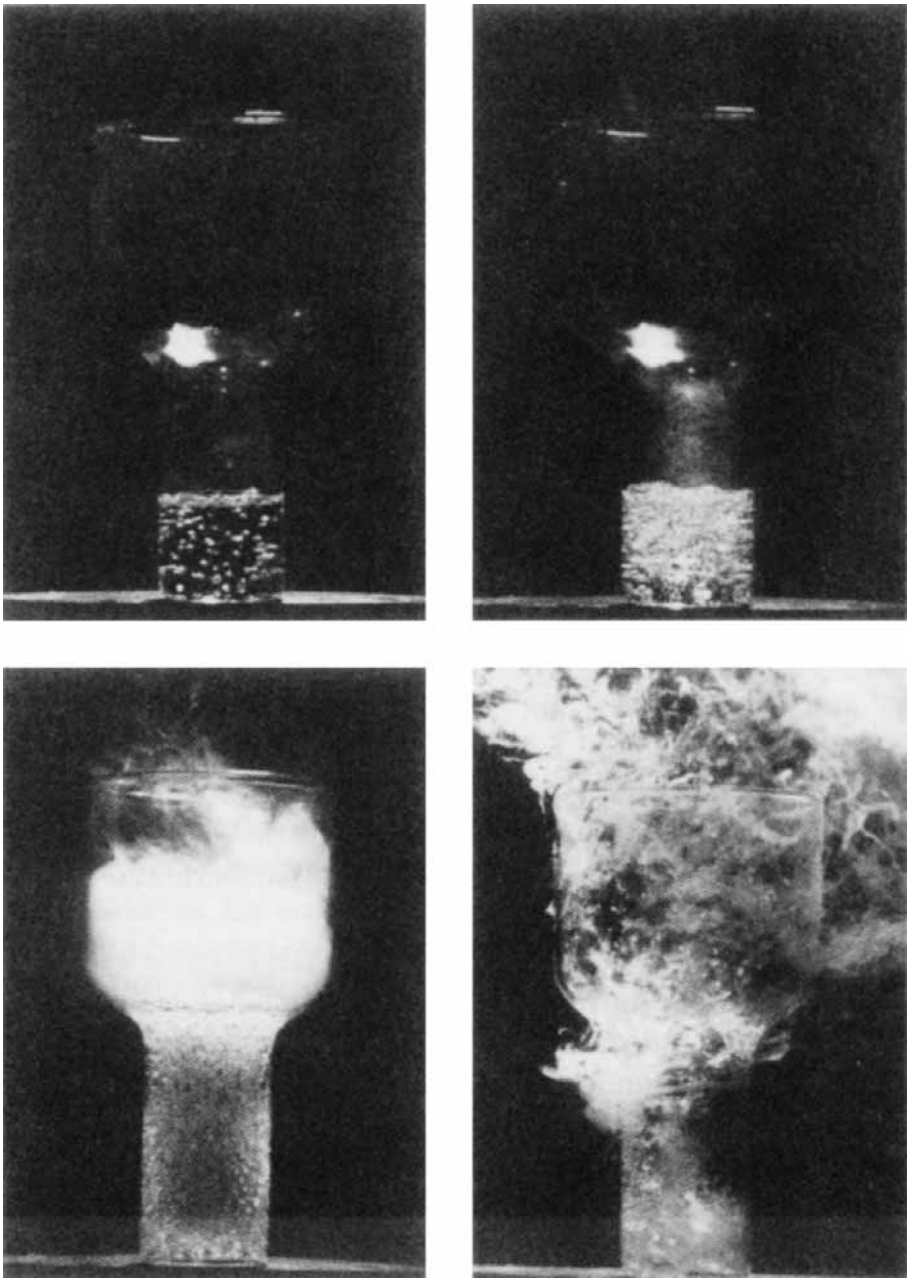
Both a larger stored quantity and a higher storage temperature result in an increase of heat generation and a decrease of heat transfer. Storage for a long period of time may accelerate the decomposition by auto-catalysis.
The effect of a runaway reaction is two-fold. The casing of the vessel will weaken by the exposure to the high temperature of the peroxide and the pressure in the containing vessel will exceed its design pressure. This will cause a violent pressure burst and a subsequent, sudden release of hot flammable vapours which may ignite spontaneously. Moreover, the released vapour cloud may produce a secondary (gas) explosion either by spontaneous ignition or by contact with an external ignition source.
Organic peroxides that are especially prone to exploding under confinement, are marked by the risk sentence R44.

The self accelerating decomposition reaction is determined by the bulk temperature of the peroxide. Apart from showing a runaway reaction a number of peroxides may deflagrate as well. A deflagration can already occur at a relatively low temperature. It is initiated by an ignition source or by self-ignition of the peroxide (or its decomposition) vapours at temperatures higher than the flash point. Hot spots by self-heating, exposure to hot surface-areas, sparks, friction, impact, etc. are frequently observed ignition sources in case of solid peroxides. The safety sentence S34 (avoid shock and friction) is used if an organic peroxide shows a high sensitivity to ignition by friction or impact.
Only a small number of commercial peroxide formulations is able to detonate. In practice, the peroxides that are prone to detonation, are desensitized (inactivated) in such a way, that they no longer possess detonation properties.

Almost all organic peroxides are composed of hydrocarbon chains, either aliphatic or aromatic. Only a very limited number of organic peroxides (e.g. di-4-chlorobenzoyl-peroxide) comprise elements such

as chlorine that are closely associated with the formation of decomposition products with toxic properties. The decomposition products of organic peroxides are mostly saturated or partially oxidized hydrocarbons (CnHm) or either or not partially oxidized carbon (COx). This implies that the toxicity of the decomposition products of organic peroxides, generally, is of a similar nature as that of hydrocarbons with small chain lengths.

For detailed information concerning toxicity and eco-toxicity of individual organic peroxides the Material Safety Data Sheet has to be consulted.



Events occurring during a self accelerating decomposition reaction

1.3 Fire hazard

The fire hazard follows either from the exposure to an external fire or from the flammability of the organic peroxide. The exposure to an external fire is identical to the exposure to hot surface-areas (see 1.2). The flammability of organic peroxides varies: some of them ignite very easily, others are very difficult to ignite. The risk of flammability is for instance reflected by the use of risk sentence R7 (may cause fire).

In most cases it is hardly possible to determine the flammability of a peroxide. The flash point of a liquid peroxide, for example, defines its flammability. The flash point, however, is often distinctly higher than the temperature range in which the peroxide is sufficiently stable for handling and storage.

Therefore, a flash point is only relevant if its value coincides with the usual temperature range of storage and handling. Ditert.butylperoxide is for instance a typical example of a peroxide, that is stored at ambient temperature, whereas its flashpoint (6ºC) is lower.

Adequate ventilation of peroxide store rooms is recommended to disperse the peroxide vapour and to reduce the risk of vapour ignition by minimizing the vapour concentration of the peroxide. Ventilation is even required if the vapour concentration in the store room can exceed a level of 20% of the lower flammability limit (LFL).

For storage rooms without active cooling ventilation to the atmosphere is recommended. The necessity to ventilate is reflected by safety sentence S9 (keep container in a well-ventilated place).

The gaseous products resulting from a peroxide decomposition are usually flammable when mixed with air. Such a gaseous mixture can ignite spontaneously or by contact with an ignition source. Therefore, the presence of potential ignition sources such as electric installations, etc., must be avoided and the storage must be provided with adequate relief panels to prevent excessive pressure rises and to vent the gaseous products to a safe place in case of an emergency.

A fire of liquid peroxides will readily spread as the peroxide leaks and spills from the collapsing peroxide-containing vessels. This implies that measures must be taken to contain spilled liquid peroxides. The fire intensity will be relatively high as its severeness is proportional to the burning surface area (which, in this case, is identical to the floor area). Special care should be paid to volatile peroxides where ignition of the vapours is possible.
Solid peroxides spread in a different way. This reduces the intensity of the fire as compared to liquid peroxides, because of the smaller burning surface-area. Adequate fire-fighting systems can largely reduce the effects of a fire if they start operating in an early stage of the fire.

It is essential in fighting a peroxide fire to use fire-extinguishing agents that cool efficiently (such as water). The supply of the cooling agent has to be continued upon extinction of the flames as the heated peroxide may self-ignite again. In general, non-cooling fire extinguishing agents are only suitable for fighting small fires.

In setting up a storage facility for peroxides, care has to be taken to avoid the use of incompatible construction materials or equipment. Incompatible materials may either stimulate the decomposition of peroxides or may break down themselves, which may result in hazardous situations.

1.4 Toxicity, eco-toxicity or corrosivity

Organic peroxides are generally of a moderate toxicity. The toxicity depends on the particular peroxide. Some are corrosive to the skin and mucous membranes and can cause severe damage to the eyes on direct contact. These types of organic peroxides are mostly marked by the combination of safety sentences S37 (wear suitable gloves) and S39 (wear eye/face protection). Inhalation of the vapours of some peroxides may cause irritation of the respiratory tract and of the lungs. Swallowing of peroxides may cause scalding of the mouth, throat, gullet and stomach.

The eco-toxicity, i.e. the longterm effects of exposure of the environment to organic peroxides, depends on the stability of the peroxide. The eco-toxic effect of the de-oxygenated decomposition product of peroxide is similar to its hydrocarbon counterpart.

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

1.5 Hazard classification

The intensity of a peroxide decomposition depends on its decomposition properties as is shown in 1.2 and 1.3. These properties shall be determined for each individual peroxide. A proper knowledge of the decomposition properties allows classification of the peroxide in five groups of decreasing intensity of decomposition or burning. These storage groups are discussed in 2.3.
A sequence of tests is required to determine the necessary properties. A useful test scheme is provided in the United Nations Recommendations on the Transport of Dangerous Goods [3]. This test scheme results in a meaningful comparison of the hazards of the various peroxides.
Still, a considerable amount of expertise remains required in working with and evaluation of test results in view of scaling and extrapolation to plant operation. Such expertise is available with peroxide producers or specialized institutions like the TNO Prins Maurits Laboratory.

2. Classification of organic peroxides

2.1 General

The hazard involved with the individual organic peroxides varies considerably. These variations shall be taken into account when storing the substances. Classification of organic peroxides into groups is therefore desirable. For the purpose of this directive the classification is based on that used for transport [3] and the burning rate.

The classification group and the amount of stored product is used to determine the safety distances around the storage facility.

The hazards giving rise to effects outside the storage and thus requiring safety distances are:
- explosive decomposition
- heat radiation as a result of rapid burning

The other hazards mentioned in chapter 1 enhance the probability of ignition, being:
- too high product temperatures
- sensitivity to impact and friction
- reaction with other materials (contamination)

These hazards are incorporated in this directive by means of storage requirements, e.g. temperature control and handling instructions.

Finally, some peroxides have additional hazards like corrosivity or toxicity. These hazards are indicated by subsidiary risk labels on the packaging, next to the primary organic peroxide risk label. Although primary risks have precedence over subsidiary risks, additional safety measures might be necessary.

The classification groups for the storage of organic peroxides are based on decomposition and burning properties. The decomposition effects of organic peroxides are strongly influenced by size and type of the packaging, in particular its mechanical strength. These aspects are taken into account in the classification scheme for organic peroxides in the transport regulations.

2.2 Transport classification

Practically all regulations for the transport of organic peroxides by sea, inland waterways, road, rail and air are based on the United Nations recommendations for the transport of hazardous goods [3]. These regulations distinguish between seven types of organic peroxides, type A to G. The hazard of the various organic peroxide types is described in table 1.
The transport regulations prescribe the maximum size, type and material of packagings allowed for each type of organic peroxide.

Table 1: Classification Principles for Transport

organic peroxide type	Hazard description of class 5.2 substances
A	organic peroxide formulations which can detonate or deflagrate rapidly, as packaged for transport.
B	organic peroxide formulations possessing explosive properties and which, as packaged for transport, do neither detonate nor deflagrate rapidly, but are liable to undergo a thermal explosion in that package.
C	organic peroxide formulations possessing explosive properties and which, as packaged for transport, cannot detonate or rapidly deflagrate or undergo a thermal explosion.
D	organic peroxide formulations 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 peroxide formulations which, in laboratory testing, do neither detonate nor deflagrate at all and show no or low effect when heated under confinement.
F	organic peroxide formulations which, in laboratory testing, do 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 peroxide formulations which, in laboratory testing, do neither detonate in the cavitated state nor deflagrate at all and show no effect when heated under confinement as well as no explosive power.

UN numbers are assigned to the organic peroxide types on the basis of its physical state (liquid/solid) and temperature control requirement (no/yes). The socalled “generic” listing for collective entries in the UN list of dangerous goods is applied. These UN numbers and the permitted maximum container capacity are given in table 2.

Table 2: Transport Classification of Organic Peroxides

organic peroxide type	U.N. number				max. container capacity	
	no temperature controlled		temperature controlled			
	liquid	solid	liquid	solid	liquid	solid
A	-	-	-	-	-[1)]	-[1)]
B	3101	3102	3111	3112	30 l	25 kg
C	3103	3104	3113	3114	60 l	50 kg
D	3105	3106	3115	3116	60 l	50 kg
E	3107	3108	3117	3118	225 l	200 kg
F	3109	3110	3119	3120	IBC tanks	IBC tanks
G	-	-	-	-	[2)]	[2)]

1) prohibited for transport as class. 5.2.

2) exempted from class 5.2.

2.3 Storage classification

The storage classification comprises five groups. The assignment to a storage group is primarily based on the transport regulations. Secondly, the burning rate of the peroxide is taken into account. The burning rate mainly determines the heat radiation from a peroxide fire. It is defined as the amount of substance burned per minute for a 10.000 kg lot engulfed in a fire. The lot shall consist of containers used for the transport and storage of organic peroxides. Representative fire tests with smaller

quantities can also be used for classification (see Annex 5). In case the burning rate is not known, the most severe classification for the type of organic peroxide shall be used.
The above described storage classification is specified in table 3. Group 1 comprises the most dangerous substances and group 5 the least dangerous substances.
The classification is based on the assumption that organic peroxides are only stored in the transport packages that are legally permitted in the Netherlands.
The hazards described in table 3 comprise of:

- explosive/hazardous, indicating that some packages may explode but no mass explosion will occur
- burning, indicating that heat radiation from the fire will endanger the surroundings.

Table 3: Classification for Storage

storage group	organic peroxide type	burning rate[1)] (kg/min)	description
1	B	all	explosive or very fast burning
	C	≥ 300	
2	C	< 300	very hazardous or fast burning
	D	≥ 60	
	E	≥ 60	
3	D	< 60	hazardous or burning like solvents
	E	< 60	
	F	> 10	
4	E	< 10	minor hazard and slow/no burning
	F	< 10	
5 [2)]	G	all	may be exempted

[1)] *) of 10000 kg organic peroxide, corrected for radiation efficiency (see Annex 5)
[2)] including those products with a low active oxygen content according to paragraph 2.4

On the basis of this classification a list has been compiled in which a majority of the organic peroxides that are used in practice are included (see Annex 2). As new products regularly appear on the market, or new fire tests with existing products will be carried out, the list needs to be updated from time to time. Requests to this extent shall be addressed to the Secretary to the Committee for the Prevention of Disasters caused by Dangerous Substances (PO box 90801, 2509 LV The Hague, The Netherlands). The request shall be submitted with documentation as extensive as possible.

2.4 Remarks

Organic peroxides of type A have not been assigned to a storage group as they are prohibited from transport as organic peroxide. The storage conditions of type A peroxides shall be specified by the competent authorities.

Samples of new organic peroxides or new formulations of currently assigned 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 would be no more dangerous than “organic peroxide type B”;
- the sample is packaged in inner receptacles of packing method OP2 (max. 0.5 l for liquids and max. 0.5 kg for solids);
- the available data indicate that the control temperature, if any, is sufficiently low to prevent any dangerous decomposition and sufficiently high to prevent any dangerous phase separation.

Organic substances can by dilution or otherwise contain only a small mass fraction of the bivalent -O-O-structure. The substances with a socalled low active oxygen content are included in storage group 5 if the formulation contains:

- not more than l.0% active oxygen from the organic peroxides when containing not more than 1.0% hydrogen peroxide;

or,

- not more than 0.5% active oxygen from the organic peroxides when containing more than 1.0% but not more than 7.0% hydrogen peroxide.

The active oxygen content (%) of an organic peroxide formulation is defined by the formula:

$$16 * \sum (n_i * \frac{c_i}{M_i})$$

where,

n_i = number of peroxygen groups per molecule of organic peroxide i;
c_i = concentration (mass %) of organic peroxide i;
M_i = molecular mass (gram/mol) of organic peroxide i.

In addition to the above substances organic peroxide formulations of type G (see table 1) are included in storage group 5 if:

- the formulation is thermally stable (SADT ≥ 60°C for a 50 kg package)

and,

- the boiling point of the diluents used for desensitization is not less than 150ºC, otherwise they have to be treated as storage group 3 or as storage group 4 peroxides.

The organic peroxides of storage group 5 can be excluded from this directive. It shall be noted, however, that they can remain dangerous substances, subject to classification according to the “Wet Milieugevaarlijke Stoffen”.

3. General guidelines for storage

Safety guidelines for the storage of organic peroxides serve two purposes:
- prevention that incidents will arise
- reduction of effects when an incident takes place

The preventive and reductive measures are obtained by special construction of the storage building, special provisions in the storage, proper management/housekeeping and appropriate safety distances from the storage to adjacent buildings.
The extent to which the safety measures shall be applied depend on the amount and hazard classification of the stored product as well as the purpose of the storage.

In general the following stores will occur at a factory:
- sample storage, small quantities of product stored for the purpose of testing or analysis.
- central storage facilities and tanks in which the main feed stock is kept.
- daily stock, an area in the vicinity of the plant where the quantity of product needed for one day is stored.

The safety measures for the above mentioned storage facilities are different and therefore described in separate paragraphs of this directive. The principles on which all these safety measures are based are nevertheless the same.

The production and processing of organic peroxides at factories are not covered by the CPR-3 (Storage of Organic Peroxides). Specific provisions and safeguards are to be observed which are beyond the scope of this directive.

The general safety principles for the storage guidelines are summarized in the following sections.

3.1 Prevention of incidents

a. The most important means of hazard prevention for organic peroxides is temperature control. Extensive safety measures are necessary to prevent organic peroxides from exceeding their maximum allowable storage temperature. For many peroxides cooling facilities will be necessary.

b. Temperature sensors with indication and alarm will mostly be necessary. The temperature recorded shall be representative for the ambient temperature of the peroxide. The temperature indication shall be supervised regularly and the response to alarms shall be guaranteed.

c. Every contamination has to be avoided.

d. Peroxide spillage has to be cleaned immediately. Storage areas shall be designed in such a way, that spillages do not extend in an uncontrolled way, e.g. by means of sloped floors, trays.

e. Peroxides shall not be exposed to heat sources or hot elements having a temperature higher than the maximum storage temperature of the peroxide. There are many examples, e.g. radiators, steam pipes, warm air, etc. The main problem is mostly to recognize sources as such.

f. Avoid ignition sources which might ignite vapours of a peroxide decomposition. For this reason explosion proof electrical equipment is generally required in peroxide stores [8].

g. Limited storage periods. As peroxides decompose slowly they cannot be kept for an unlimited period of time.

h. Last but not least the personal means of protection shall be used to prevent direct contact (skin and eyes) and inhalation. Proper ventilation is important but is as such not a means of personal protection. The industrial hygiene guidelines in this respect are proper ventilation and avoidance of direct skin contact.

3.2 Reduction of effects

a. The main means of reduction of the fire and the decomposition of peroxides is deluging with water. Water extinguishes the fire and cools down the self-heating process of the peroxide decomposition. Adequate fire-fighting provisions are recommended for peroxide storage facilities.

b. Detectors (smoke, fire, temperature etc.) shall detect the onset of fires and decompositions at their early stage. The timely suppression of starting fires and decompositions limits the extent of the accident.

c. Emergency reliefs to vent the gases generated by a peroxide decomposition do prevent major damage to the construction of the storage building.

d. To avoid environmental pollution gutters and basins are recommended to channel and catch the fire-fighting water. These provisions shall be constructed in such a way that the spreading of the fire to other buildings can be prevented and pressure build-up in ducts is avoided.

e. Safety distances between the peroxide store and its adjacent buildings shall be observed. This directive gives values for safety distances to property boundaries and other storage rooms.

4. General requirements for storage

All requirements enumerated in this chapter are applicable to storage rooms. The requirements given in 4.1, 4.1.1, 4.1.2, 4.3, 4.5, 4.6 and 4.7 are also applicable to storage tanks. Additional requirements for tanks are given in 6.

4.1 Temperature control

For reasons of safety organic peroxides shall be kept cool (see 1.1). In order to avoid self accelerating decomposition a maximum storage temperature is assigned to each organic peroxide. The prescribed maximum storage temperature is equal to the control temperature (TC) given in annex 2 and 45ºC when no control temperature is listed.
Under climatical conditions met in the Netherlands the recommended means of cooling are:
- passive cooling when $T_c \geq 30°C$ or no T_c value is given in annex 2
- active cooling when $10ºC < T_c < 30ºC$
- thermal insulation and active cooling when $T_c \leq 10°C$

4.1.1 Cooling requirements

a. The passive means of cooling can comprise of:
sunroof, double roof, insulating walls, air ventilation, a water spray installation on the roof, etc. Particular care shall be taken to avoid heat input by sun-radiation; e.g. no windows or plastic shields. Most means of passive cooling can be achieved by proper constructive measures.

b. Active means of cooling can comprise of:
- mechanical refrigeration units with the provision that, except for the vaporizer section, the cooling unit is located outside the storage room,

or:
- coolant systems such as solid carbon dioxide, liquid nitrogen, ice, provided that the storage facility is thermally insulated. This type of cooling has to be restricted to small storage facilities for less than 150 kg organic peroxide. Ample spare capacity of coolant shall be present.

c. Thermal insulation and active cooling consist of:
- a storage facility which is completely insulated. The insulation material shall be non combustible or be protected with material which is fire proof according to NEN 6064 [9].

and
- mechanical refrigeration unit(s) where, except for the vaporizer section, the cooling unit is located outside the storage room

and
- spare or back-up cooling facilities to overcome cooling failures.

d. Storage facilities with active cooling shall be provided with temperature sensors. The temperature read-out shall be observable near the storage unit. The temperature has to be checked at regular intervals. Remote warning systems to permanently manned locations are required when more than 150 kg organic peroxides with a $T_c \leq 20°C$ are stored.

e. General requirements for refrigerated rooms as described in P142 [10] are applicable.

4.1.2 Heating restrictions

If in a storage unit heating is necessary, e.g. to prevent freezing or phase separation, the following provisions shall be made:

a. Measures shall be taken to prevent the temperature of the packages rising above the maximum storage temperature as a result of the heating. The heating shall be switched off below the maximum storage temperature. The heating shall be switched on at a temperature depending on the required physical state (solid, liquid) of the organic peroxides (e.g. freezing point, phase separation);

b. Heating shall be effected with hot air or with equipment in which hot water is used as the heating medium. The surface temperature of heating equipment in the storage unit shall remain below 60ºC. The temperature of the air entering the storage unit shall remain below 60ºC;

c. The heating equipment shall be installed in such a way that no packages containing organic peroxides can be placed against it, on top of it, or directly over it;

d. Measures shall be taken to prevent any hot air stream or heat radiation being directed to the packages containing organic peroxides. The distance between the packages containing organic peroxides and the heating equipment shall be at least 0.5 m;

e. Storage facilities with active heating shall be provided with temperature sensors. The temperature read-out shall be observable near the storage unit. The temperature has to be checked at regular intervals. Remote warning systems to permanently manned locations are required when more than 150 kg organic peroxides are stored.

4.1.3 Air circulation and ventilation

Air circulation

Circulation of air in the storage facility is extremely important to prevent self-heating of the peroxide. To enhance natural air circulation the following measures are required:

- packages shall be placed 0.15 m from the wall
- ample space (0.1 m) is to be provided between stacks of packages or pallets so that air circulates along at least two sides
- peroxides shall not be stacked in unit quantities of more than 1500 kg

Ventilation

Ventilation is required if the vapour concentration in the store room can exceed 20% of the lower flammability limit (LFL). In this case the ventilation rate shall be large enough to keep the vapour concentration below 20% of the LFL [8].

This shall be effected by means of openings in the walls, which

- are situated near the floor, above the level of the door threshold and near the ceiling
- are distributed equally over the length of the walls
- have a cross section of at least 0.5 % of the floor area with a minimum of 0.01 m^2
- cannot be obstructed
- shall not affect the fire resistancy of the wall or door construction.

4.2 Emergency relief venting

The decomposition or explosion of peroxides results in the evolution of gases and subsequent pressure increases. In order to prevent demolition of the storage facility by internal overpressure, emergency relief venting is necessary.

For large storage facilities it will be necessary to make the roof or one side wall of a light weight construction material which will readily give way. Additionally, a small relief panel of about 0.25 m^2 may be fitted to prevent damage in case of minor decompositions of the stored peroxides.
For smaller facilities it will generally suffice to use venting panels or to construct the door as an emergency relief. In the latter case door closures or hinges should readily open or tear off, e.g. magnetic locks of refrigerators. In any case it should be avoided that parts of the emergency relief are blown off.
Typical sizes for the emergency relief are:
- 1 m^2/1000 kg for products of storage group 1
- 0.5 m^2/1000 kg for products of storage group 2
- 0.25 m^2/1000 kg for products of storage group 3 and 4

The opening pressure of the emergency relief shall be sufficiently below the mechanical strength of the storage facility e.g. 0.01 barg vs 0.03 barg.

4.3 Materials

Materials which come in contact with the peroxide shall have no detrimental influence on the thermal stability of the peroxide e.g. heavy metals (copper), accelerators, acids, amines, etc.

If construction materials are used, they shall be fire resistant according to NEN 6069 [19] for at least 30 minutes. When a higher resistance is required it is specified in the text. A higher resistance is not required for the emergency vent.

The areas in front of emergency reliefs shall be kept free. No obstacles like brushwood, trees etc. shall remain in the emergency area.
For large storage rooms (> 1000 kg) the peroxide shall be stocked at least 0.5 meter away form the outlet of the emergency relief.

4.4 Catch basin

In order to prevent spreading of the fire and to prevent soil pollution it is required that fire fighting water and leaking peroxide is channelled to a liquid tight basin.
The basin can be situated either on the floor of the storage facility or at a safe outside location. More than one storage facility may be connected to the outside catch basin.
The catch basin shall have a capacity of:

- 10% of the volume of the maximum amount of stored product (or largest connected storage room), plus,
- 40 minutes of water supply of the installed system.

The capacity shall at least be large enough to contain the maximum amount of stored product (from the largest connected storage room).

Confinement of peroxides in channels and basins is to be avoided. The maximum thickness of the peroxide layer in a catch basin shall therefore be restricted to 0.5 meter.

Safety distances as given in 7 shall be observed for catch basins.

Channels or gutters directing the fire fighting water to the basin shall not endanger neighbouring objects. Flooding of basin and channels has to be avoided during the fire fighting, e.g. by pumping the (water)layer to a suitable sewer.

Since fire fighting can be rather complex an emergency response plan has to be worked-out with the local fire brigade (see 10.1).

4.5 Fire fighting

According to the Ministry of Interior, all buildings, including storage rooms for organic peroxides, are to be safeguarded in such a way that a fire can be controlled by the fire brigade. A fire is said to be controllable if the fire remains within the fire area during the fire.
A fire is expected to be controllable if measures and provisions as described in this directive (stored amount in relation with the fire resistance of construction materials, fire fighting measures, distances to other objects) are followed. It is assumed that the time period of a fire of an organic peroxide will not exceed 30 minutes.
The wall of a storage building will be subjected to a temperature according to the curve for hydrocarbons. This curve shows a higher temperature increase and a higher maximum value of the temperature.

Fires of organic peroxides shall be fought with adequate fire fighting equipment.
At least one small portable fire extinguisher (CO_2, powder, foam) or hose reel shall be present within a distance of 15 m of the entrance of the storage facility. Portable extinguishers and hose reels shall comply with NEN 2559 and NEN 3211 respectively [12,13]. Cooling the remaining peroxide, after a fire has been extinguished remains necessary to avoid reignition.
Fire fighting equipment as mentioned above is suitable to fight small fires only. Fire fighting systems to fight large fires of organic peroxides shall make use of water sprays or fog. A thin foam layer and powdersystems are suitable to prevent spreading of the fire outside the building. When fire-fighting equipment will be installed to fight large fires, three different systems are distinguished :

a. Automatic sprinkler
Characteristics:
- a fire is detected by temperature or heat (NEN 2535, [16])
- when activated, only the surface area below the sprinkler head is covered
- the capacity of the system equals at least
  10 l/min.m^2 for storage group 3 peroxides
  15 l/min.m^2 for storage group 2 peroxides
  20 l/min.m^2 for storage group 1 peroxides
- the system complies with VAS 1987 or NFC 13. [14,15]

b. Automatic deluge
Characteristics:
- a fire shall at least be detected by temperature or heat, in addition smoke detection may be applied (NEN 2535, [16])
- when activated, the water spray covers the total surface area of the storage facility
- the capacity of the system equals at least
  10 l/min.m^2 for storage group 3 peroxides
  15 l/min.m^2 for storage group 2 peroxides
  20 l/min.m^2 for storage group 1 peroxides
- the system complies with NFC 15 [17]

c. Dry deluge system and assistance of fire brigade (local or company)
The fire brigade shall be present within 6 min and equipped with 1 fire pump truck with complete occupation (6 persons), and a second fire pump which should be available within 10 minutes.
Characteristics:
- a fire shall at least be detected by temperature, in addition smoke detection may be applied (NEN 2535, [16])
- when activated, a water spray covers the total surface area of the storage facility
- the capacity equals at least
  10 l/min.m^2 for storage group 3 peroxides
  15 l/min.m^2 for storage group 2 peroxides
  20 l/min.m^2 for storage group 1 peroxides
- the system complies with NFC 15 [17]

Fire fighting systems, in particular system c. or alternative systems shall be discussed with the local fire brigade with respect to alarm procedures and response time of a local fire brigade.

4.6 Electrical requirements

Electrical equipment within the facility shall satisfy the requirements of zone 2 and temperature group T3 [8]. The compressors of the cooling equipment shall be placed outside the storage facility but not within the emergency relief zone.

4.7 Placards

The following placards shall be shown clearly on the door(s) or covers of the storage facilities:
- a peroxide (transport) label as shown in annex 4
- a placard to prohibit smoking
- a placard to wear safety goggles.

5. Storage facilities

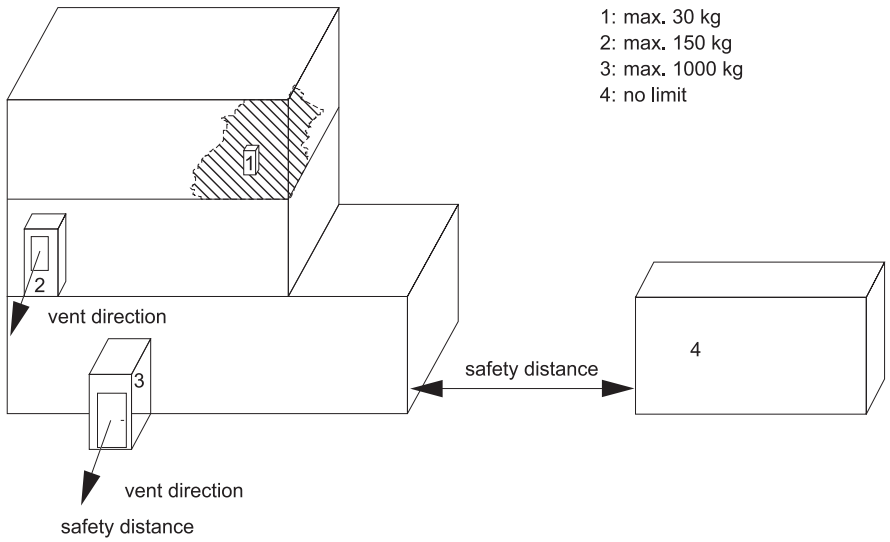
Storage facilities as meant in this chapter are facilities suitable for the long and short term storage of packaged organic peroxides. The storage of organic peroxides shall in general take place in dedicated storage facilities. Mostly the facilities should comprise of a detached store and in a few cases facilities integral with a building are allowed[1)]. For long term storage, four different types of storage facilities are distinguished, depending on the amount of peroxide to be stored:

- storage of sample quantities - < 30 kg see 5.1
- storage of small quantities - < 150 kg see 5.2
- storage of medium quantities - < 1000 kg see 5.3
- storage of large quantities - > 1000 kg see 5.4

For short term storage, a daily stock facility is to be used, see 5.5.

The general requirements for the storage facilities of organic peroxides concern construction of the building, fire fighting provisions, electrical installations and safety distances. Safety distances are the necessary distance between the storage facility and its surrounding endangered objects (houses, plants, etc.) The distances depend on the amount of peroxide, type of peroxide, safety provisions and type of exposed objects. The required distances are given in 7.

Figure 1: Example of possible sites for storage facilities



1) detached: a building or outside location solely used for the storage of organic peroxides
integral: part of or inside a building separated from other activities by partition walls

The general requirements for fire fighting systems, emergency basins and construction materials are given in 4. All safety provisions given in this chapter are based on the assumption that the organic peroxides are stored in packages permitted for transport.

5.1 Storage of sample quantities, < 30 kg

Sample quantities of peroxides can be stored in the following facilities:
- cupboard
- refrigerator
- freezer (cabinet of box)

Requirements for the storage are:

a. Location: the facility shall be located at a readily accessible, quiet place provided with an exhaust system, for the removal of incidental decomposition vapours. Not suitable are: canteens, utility rooms, basements, corridors and escape routes.
Samples may be stored in inner receptacles that are allowed for transport (thus without outer packaging) [7].

b. Construction and materials: 4.3 is applicable, except for the fire resistancy.

c. Emergency relief: doors shall open easily in case of a decomposition of the peroxide.

d. Temperature control:
- cupboard, for peroxides with $T_c \geq 30$ºC, apply passive cooling, place out of direct sunlight
- refrigerator for peroxides with 10ºC $\leq T_c < 30$ºC
- freezer for peroxides with $T_c < 10$ºC
Add (dry) ice when cooling unit fails.

e. Safety distances: No safety distances have to be observed. Materials in the vicinity of the facility shall be non-combustible (NEN 6064, [9]). Smoking and open flames shall be prohibited within a distance of 1 m from the facility.

f. Catch basin: The packages, preferably of plastic, (polyethylene) of maximum 1.0 kg each, shall be placed in a liquidtight tray.

g. Fire fighting: a handoperated extinguisher shall be placed near the facility.

h. Electrical requirements: only explosionproof electrical equipment shall be applied inside the storage facility.

i. Placarding: 4.7 is applicable.

5.2 Storage of small quantities, < 150 kg

Small quantities of organic peroxides can be stored in outside or inside vaults/fixed cupboards. The facility shall have an emergency relief directly to outside.

Requirements for the storage are:

a. Location: - outside or inside another building:
for storage group 1 peroxides only outside facilities are allowed.

b. Construction and materials: 4.3 is applicable.
The facility shall be capable to withstand a static internal overpressure of 0.06 bar except for the emergency relief.

c. Emergency relief: 0.25 m^2 opening connected directly to the outside.
Opening pressure shall be substantially lower than 0.06 bar (overpressure).

d. Temperature control: 4.1 is applicable.

e. Distance requirements: no objects are allowed within 2 m from the emergency relief vent.
Smoking and open flames are prohibited in this area.
Apart from this no safety distances are required.

f. Catch basin: The basin should at least be large enough to contain the maximum amount of stored product.

g. Fire fighting: a handoperated fire extinguisher.

h. Electrical requirements: 4.6 is applicable.

i. Placarding: 4.7 is applicable.

5.3 Storage of medium quantities, 150 - 1000 kg

Medium quantities of organic peroxides can be stored in facilities which may be detached or integral with a building. Peroxides of group 1 are allowed in detached facilities only.

Requirements for the storage are:
a. Location: a detached facility shall be located at a safe distance from other buildings.
The integral facility shall be located adjacent to an outside wall or the roof to facilitate emergency venting.

b. Construction and materials: for a detached facility 4.3 is applicable.
For an integral facility the partition walls and inside doors and ceiling shall have a fire resistance according to NEN 6069 of at least 60 min. Inside door(s) shall be self-closing to the inside of the integral facility. The integral facility shall have a mechanical strength of 0.06 bar overpressure with the exception of the emergency relief.

c. Emergency relief: 4.2 is applicable.
The opening pressure shall be sufficiently lower than the mechanical strength of the building.
The walls within a distance of 2 m horizontally and 4 m vertically of the emergency relief should be fire resistant according to NEN 6069 [19]) for at least 60 minutes.
No objects are allowed within 5 m of the emergency relief (vent zone). Smoking and open flames are prohibited in the vent zone.

d. Temperature control: 4.1 is applicable.

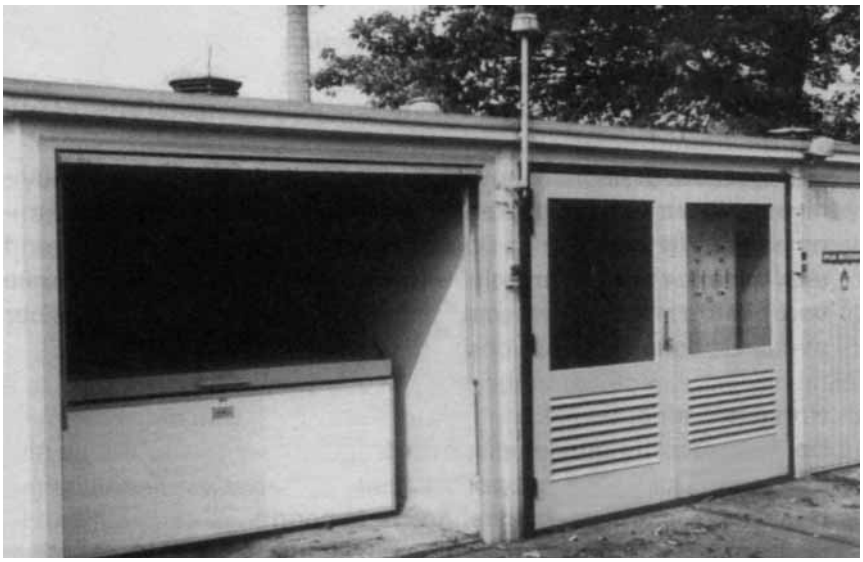
e. Distance requirements: chapter 7 is applicable for detached storage facilities.
In front of the emergency relief of an integral facility 7 is applicable.

f. Catch basin: 4.4 is applicable, with the provision of 15 min. water supply instead of 40 minutes.

g. Fire fighting: For integral facilities one of the fire fighting systems described in 4.5 for large fires is to be applied

h. Electrical requirements: 4.6 is applicable.

i. Placarding: 4.7 is applicable.



Example of storage facility with less than 1000 kg

5.4. Storage of large quantities, >1000 kg

Large quantities of organic peroxides shall be stored in detached facilities only. The facility may consist of several smaller units, compartments, each having an outside door.
In case the facility is divided into compartments the requirements with respect to safety distances and emergency venting can be applied to each compartment provided that:

- the separation walls shall have a fire resistancy according to NEN 6069 of at least 60 min.
- the walls adjacent to the wall or roof containing the emergency relief are extended by 0.5 m.

Requirements for the storage are:

a. Location: at a safe distance from other buildings in particular offices.
   The storage facilities shall be easily accessible for fire brigades.

b. Construction and materials: the facility shall be such that the packages are weather protected (rain/snow, storm, direct sunlight). Paragraph 4.3 is applicable.

c. Emergency relief: 4.2 is applicable.

d. Temperature control: 4.1 is applicable. Two independent temperature indicators with temperature alarms are required for storage facilities in which peroxides with a prescribed T_c are stored. An alarm is to be given when T_E is exceeded. One of the indicators may be replaced by a smoke or gas detector connected to a warning system.
   In case more than one product is stored in one room, the lowest T_c and T_E do apply.

e. Distance requirements: chapter 7 is applicable.

f. Catch basin: 4.4 is applicable.

g. Fire fighting: the safety distances may be reduced when one of the fire fighting systems mentioned in 4.5 is applied.

h. Electrical requirements: 4.6 is applicable.

i. Facilities have to be protected against lightning according to NEN 1014 [18].

j. Placarding: 4.7 is applicable.

Example of a storage building

5.5 Daily stock

The “daily stock storage unit” is a facility used for the temporarily (max. 72 hrs.) storage, tapping and distribution of the amounts of organic peroxides required for the production process and for the installation of apparatus required for the above mentioned activities. Daily stock facilities may be detached or integral with a production building.

a. Location: daily stock facilities which are integral with a production building shall be located at an outside wall or the roof.

b. Construction and materials: Except for the emergency vent the walls, roof and floor shall have a fire resistancy according to NEN 6069 of at least 60 min. for peroxide quantities less than 1000 kg and a fire resistancy of 90 min for quantities more than 1000 kg. The facility shall have a mechanical strength of 0.06 bar. Inside doors shall be self closing and have a fire resistancy of at least 60 min. For quantities larger than 1000 kg this door opening shall be closed with a fire door of at least 90 min fire resistancy.

c. Emergency relief: 4.2 is applicable.
The opening pressure shall be sufficiently lower than the mechanical strength of the building.
The walls within a distance of 2 m horizontally and 4 m vertically of the emergency relief should be fire resistant according to NEN 6069 [19]) for at least 60 minutes.
No objects are allowed within 5 m of the emergency relief (vent zone). Smoking and open flames are prohibited in the vent zone.

d. Temperature control: 4.1 is applicable.

e. Safety distances: no obstacles shall be allowed in the venting zone of the emergency relief within a distance of:
- 2 m for peroxide quantities less than 150 kg
- 5 m for peroxide quantities less than 1000 kg
- 10 m for peroxide quantities more than 1000 kg

Smoking and open flames are prohibited within a distance of 2 m from daily stock facilities.

f. Catch basin: 4.4 is applicable, with the provision of 15 min water supply if the stored amount does not exceed 1000 kg

g. Fire fighting: 4.5 is applicable. One of the fire fighting systems mentioned in 4.5 has to be applied.

h. Electrical requirements: 4.6 is applicable.

i. Placarding: 4.7 is applicable.

6. Storage in tanks and vessels

In order to facilitate the safe storage and handling of liquid organic peroxides it can be advantageous to store organic peroxides in tanks or supply installations such as dosing vessels. Storage of this type shall be designed and operated with great care as peroxide decompositions in metal containers can result in violent explosions with fragmentation of the container. A basic safety requirement is that such accidents do not cause casualties. The accidents can be prevented for some peroxides in tanks of restricted volume and equipped with adequate venting devices. Detailed guidelines to this extent are hard to give as practical experience and test data are still limited.
By dilution of concentrated peroxides safe storage in tanks is feasible for most peroxides. Organic peroxides type F, listed in Annex 2, may be considered for storage in tanks. Dilutions of concentrated peroxides made by the users themselves are not listed in annex 2. The decomposition reaction may be less violent than that of the concentrated peroxide. Nevertheless, the reduction in violence depends on the type of diluent used. Any change in classification shall be based on tests, in a similar way as for the listed peroxides. If tested, these dilutions have to be treated accordingly. Information on this can be obtained from the supplier of the peroxide or a specialized institute, like TNO Prins Maurits Laboratory.
Investigations carried out so far do make it possible to issue some general guidelines on the safety requirements for storage tanks and dosing vessels.

6.1 Storage tanks

The storage in tanks is allowed for certain organic peroxides, type F. The safety of the peroxide in the tank has to be proven. Emergencies to be taken into account are self accelerating decomposition of the peroxide and fire engulfment of the tank (heat load 110 kW/m^2).

Application for tank storage has to be supported by a test report covering among others the following items:
- compatibility of all materials normally in contact with the peroxide
- data to enable the design of the pressure and emergency relief devices taking into account the design characteristics, such as mechanical strength, of the tank. 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.
- data to support the proposed storage- and emergency temperature. Tank size, insulation etc. influence the temperature at which self-heating will occur i.e. the SADT of peroxides in tanks differs from the SADT of peroxides in (smaller) packages.
- any special requirements necessary for the safe storage of the peroxide.
- the safety provisions on the service equipment (external piping, valves, pumps, etc.).

The requirements with respect to the storage tank are:
a. The maximum contents of the tank shall not be more than 100 m^3.

b. If the SADT of the peroxide in the tank is 55ºC or less, or if the tank is constructed of aluminium, the tank shall be completely insulated. The insulating material shall be non-combustible [9,27].

c. The temperature of the tank contents has to be monitored by at least three thermometers of which:
   - two independent thermometers shall be located in the liquid phase with alarm set points at the maximum storage temperature and high alarm set points at the emergency temperature
   - at least one thermometer in the vapour phase with alarm set at 50ºC or lower.

d. Organic peroxides which are stored at temperatures above their flash point, require inertisation of the vapour space to avoid explosive vapour/air mixtures.

e. Each tank has to be connected to a catch basin. Several tanks may be connected to one basin. The capacity of the basin shall be 150% of the content of the largest connected tank.

f. For the determination of safety distances according to 7.3, peroxides stored in tanks shall be treated as “storage group 2” peroxides although they are classified as storage group 3 peroxides.
   The distance from peroxide tank (peroxide type F) to peroxide tank can be reduced to half the diameter of the tank measured from wall to wall and limited safety provisions for distances are applicable (see 7.3), if
   - the tanks are insulated with a material with a fire resistancy according to NEN 6069 [19] of at least 60 min.

   or
   - adequate deluge systems are installed at the outside of the tank to protect the tank against external fires and to provide additional cooling.

g. In addition to the cooling requirements given in 4.1.1 tanks containing cooled peroxides shall be equipped with a back-up system.

h. Pipe connections to the tank shall be provided with valves, close to the tank and readily accessible. The valves shall be closed except for loading, unloading and recirculation operations. The connections of the peroxide tank shall be distinctly different from other non-peroxide tank connections.

i. Peroxide tanks shall be provided with lightning protection according to NEN 1014[18].

The general guidelines for the construction, inspection and maintenance of tanks for flammable liquids [20] shall be observed where the above requirements prevail in case of conflict.

6.2 Dosing vessels

Supply vessels, day tanks, etc. are covered in this directive by the term dosing vessels. They are to be regarded as storage or daily stocks for organic peroxides.
In general, the contents of dosing vessels which may be allowed for peroxides depend on the type of peroxide:
- Organic peroxide type C, max. 100 l.
- Organic peroxide type D, max. 200 l.
- Organic peroxide type E, max. 1500 l.
- Organic peroxide type F, max. 5000 l. (10000 l for storage group 4 peroxides)

All vessels should be adequately vented to cope with vapours released during a decomposition reaction. This can be achieved for instance by a hinged lid, covering the entire top of the vessel. For larger quantities explosion of the vessel in the event of a self accelerating decomposition reaction of the peroxide, may not be avoided. Blast cells would be necessary to arrive at a safe design.

The dosing vessels with a content larger than:
- 30 l for type C peroxides or,
- 60 l for type D peroxides or
- 225 l for type E peroxides

shall be located in:
- a separate building, taking into account safety distances as given in chapter 7. Guidelines for storage rooms are applicable

or,
- a separate room, satisfying the requirements of a daily stock room. Maximum allowable total quantity per room is 5000 litres with a maximum of five vessels.

Adequate measures to control the temperature of the dosing vessels themselves or the whole room/building shall be applied.

The temperature of the peroxide inside the vessel has to be monitored:
- for peroxides with a $T_c \leq 20°C$ by at least two thermocouples
- for peroxides with a $T_c > 20°C$ by at least one thermocouple.

The alarm set point shall be at the storage temperature and at the emergency temperature. Higher temperatures are allowed if additional safeguards are applied.

The temperature of the vapour phase inside vessels shall be measured for vessels larger than 200 l with an alarm set at 50ºC.

Peroxides which are stored at temperatures above their flash point, require inertisation of the vapour space to avoid explosive vapour/air mixtures.

6.3 Auxiliary equipment

General guidelines to be observed in the design of auxiliary equipment are:

- compatibility of the peroxide with the construction materials of the equipment;
- temperature control of the peroxide in the equipment and avoiding operations which cause heat developments;
- adequate safety provisions like relief valves and rupture discs to cope with uncontrolled decompositions of the peroxide in the equipment;
- residence times shall be limited and purging of the equipment with suitable solvents is recommended to avoid hold-up.

Specific design rules concerning dosing equipment are beyond the scope of this booklet. Experts are to be consulted to obtain the best practical and technical means.

7. Safety distances to be applied

External safety distances (distances to objects outside the property boundary) between storage rooms for organic peroxides and sensitive objects are not required. If one wants to take into account effect distances to objects the procedure as outlined below can be followed.

In determining the distance between stores for organic peroxides and surrounding objects, allowance shall be made for a fierce fire in the peroxide store. Furthermore, a store shall give protection against an external fire as such a fire may lead to decomposition and ignition of the peroxides. Peroxides of storage group 1 may additionally show explosions of individual packagings.

Scenarios used to determine the separation distances for stores of organic peroxides are:
a. Fire in the peroxide store
   Determines the distances relative to surrounding objects on the basis of the effect that burning peroxides may have on these objects.
b. Fire in an object in the vicinity of the peroxide store.
   The result may be fire in the 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 on the assumption that as a result of the heat radiation of the burning object on the peroxide store a decomposition or explosion of the peroxide can be initiated. It should be mentioned here that explosions are to be expected only for peroxides of storage group 1 with an explosive subsidiary risk label for transport, see Annex 3.

In determination of the distances between organic peroxide stores and other objects, the heat radiation of a peroxide fire has been used. The technical data given in references 21 to 24 served as an information basis on peroxide fires.
The acceptable heat radiation values for exposed objects within the property boundary were taken from the limit values issued by the Ministry of Interior.

7.1 Limit values

The required safety distance between storage facilities of organic peroxides and other objects depends on:
- storage group of the peroxide
- stored amount of peroxide
  - safety provisions of the storage facility
- type and safety provisions of the exposed object
- allowable limit values for exposed objects

The Ministry of the Interior, Fire Services and Crisis Management Directorate in the Netherlands is using the following limit values with respect to heat radiation intensity:
- Man, prolonged exposure 1 kW/m^2

- Man, in rapid flight (10 seconds) 3 kW/m^2
- Man, exposure for 5 seconds 10 kW/m^2
- Equipment, including tanks 10 kW/m^2
- Scorch damage to wood 10 kW/m^2

7.2 Types of objects

Three types of exposed objects are distinguished:

Type 1 objects are facilities outside the property boundary. External safety distances are not required to type 1 objects. The distances given in 7.3 are recommended safety distances based on the fire hazard (heat radiation ≤ 1 kW/m^2).

Type 2 objects are facilities within the property boundary where people are at work, e.g.:
workshops, offices and control rooms on the site
The property boundary itself is also regarded as a type 2 object.
The allowed heat radiation for type 2 objects is 3 kW/m^2.

Type 3 objects are facilities where in general no people are at work, e.g.:
- other storage facilities
- buildings and production facilities without permanent occupation

The allowed heat radiation for type 3 objects is 10 kW/m^2.

7.3 Effect distances

The required distance for peroxides of storage group 1, 2 and 3 with respect to objects of type 2 and 3, are given in table 4. Those mentioned for type 1 objects are recommended distances based on the fire hazard.
Peroxides of group 4 do not require distances for reasons of peroxide hazards. For these peroxides the distances to be observed are still subject to general (local) regulations. When peroxides of different storage groups are stored in one room, the most severe classification shall be used for the determination of distances. The distances shall further be based on the total stored amount. Peroxides of storage group 4 and 5 do not have to be included.

The safety distances given in table 4 are required for quantities larger than 150 kg. Table 4 provides distances as a function of the floor area, A. It is assumed that 1 m^2 floor area contains 500 kg product. For the determination of safety distances the following formula is applicable:

$$d = c * A^{1/3} = \frac{c}{8} * m^{1/3} \quad \text{en} \quad A = \frac{m}{500}$$

in which: A = floor area (m^2)
m = total mass (kg)
d = effect distance (m)
c = constant, values listed in table 4

The effect distances shall be determined both on bases of the surface area and the total amount of product stored. The largest distance of the two calculations is applicable.
For products of group 3 fixed distances, independent of mass and floor area, are given in table 4.

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

The effect distances for storage facilities with storage group 1 peroxides are based on a burning rate (BR) of 1200 kg/min (see Annex 5). Since many peroxides burn less vigorous, the distance for organic peroxides type C of storage group 1, is given by the formula

$$d = c * A^{1/3} * \sqrt{\frac{BR_c}{1200}}$$

BR_c can be obtained from the burning tests in packages as elucidated in Annex 5.

Table 4: Effect distances (in meters) of storage facilities to other objects

	safety-provisions	**storage group 1**[1)] **c * A$^{1/3}$**	**storage group 2**[1)] **c * A$^{1/3}$**	**storage group 3**
type 1 objects	NO	36 * A$^{1/3}$	16 * A$^{1/3}$	25
	LIMITED	24 * A$^{1/3}$	11 * A$^{1/3}$	16
	EXTENDED	16 * A$^{1/3}$	7 * A$^{1/3}$	10
type 2 objects	NO	24 * A$^{1/3}$	11 * A$^{1/3}$	16
	LIMITED	16 * A$^{1/3}$	7 * A$^{1/3}$	10
	EXTENDED	11 * A$^{1/3}$	4.5 * A$^{1/3}$	5
type 3 objects	NO	16 * A$^{1/3}$	7 * A$^{1/3}$	10
	LIMITED	11 * A$^{1/3}$	4.5 * A$^{1/3}$	5
	EXTENDED	7 * A$^{1/3}$	3 * A$^{1/3}$	0

[1)] The minimum distances are equal to the fixed distances of storage group 3.

The provisions given in column 2 of table 4 refer to:

‘NO’: The storage facility has no provisions other than the minimum requirements of chapter 4, liquid tight floor/basin as described in 4.4;

‘LIMITED’: The storage facility is provided with a limited set of safety provisions being:
- a liquid tight floor/basin (see 4.4)

and
- one of the fire fighting systems as described in 4.5;

‘EXTENDED’ (not in vent direction) The storage room is provided with an extended set of safety provisions, being:
- a liquid tight floor/basin (see 4.4)

and
- one of the fire fighting systems as described in 4.5.

and
- walls with a fire resistancy according to NEN 6069 [19] of at least 60 minutes, except when it constitutes the emergency relief vent

and
- an emergency relief vent as described in 4.2 with a fire resistancy according to NEN 6069 of at least 30 min

and
- the facility shall be capable of withstanding an internal pressure of 0.2 barg when storage group 1 peroxides are stored or 0.06 barg when storage group 2 peroxides are stored;

‘EXTENDED’ (in vent direction)
- The storage room is provided with: an extended set of safety provisions as indicated for extended

and
- the walls of endangered object facing the emergency vent, within the hazard zone, are fire resistant according to NEN 6069 for at least 60 min.

The effect distances given in table 4 are shown as a function of floor area or amount of stored product in fig. 4a and 4b.
An example of how to apply these rules is given in figure 2.

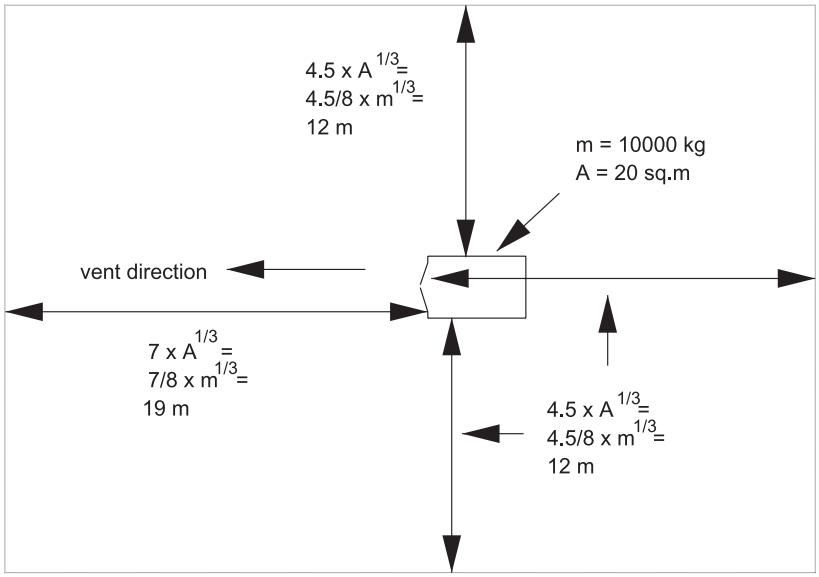


Figure 2: Effect distances to property boundaries (type 2 object) for 10,000 kg organic peroxides of storage group 2 in a storage facility with extended safety provisions and with the doors as emergency relief vent

In a few cases the safety distances can be reduced to zero when a fire protection wall effectively shields the endangered object against a fire in the storage facility, and if the endangered object fulfils certain requirements. The required provisions are:

- the fire protection wall separating the storage facility from the endangered object shall have a fire resistance according to NEN 6069 of 120 minutes, 90 minutes and 60 minutes for storage group 1, storage group 2 and storage group 3 peroxides respectively. The fire protecting part shall be extended vertically until the roof of the tallest building and be extended horizontally over a distance equal to the width of the endangered object, but more than the distance as required in table 4 for "EXTENDED" safety provisions is not required,

and,

- the storage facility satisfies the criteria for an "EXTENDED" set of safety measures, with the provision that an automatic fire fighting system is installed,

and,

- the roof of the endangered object shall be fire resistant for at least 30 minutes,

and,

- for type 1 and type 2 objects, the emergency vent shall be directed in the opposite direction of the endangered object,
- for type 3 objects, the emergency vent shall not be directed towards the endangered object.

Elucidation

Precise guidelines for the reduction to 0 meters are hard to specify as the additional safety provisions shall be adopted to the local situation. In stead of a fire wall it is also possible to construct the endangered object of materials which fulfil the same requirements.
An example is given in figure 3.

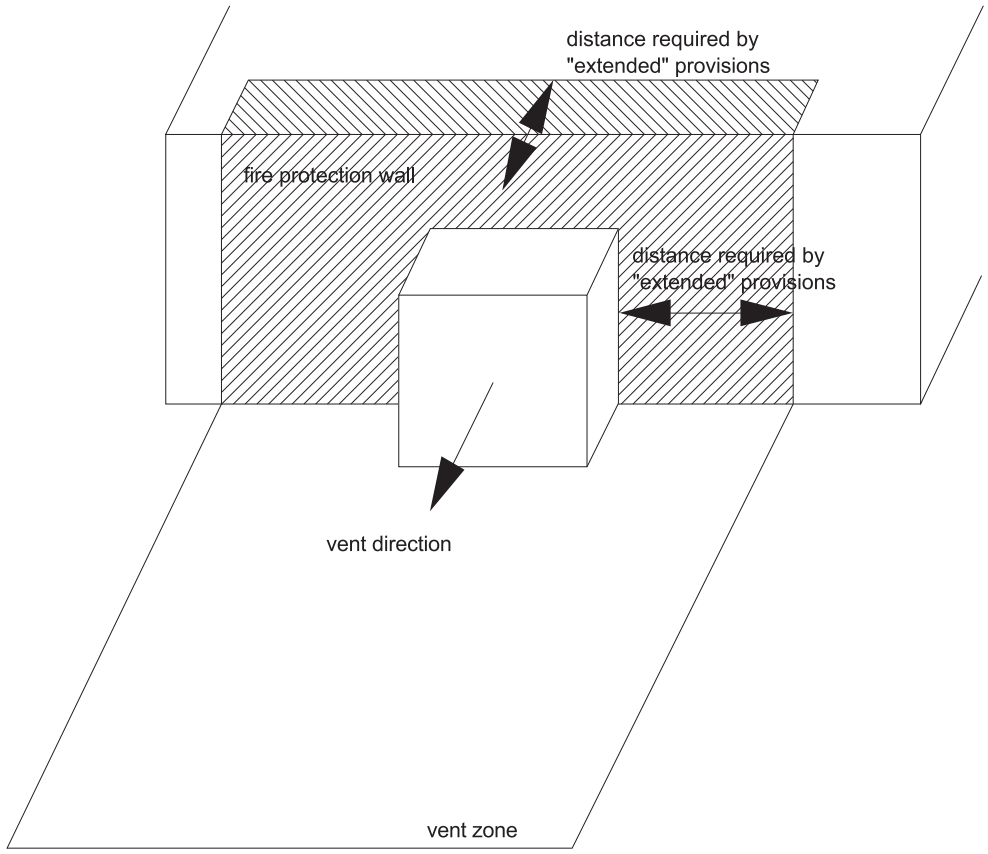


Figure 3: Example of a reduction to zero meters

Figure 4a: Effect distances for storage group 1 peroxides

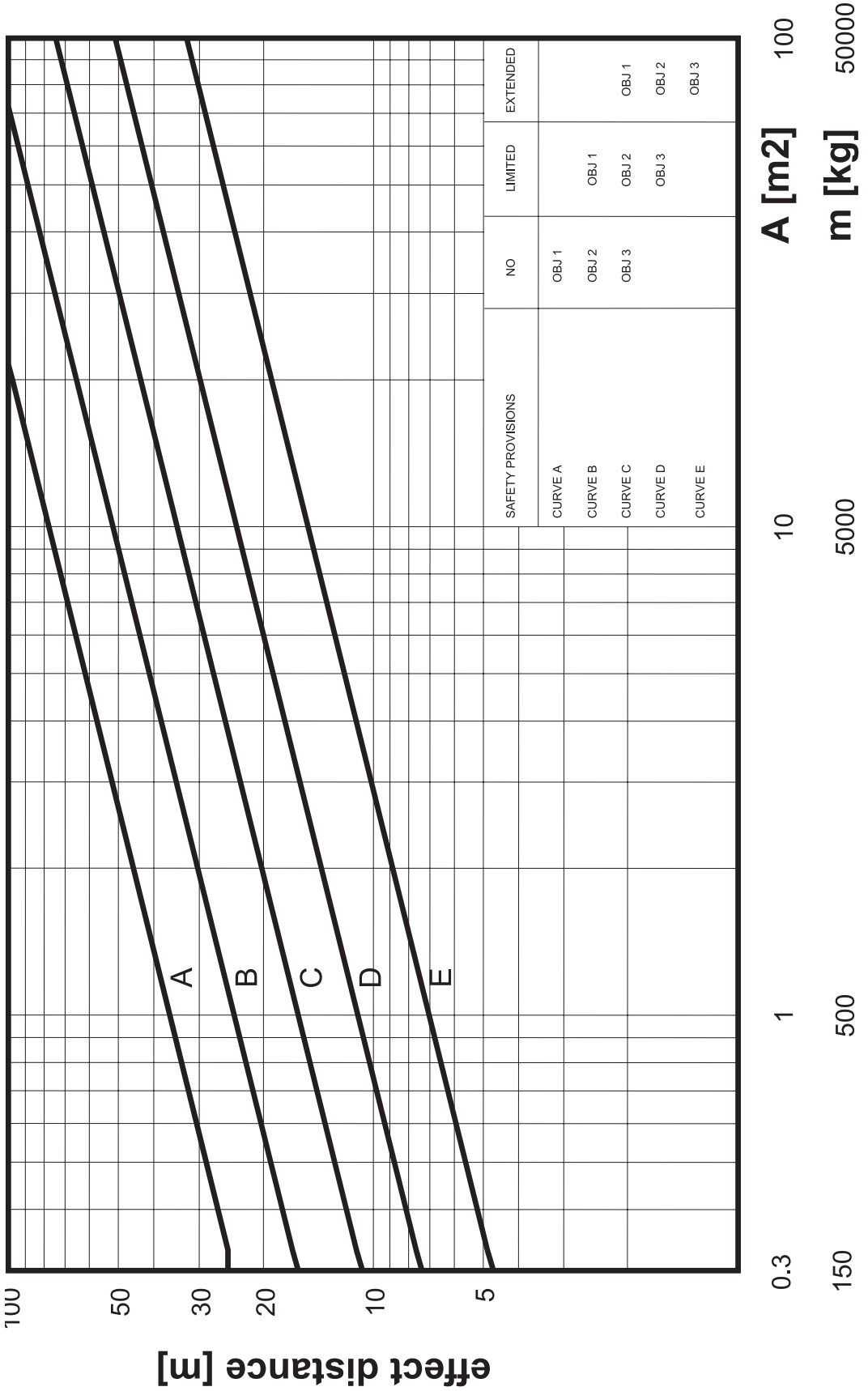
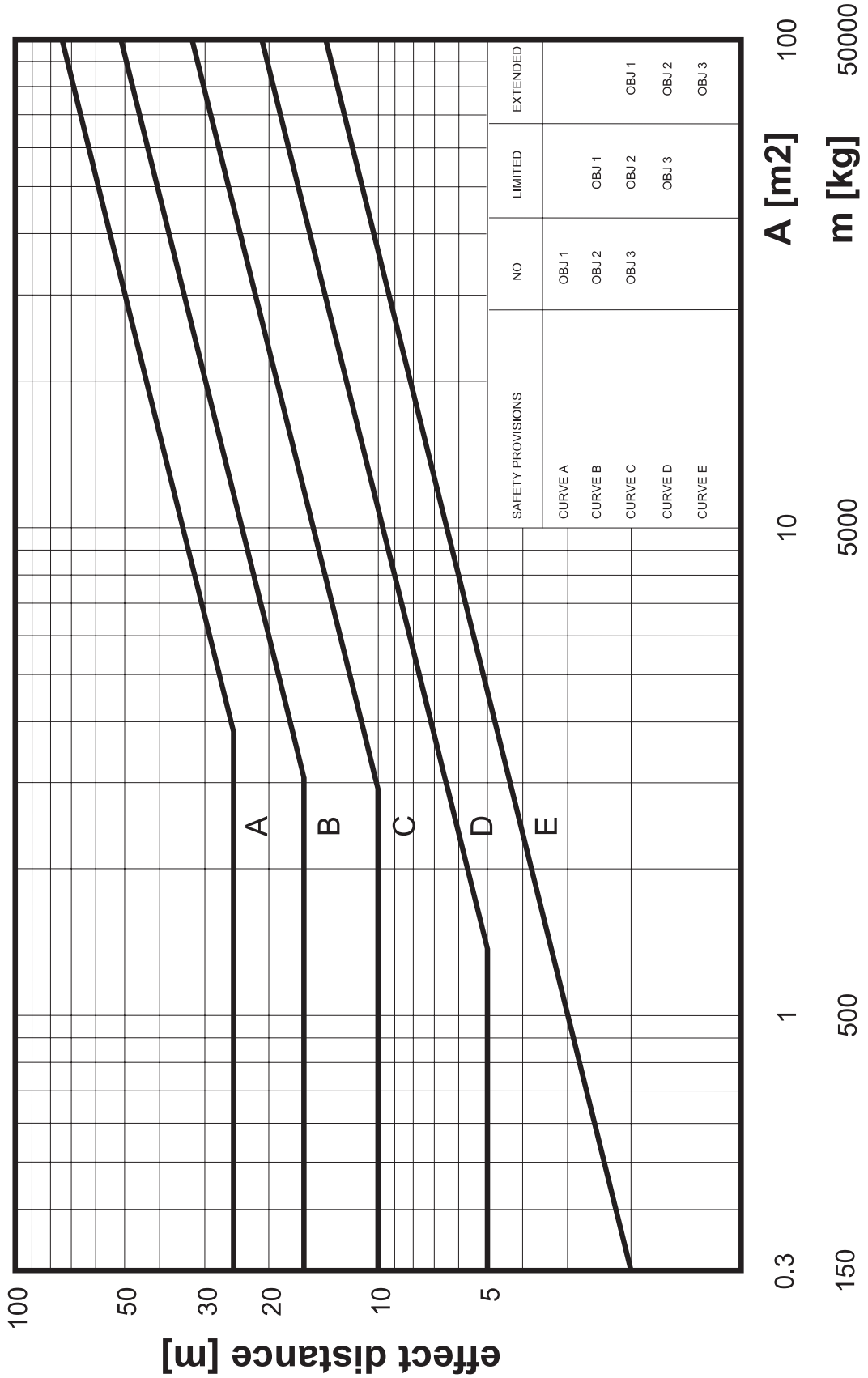


Figure 4b: Effect distances for storage group 2 peroxides



8. Marking and labelling

8.1 Stores

Stores, storerooms, cupboards and bins must be clearly marked with the organic peroxide label for transport (see annex 3). If direct marking is not reasonably perceptible or effective, the marking shall be displayed close to the store.
No-smoking signs shall be clearly displayed outside the buildings and inside the areas and rooms containing organic peroxides.
The areas, stores and storerooms with organic peroxides shall be marked by a placard requesting the wearing of safety goggles.
The maximum temperature of cooled stores shall be clearly visible outside the store.

8.2 Packages

A package with organic peroxides shall be labelled with the organic peroxide label for transport (see Annex 3) and the relevant symbols according to the Wet Milieugevaarlijke Stoffen. It shall further carry the proper shipping name, the chemical name, and the commercial name, if any, to indicate its contents [3].
Packages with organic peroxides that have explosive properties for transport, must bear a subsidiary explosive risk label [3].
Packages with organic peroxides that have corrosive properties for transport, must bear a corrosion label [3].
The main hazards of the organic peroxide in a package shall be pointed out by showing the appropriate Risk sentences and the basic safety precautions shall be shown by providing the relevant Safety sentences (see Annex 4).

9. Operations

9.1 Logistics

9.1.1 Supervision of stores

Only well-instructed personnel shall be appointed to manage and supervise the stores of organic peroxides. Each store shall have a supervisor.

9.1.2 Supply

Upon arrival, a consignment of organic peroxides shall be unloaded and appropriately stored as quickly as possible.
The temperature inside a transport unit or van shall be measured before unloading the peroxides. This temperature, the name of the peroxides, the batch number, the date of receipt and the name of the supplier shall be taken down in the stock administration. The temperatures shall not be measured with mercury thermometers.
If the measured temperature exceeds the emergency temperature, the consignment shall not be unloaded, and the responsible management and the management of the supplying firm shall be notified. The van carrying the consignment must be moved to a pre-determined safe place, pending the decision of the responsible management. The responsible management will decide on a final destination of the peroxide in consultation with the supplier of the peroxide (see also chapter 10).
If the temperature in the refrigerated van is between the control and the emergency temperature, the organic peroxide can be unloaded, but must be kept under surveillance until the control temperature is reached.
Cooled organic peroxides shall always be unloaded in such a way that heating of the organic peroxide by contact with ambient air and/or by any other heating source is minimised (e.g. to less than 30 minutes).
Damaged packages showing a leakage or a high potential to leakage shall not be placed in the storage facility. The contents of the damaged packages shall be transferred to a suitable packaging or reservoir, and be used immediately. “Spilled” product shall be destroyed.

9.1.3 Disposal

The correct disposal procedures for waste materials shall be considered carefully and advice shall be sought from the supplier.
Organic peroxides can be destroyed by burning, neutralising or dilution till the active oxygen content < 1% (see 2.4). This may be carried out by the factory itself in a justified and knowledgeable manner, otherwise the organic peroxides shall be sent to an official waste processing industry with a well-defined indication of the type of substance.
The destruction of spilled or contaminated organic peroxides shall be effected in a safe manner in order to eliminate the risk of fire and/or explosion. For example, methyl ethyl ketone peroxide can be destroyed by adding small quantities to a 20% sodium hydroxide solution under continuous stirring. The mass of the solution shall exceed the mass of the peroxide by a factor of ten. In case of benzoyl peroxide a 10% sodium hydroxide solution can be applied using four times the mass of the spill.

Empty packages of organic peroxides shall be treated and dispatched as dangerous goods until they are adequately cleaned. They shall be stored in an appropriate place on the site but not in the peroxide storage facilities.

9.1.4 Stock administration

The stored amount and types of organic peroxides shall be known at any time e.g. from a stock administration. The supervisor shall check the stock and stock administration once a month. The administration can a.o. contain the following entries:

- date of entry and of issue,
- type and quantity involved,
- storage data (maximum, minimum storage temperature, package size, etc.),
- supplier or consumer.

The supervisor will administer store particulars, such as:

- date and times of inspections,
- observations of inspections and actions taken,
- abnormalities in store such as leaking packages, failure of cooling equipment, etc., and the subsequent actions taken.

9.2 Handling

9.2.1 Protective measures

Peroxides shall preferably be used, handled and stored in dedicated areas, which are adequately ventilated and which can be adequately and regularly cleaned.
Access to the stores shall be restricted to authorised personnel only.
The contact between peroxides and eyes or skin must be avoided. Especially during maintenance. and in the event of failures and leakages, brief moments of exposure to organic peroxides may occur. Therefore, when working with peroxides a face shield or closefitting safety goggles are necessary for eye protection and the use of suitable protective gloves is required for skin protection.
The use of protective clothing like overalls, laboratory coats, etc. is recommended as well.
Smoking in the stores, and storage and handling areas shall be prohibited and warning signs shall be well displayed accordingly.
The consumption of food is prohibited in the storage and handling areas. Protective clothing shall not be worn in the areas dedicated to the consumption of food and drinks.

9.2.2 Storage

The storage facilities shall only contain organic peroxides in original packagings that are allowed for transportation [7].
Organic peroxides shall be stored in dedicated stores of organic peroxides only. The stores shall not comprise any other chemicals, substances, or materials, except peroxides of storage group 5 (see 2.4).
Organic peroxides decompose slowly and as such cannot be kept for an unlimited period of time. Therefore, they shall be used on a stock rotation basis. If organic peroxides are no longer used they shall be removed and destroyed in a safe manner (see 9.2.4).
The packages with peroxides shall be stacked in a stable manner with a maximum stack height of three meters at maximum, in such a way that escape routes are not obstructed.
Packages with organic peroxides that must be kept at temperatures below ambient, shall be stored in such a way that adequate cooling is ensured [see 4.1.1].

Packages or pallets with organic peroxides shall not be stored in contact with the walls of the store. In general, a gap of at least 0.1 m is required. However, refrigerators or freezers containing packages with organic peroxides may contact the walls provided that the cooling efficiency is not interfered with.
The organic peroxides in store shall be inspected at least once weekly. Leaking or bulging packages shall immediately be removed and repackaged or destroyed (see 9.2.4).

Peroxides packagings shall not be opened in the stores except for sampling purposes.
The transfer of liquid peroxides shall be performed using dedicated clean dispensers/siphons or

pumps. The advice of the supplier can be sought on suitable equipment and materials. Particular care is required in the design of pump systems where frictional heating, confinement, overpressurisation or generation of static electricity may occur.
Where appropriate, fork lift trucks and other vehicles used within the hazardous areas associated with package storage and handling areas shall be protected against igniting flammable vapour [25,26]. Indoors the use of electrically-powered vehicles is recommended Outdoors both electrically and Diesel powered vehicles can be used. Battery charging shall not be carried out in hazardous areas and vehicles shall neither be parked in such areas.

9.2.3 Handling

The packages shall be closed immediately after use. Surplus material shall never be returned to the original packages.
Whenever organic peroxides are handled, safety goggles and suitable protective gloves shall be worn as a minimum. Only a daily quantity of peroxide shall be present at the work area. All packages and equipment which come into contact with peroxides must be compatible. Suitable materials include glass, porcelain, polyethylene and certain types of stainless steel.
After termination of activities involving the use of organic peroxides, the remaining organic peroxides shall be returned to the appropriate stores.

9.2.4 Spillages, leakage and destruction

Packages containing organic peroxides shall be inspected at least once weekly. Leaking or bulging packages must be removed and subsequently emptied and disposed of as quickly as possible.
A supply of suitable non-combustible material such as vermiculite, kieselguhr or sand shall be kept readily available for absorption of any spillages which shall be cleared immediately. Spillages shall not be allowed to contaminate drainage or other water systems. Incompatible materials such as rags, sawdust or paper shall not be used.
Spilled peroxides and peroxide soaked adsorbents shall be removed immediately, shall not be confined, and shall be carried off for destruction in an appropriate and properly labelled packaging.
Contaminated areas shall be cleaned with water where necessary.
If the quantity needed is less than the contents of the supply package, the remainder shall be kept free of all incompatible materials and combustibles.

Dispensing of liquid peroxides shall be carried out over a suitable clean spillages retention tray, which is capable of holding the entire contents of the supply package.
All remaining peroxides shall be returned to the appropriate stores.

9.3 Housekeeping

9.3.1 Instrumentation and inspections

All instruments used for normal operation and for emergencies shall be inspected at regular time intervals. A typical inspection scheme is shown in Table 5.

Table 5: Typical Instruments Inspection Schedule

Device	Operational Instrument Check (presence, data output etc.) frequency	Extensive Instrument Check (maintenance, calibration etc.) frequency
temperature indicators	twice weekly	every six months
alarmen	once monthly	every six months
koelinstallatie	once monthly	every six months
sprinkler, deluge systems	according to supplier recommendations	
additional water systems	once yearly	
fire extinguishers	once yearly	

9.3.2 Maintenance and repairs

Prior to maintenance or repairs being carried out in a place where organic peroxides are stored, a work permit in which the assignment, the work conditions and the required safety measures are specified, shall be issued by a competent person. The permit shall be signed by the acting manager, and countersigned by the store supervisor.
Organic peroxides shall be removed, before open flames are used.

The store supervisor will only sign the permit after checking the safe working conditions. The maintenance personnel involved shall be instructed about the required safe working conditions.

10. Emergency response

10.1 Emergency planning

If in a factory the amount of organic peroxides to be stored is such as to require one or more storage buildings, it is imperative that an emergency response plan is available. This emergency response plan may be incorporated in an emergency plan for the whole factory. However, it must be clearly identified for the specific storage facilities. The size and the impact of the plan will reflect the proportions and hazards of the stored quantities.
The emergency response plan, at least, shall provide directions for:

- actuation of an alarm signal,
- actions to be taken in case of dangerous situations with respect to peroxides, such as failure of cooling equipment (see 9.2), fire (nearby or instore), spillages, contamination, self-heating (run-away), etc.,
- installation of an emergency management and crew,
- procedures for notification of responsible management and authorities,
- fire-fighting activities (on-site and off-site),
- first-aid and further medical treatment,
- evacuation procedures (e.g. warning system, evacuation routes, registration and care of evacuees)

All personnel directly or indirectly involved in the storage and use of organic peroxides shall be familiar with the emergency response plan. The emergency response plan shall also be discussed with and made available to the local authorities. This is especially important for the parts concerning off-site help (e.g. fire-brigade, hospital).
The emergency response plan shall be checked and updated at regular intervals, at least once a year. The effectiveness of the emergency procedures shall regularly be tested in practice. Trial alarm in which the complete organization with respect to alarm signalling, rescue service, etc. is tested shall in general be organized in such a way that each staff member involved experiences such an event once a year.

10.2 Cooling equipment

The refrigeration equipment for refrigerated or cooled stores shall be located outside the storeroom. Sufficient space shall be left between the stacks individually and between the stacks and the walls to allow for air circulation (see 4.1.3).
Proper cooling arrangements shall ensure a uniform cooling of all parts of the storeroom.
A temperature alarm, set at the emergency temperature, shall be installed giving a warning to a permanently manned location.
A spare or back-up cooling system is required if the control temperature is ≤ 10ºC, or if the system cannot be repaired within the period of time during which the peroxides heat to the emergency temperature.
A plan of action shall be drawn up that can be used in case of failure of the cooling equipment. This plan of action shall include the following:

- the personnel to be notified in case of 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 repair of the cooling aggregate,
- where ice or dry ice can be obtained that can be placed in the cold store in order to keep the temperature at a certain level in the case of prolonged failure of the cooling aggregate,
- whether water can be used as an emergency coolant (e.g. when the emergency storage temperature is +15ºC),
- whether it is possible to switch to an emergency power supply in case of power failure, and how this can be achieved,
- whether it is possible to transfer the organic peroxides to another cold store and where such a store is located.
- re-entry procedures to the storeroom (e.g. because of increased flammability, lack of oxygen or toxicity in the store).

10.3 Fire fighting

Suitable fire-fighting equipment must be available at all places where organic peroxides are stored and handled. The fire-fighting equipment must be easily accessible in such a way that a fire can be attacked in its early stages. All personnel must be trained to use the small-size equipment. Fire fighting personnel must be available and well-trained with the available equipment.
Large fires shall not be attacked single-handed.
A very small organic peroxide fire can be extinguished with CO_2, although foam, dry powder or water can be used as well. Only water is suitable for larger fires because of its cooling effect. The effect of air sealing is of no importance with organic peroxides: the decomposition of these substances continues even in the absence of oxygen.
A large organic peroxide fire can best be attacked with water which shall be sprayed from a safe distance. When practical, the use of water fog is very effective.
If fire occurs near an organic peroxide stock which cannot be moved away from the fire, apply water for cooling.
In a large scale organic peroxide fire, fire fighting personnel must be protected from potential thermal explosions and ejection of burning peroxide material. Personnel and fire fighting equipment must be stationed a safe distance from the fire.
After extinguishing an organic peroxide fire, an ample amount of water shall be used for cooling of the fire remains to prevent the unburned organic peroxides from reigniting.

10.4 First aid

Organic peroxides are corrosive to the skin and mucous membranes and can cause severe damage to the eyes on direct contact (see 1.4). At any place where organic peroxides are stored or handled, appliances must be available for extensively washing skin and eyes.
Unless mentioned otherwise, in case of an accident the following actions may be carried out by any person, whether or not trained in first aid.

Skin exposure
- Rinse with copious amounts of cold water,
- If skin burns develop, rinse continuously with cold water for 15 minutes,
- Immediately remove contaminated cloths, avoid own skin contact (place cloths in water to prevent spontaneous ignition),
- Cover burnt skin with sterile gauze,
- Consult a doctor.

Eye exposure
- Immediately rinse with lukewarm, slowly running water, during which the eyes shall be kept open; this shall be maintained for at least 15 minutes,
- Cover up serious eye injuries with sterile material,
- Immediately consult an oculist.

Swallowing
- Rinse mouth,
- Give plenty 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 half upright position,
- Administer oxygen 8-10 litres per minute (trained personnel only!),
- Consult a doctor.

11. Management

The management shall appoint a sufficient number of well-instructed personnel to manage, to supervise, and to handle the organic peroxides. The handling of organic peroxides shall only be entrusted to personnel at least 18 years of age, unless in training and continuously supervised according to “Arbeidsbesluit jeugdigen”.

The management provides written instructions concerning
- the safe handling of peroxides,
- the hazards involved with the handling of organic peroxides,
- the use of personal means of protection,
- temperature detection and control in stores,
- the plans and procedures to be followed in case of an emergency.

The management shall
- provide the technical means and facilities to store the peroxides in a correct and safe manner,
- provide accurate and unambiguous instructions for proper handling of peroxides,
- introduce adequate and sufficient inspections and operating procedures,
- introduce emergency and fire-fighting plans, etc.
- introduce a plan in which the actions upon failure of the cooling system are bundled. The actions depend on the type of cooling system, the type of organic peroxides, the temperature limits and the location of the cooling facility.

The management shall audit the technical means and facilities, the instructions, the inspections and operating procedures, the emergency and fire-fighting plans, and the plan of actions upon failure of the cooling system once a year.

The management shall take care that the personnel involved in storage and handling of peroxides shall be given adequate instruction and training, both in unsafe and proper handling of organic peroxides, and in emergency procedures to deal with spillages, contamination, self-heating, fires, loss of refrigeration, ingestion, inhalation, skin and eye contact. Refreshment courses shall be given at least once a year. Instructions and training sessions shall also proceed from the relevant provisions in the Arbowet.

ANNEX 1: Glossary

Active/Available Oxygen Content	The relative amount of peroxygen groups in the molecule as defined in 2.4
Air (circulation of)	Internal flow of air without supply of outside air (see 4.1.3)
Air (ventilation of)	Continuous air supply to and removal from store(see 1.3 and 4.1.3)
Blast cells	Strengthened concrete cells capable of withstanding an explosion (see 6.3)
Bund area	Total area available for leaking peroxide (=Floor area) (see 1.3)
Catch basin	Catch basin for peroxide and fire fighting water to prevent spreading of fire and ground pollution (see 4.4 and 5.1)
Control temperature (T_C)	Maximum transport/storage temperature(see 1.1 and Annex 2)
Daily stock	Intermediate storage area to cover the production of one day or weekend (see 3)
Decomposition	Reaction by which a molecule splits into two or more smaller molecules (see 1 and 1.2)
Deflagration	Heterogeneous decomposition reaction proceeding layer-wise with a velocity rate of the reaction front lower than the velocity of sound in the substance (see 1.2)
Detonation	Heterogeneous decomposition reaction proceeding layer-wise with a velocity rate of the reaction front higher than the velocity of sound in the substance (see 1.2)
Dosing tank	Tank vessel used for supply of peroxide to the reaction vessel or processing equipment(see 6.3)
Emergency relief (vent)	Part of the building e.g. door or panel provided for venting excessive amounts of gases and/or liquids that is sufficiently large to keep the pressure below the strength of the building (see 3.2, 4.2 and 4.3)
Emergency temperature (T_E)	High alarm temperature at which emergency procedures have to be started (see 1.1 and Annex 2)
Exothermic reaction	Reaction which generates heat during conversion (see 1)
Fire resistant	Fire resistance according to NEN 6069 for a specified period of time
Flammability Limit (Lower = LFL)	Lowest gas concentration in air at which no ignition is observed under stagnant conditions (= lower explosion limit) (see 1.3)
Flammability Limit (Upper = UFL)	Highest gas concentration in air at which no ignition is observed under stagnant conditions (upper explosion limit) (see 1.3)
Flash point	Lowest temperature at which a partly condensed vapour can be ignited by a flame (see 1.3)
Freezer	Storage facility that is temperature controlled down to a temperature of less than 0ºC (see 5.1)
Hazard	A chemical or physical condition that has the potential for causing damage to people, property of the environment
High alarm	Alarm to be given at the emergency temperature (see 1.1)
Non-combustible	Material that cannot burn in the sense of NEN 6064
Organic peroxide	Organic chemical which contains the -O-O-peroxy linkage in its molecular structure (see 1)
Peroxide	In this directive identical to organic peroxide (see 1)
Refrigerator	Facility or storage vessel that is temperature controlled down to temperature of 0ºC
Risk	A measure of economic loss or human injury on terms of both the incident of likelihood and the magnitude of the loss or injury

Risk sentence	A warning phrase specifying a potential hazard involved with the chemical under consideration (see 1.2)
Runaway reaction	A reaction which accelerates beyond control and which may result in large changes in temperature (see 1.2)
SADT	Self Accelerating Decomposition Temperature; the lowest temperature at which hazardous self-accelerating decomposition will occur with a substance in the packaging used for transport (see 1.1)
Safety distance	Required distance between the storage location and surrounding objects (see 7.3)
Safety sentence	A phrase providing advise on handling issues to avoid the occurrence of an incident with chemical under consideration (see 1)
Self-accelerating decomposition	Decomposition which accelerates as a function of temperature and/or conversion (see 1)
Stock rotation	Supply and removal of stock according to the first-in/first-out principle (see 9.2.2)
Storage (Central)	Facilities in which main stock is stored
Storage facility	Place or area for the storage of chemicals (see 5)
Storage facility (Detached)	Storage facility that is not integrated with other buildings (see 5)
Storage facility (Integral)	Storage facility that is part of another building (see 5)
Storage group	Subdivision of organic peroxides into five groups with respect to storage hazard (see 2.3)
Storage (Sample)	Facilities in which small quantities are stored for testing or analysis (see 2.3 and 5.1)

ANNEX 2: Currently assigned organic peroxides

Elucidation to the table:

Column	**Description**
Storage group	Classification of the peroxide with respect to storage requirements
Organic peroxide	The chemical name of the peroxide
Concentration	The minimum and/or maximum concentration of the peroxide
Diluent type A	Diluent as defined by the transport regulations as: organic liquids which are compatible with the peroxide and which have a boiling point of not less than 150 ºC. Type A diluents may be used for desensitizing all organic peroxides.
Diluent type B	Diluent as defined by the transport regulations as: organic liquids which are compatible with the organic peroxide and which have a boiling point of less than 150 ºC but not less than 60 ºC and a flash point of not less than 5 ºC. Type B diluents may be used for desensitization of all organic peroxides provided that the boiling point is at least 60 ºC higher than the SADT in a 50 kg package.
Inert solid	Organic or inorganic solids used for the desensitization of organic peroxides provided that they are compatible
Water	The concentration of water
Packing method	Maximum package size for the peroxide as allowed by transport regulations
Control temperature	Maximum storage temperature (see 1.1)
Emergency temperature	Temperature at which emergency actions have to be taken
Number (generic entry)	Generic entry number listed in transport regulations specifying: • organic peroxide type (B to F) • physical state (liquid/solid) • temperature control (when required)
Subsidiary risks and remarks	the class(es), division(s), etc. of important subsidiary risks identified for those products

List of currently assigned peroxides

Stor-age group	Organic peroxide	Concen-tration (%)	Diluent type A (%)	Diluent type B (%)	Inerte solid (%)	Water	Packing Method	Control Temper-ature (°C)	Emergency Temper-ature (°C)	Number Generic entry	Subsidiary risk and remarks
2	ACETYL ACETONE PEROXIDE	≤ 42	≥ 48			≥ 8	OP7			3105	2)
3	„	≤ 32 as a paste					OP7			3106	20)
2	ACETYL BENZOYL PEROXIDE	≤ 45	≥ 55				OP7			3105	
1	ACETYL CYCLOHEXANE-SULPHONYL PEROXIDE	≤ 82				≥ 12	OP4	– 10	0	3112	3)
3	„	≤ 32		≥ 68			OP7	– 10	0	3115	
2	tert-AMYL HYDROPEROXIDE	≤ 88	≥ 6			≥ 6	OP8			3107	
2	tert-AMYL PEROXYACETATE	≤ 62	≥ 38				OP8			3107	
2	tert-AMYL PEROXYBENZOATE	≤ 96	≥ 4				OP7			3105	
2	tert-AMYL PEROXY-2-ETHYL HEXANOATE	≤ 100					OP7	+ 20	+ 25	3115	
2	tert-AMYL PEROXY-2-ETHYLHEXYL CARBONATE	≤ 100					OP7			3105	
2	tert-AMYL PEROXYNEODECANOATE	≤ 77		≥ 23			OP7	0	+ 10	3115	
2	tert-AMYL PEROXYPIVALATE	≤ 77		≥ 23			OP5	+ 10	+ 15	3113	
1	tert-AMYLPEROXY-3,5,5-TRIMETHYLHEXANOAT	≤ 100					OP5			3101	3)
2	tert-BUTYL CUMYLPEROXIDE	> 42 - 100					OP7			3105	
2	„	≤ 42			≥ 58		OP7			3106	
1	n-BUTYL-4,4-DI-(tert-BUTYL-PEROXY) VALERATE	> 52 - 100					OP5			3103	
3	„	≤ 52			≥ 48		OP7			3106	
3	„	≤ 42			≥ 58		OP8			3108	
1	tert-BUTYL HYDROPEROXIDE	> 79 - 90				≥ 10	OP5			3103	13)
2	„	≤ 80	≥ 20				OP7			3105	4), 13)
2	„	≤ 79				> 14	OP8			3107	13), 23)
3	„	≤ 72				≥ 28	OP8,M			3109	13)
1	tert-BUTYL HYDROPER OXIDE + DI-tert-BUTYLPEROXIDE	≤ 82 + ≥ 9				≥ 7	OP5			3103	13)
1	tert-BUTYL MONOPEROXYMALEATE	> 52 - 100					OP5			3102	3)
2	„	≤ 52	≥ 48				OP6			3103	
2	„	≤ 52				≥ 48	OP8			3108	
2	„	≤ 52 as a paste					OP6			3108	
1	tert-BUTYL MONOPEROXYPHTHALATE	≤ 100					OP5			3102	3)
1	tert-BUTYL PEROXYACETATE	> 52 - 77	≥ 23				OP5			3101	3)
2	„	> 32 - 52	≥ 48				OP6			3103	
3	„	≤ 32	≥ 68				OP8,N			3109	
3	„ (in tanks)	≤ 32		≥ 68			M	+ 30	+ 35	3119	
3	„	≤ 22		≥ 78			OP8			3109	25)
2	tert-BUTYL PEROXYBENZOATE	> 77 - 100	≤ 22				OP5			3103	
2	„	> 52 - 77	≥ 23				OP7			3105	

2	„	≤ 52		≥ 48		OP7			3106	
2	tert-BUTYL PEROXYBUTYL FUMARATE	≤ 52	≥ 48			OP7			3105	
2	tert-BUTYL PEROXYCROTONATE	≤ 77	≥ 23			OP7			3105	
1	tert-BUTYL PEROXYDIETHYLACETATE	≤ 100				OP5	+ 20	+ 25	3113	
1	tert-BUTYL PEROXYDIETHYLACETATE + tert-BUTYLPEROXYBENZOATE	≤ 33 + ≤ 33	≥ 33			OP7			3105	
2	tert-BUTYL PEROXY-2-ETHYLHEXANOATE	> 52 - 100				OP5	+ 20	+ 25	3113	
2	„	> 32 - 52		≥ 48		OP8	+ 30	+ 35	3117	
2	„	≤ 52		≥ 48		OP8	+ 20	+ 25	3118	
3	„	≤ 32		≥ 68		OP8	+ 40	+ 45	3119	
3	„ (in IBC's)	≤ 32		≥ 68		N	+ 30	+ 35	3119	
3	„ (in tanks)	≤ 32		≥ 68		M	+ 10	+ 15	3119	
2	tert-BUTYLPEROXY-2-ETHYLHEXANOATE + 2,2-Dl-(tent-BUTYLPEROXY) BUTANE	≤ 12 + ≤ 14	> 14		≥ 60	OP7			3106	
2	„	≤ 31 + ≤ 36		≥ 33		OP7	+ 35	+ 40	3115	
2	tert-BUTYL PEROXY-2-ETHYLHEXYLCARBONATE	≤ 100				OP7			3105	
1	tert-BUTYL PEROXYISOBUTYRATE	> 52 - 77		> 23		OP5	+ 15	+ 20	3111	3)
2	„	≤ 52		> 48		OP7	+ 15	+ 20	3115	
2	tert-BUTYLPEROXY ISO-PROPYLCARBONATE	≤ 77	≥ 23			OP5			3103	
2	1-(2-tert-BUTYLPEROXY ISOPROPYL) -3-ISOPROPENYLBENZENE	≤ 77	≥ 23			OP7			3105	
2	„	≤ 42			≥ 58	OP8			3108	
1	tert-BUTYL PEROXY-2-METHYLBENZOATE	≤ 100				OP5			3103	
2	tert-BUTYL PEROXYNEODECANOATE	> 77 - 100				OP7	– 5	+ 5	3115	
2	„	≤ 77		≥ 23		OP7	0	+ 10	3115	
4	„	≤ 42 as stable dispersion in water				OP8	0	+ 10	3117	
4	„	≤ 42 as stable dispersion in water (frozen)				OP8	0	+ 10	3118	
2	tert-BIJTYL PEROXYNEOHEPTANOATE	≤ 77	≥ 23			OP7	+ 5	+ 10	3115	
2	3-tert-BUTYLPEROXY-3-PHENYLPHTEIALIDE	≤ 100				OP7			3106	
2	tert-BUTYL PEROXYPIVALATE	> 67 - 77	≥ 23			OP5	0	+ 10	3113	
2	„	> 27 - 67		≥ 33		OP7	0	+ 10	3115	
3	„	≤ 27		≥ 73		OP8	+ 30	+ 35	3119	
3	„ (in IBC's)	≤ 27		≥ 73		N	+ 10	+ 15	3119	
3	„ (in tanks)	≤ 27		≥ 73		M	– 5	+ 5	3119	
2	tert-BUTYLPEROXY STEARYLCARBONATE	≤ 100				OP7			3106	
2	tert-BUTYL PEROXY-3,5,5-TRIMETHYL-HEXANOATE	> 32 - 100				OP7			3105	
3	„	≤ 32	≥ 68			OP8,N			3109	
3	„ (in tanks)	≤ 32		≥ 68		M	+ 35	+ 40	3119	
1	3-CHLOROPEROXYBENZOIC ACID	> 57 - 86			≥ 14	OP1			3102	3)
2	„	≤ 57			≥ 3	≥ 40	OP7			3106
2	„	≤ 72			≥ 6	≥ 17	OP7			3106
3	CUMYL HYDROPEROXIDE	> 90 - 98	≤ 10			OP8			3107	13)
3	„	≤ 90	≥ 10			OP8,M			3109	13), 18)

Storage group	Organic peroxide	Concentration (%)	Diluent type A (%)	Diluent type B (%)	Inerte solid (%)	Water	Packing Method	Control Temperature (°C)	Emergency Temperature (°C)	Number Generic entry	Subsidiary risk and remarks
2	CUMYL PEROXYNEODECANOATE	≤ 77		≥ 23			OP7	– 10	0	3115	
3	„	≤ 52 as stable dispersion in water					OP8	– 10	0	3119	
2	CUMYLPEROXYNEOHEPTANOATE	≤ 77	≥ 23				OP7	– 10	0	3115	
2	CUMYL PEROXYPIVALATE	≤ 77	≥ 23				OP7	– 10	0	3115	
1	CYCLOHEXANONE PEROXIDE(S)	≤ 91				≥ 9	OP6			3104	13)
2	„	≤ 72	≥ 28				OP7			3105	5)
2	„	≤ 72 as a paste					OP7			3106	5), 20)
5	„	≤ 32			≥ 68					Exempt	
2	DUACETIBE ALCOHOL PEROXIDES	≤ 57		≥ 26		≥ 8	OP7	+ 40	+ 45	3115	6)
2	DIACETYL PEROXIDE	≤ 27		≥ 73			OP7	+ 20	+ 25	3115	7), 13)
2	DI-tert-AMYL PEROXIDE	≤ 100					OP8			3107	
1	1,1 DI-(tert-AMYLPEROXY) CYCLOHEXANE	≤ 82	≥ 18				OP6			3103	
1	DIBENZOYL PEROXIDE	> 51 - 100			≤ 48		OP2			3102	3)
1	„	> 77 - 94				≥ 6	OP4			3102	3)
2	„	≤ 77				≥ 23	OP6			3104	
2	„	≤ 62			≥ 28	≥ 10	OP7			3106	
2	„	< 56.5 (as a paste)				≥ 15	OP8			3108	
2	„	> 52 - 62 as a paste					OP7			3106	20)
2	„	> 35 - 52			≥ 48		OP7			3106	
2	„	> 36 - 42	≥ 18			≤ 40	OP8			3107	
2	„	> 36 - 42	≥ 58				OP8			3107	
2	„	≤ 52 as a paste					OP8			3108	20)
3	„	≤ 42% as stable dispersion in water					OP8,N			3109	
5	„	≤ 35			≥ 65						Exempt
1	DIBENZYL PERIOXYDICARBONATE	≤ 87				≥ 13	OP5	+ 25	+ 30	3112	3)
2	DI-(4-tert-BUTYLCYCLO-HEXYL) PEROXYDICARBONATE	≤ 100					OP6	+ 30	+ 35	3114	
4	„	≤ 42 as stable dispersion in water					OP8,N	+ 30	+ 35	3119	
2	DI-tert-BUTYL PEROXIDE	> 32 - 100					OP8			3107	
3	„	≤ 52		≥ 48			OP8,N,M			3109	25)
2	DI-tert-BUTYL PEROXYVAZELATE	≤ 52	≥ 48				OP7			3105	
2	2,2-DI-(tert-BUTYLPEROXY) BUTANE	≤ 52	≥ 48				OP6			3103	
1	1,1-DI-(tert-BUTYLPEROXY) CYCLOHEXANE	> 80 - 100					OP5			3101	3)
1	„	> 52 - 80	≥ 20				OP5			3103	
2	„	> 42 - 52	≥ 48				OP7			3105	
3	„	≤ 42	≥ 58				OP8,N			3109	
3	„	≤ 42	≥ 13		≥ 45		OP7			3106	
3	„	≤ 27	≥ 36				OP8			3107	21)
3	„	≤ 13	≥ 13	≥ 74			OP8			3109	
2	DI-n-BUTYL PEROXYDICARBONATE	> 17 - 52		≥ 48			OP7	– 15	– 5	3115	
4	„	≤ 42 as stable dispersion in water (frozen)					OP8	– 15	– 5	3118	

3	„	≤ 27		≥ 73			OP8	– 10	0	3117	
1	DI-sec-BUTYL PEROXYDICARBONATE	> 52 - 100					OP4	– 20	– 10	3113	
2	„	≤ 52		≥ 48			OP7	– 15	– 5	3115	
2	DI-(2-tert-BUTYLPEROXY-ISOPROPYL)-BENZENE(S)	> 42 - 100			≤ 57		OP7			3106	
5	„	≤ 42			≥ 58					Exempt	
2	DI-(tert-BUTYLPEROXY) PHTHALATE	> 42 - 52	≥ 48				OP7			3105	
2	„	≤ 52 as a paste					OP7			3106	20)
2	„	≤ 42	≥ 58				OP8			3107	
2	2,2-DI-(tert-BUTYLPEROXY) PROPANE	≤ 52	≥ 48				OP7			3105	
3	„	≤ 42	≥ 13		≥ 45		OP7			3106	
1	1,1-DI-(tert-BUTYLPEROXY)-3,3,5-TRIMETHYLCYCLOHEXANE	> 90 - 100					OP5			3101	3)
1	„	> 57 - 90	≥ 10				OP5			3103	
2	„	≤ 57			≥ 43		OP7			3106	
4	„	≤ 57	≥ 43				OP8			3107	
2	„	≤ 32	≥ 26	≥ 42			OP8			3107	
2	DICETYL PEROXYDICARBONATE	≤ 100					OP7	+ 30	+ 35	3116	
4	„	≤ 42 as stable dispersion in water					OP8,N	+ 30	+ 35	3119	
1	DI-4-CHLOROBENZOYL PEROXIDE	≤ 77				≥ 23	OP5			3102	3)
2	„	≤ 52 as a paste					OP7			3106	20)
5	„	≤ 32		≥ 68						Exempt	
3	DICUMYL PEROXIDE	> 42 - 100			≤ 57		OP8,M			3110	12)
5	„	≤ 52	≥ 48							Exempt	
5	„	≤ 42			≥ 58					Exempt	
1	DICYCLOHEXYL PEROXYDICARBONATE	> 91 - 100					OP3	+ 5	+ 10	3112	3)
2	„	≤ 91				≥ 9	OP5	+ 5	+ 10	3114	
2	DIDECANOYL PEROXIDE	≤ 100					OP6	+ 30	+ 35	3114	
3	2,2-DI-(4,4-Di(tert-BUTYL-PEROXY) CYCLOFIEXYL)-PROPANE	≤ 42			≥ 58		OP7			3106	
1	DI-2,4-DICHLOROBENZOYL PEROXIDE	≤ 77			≥ 23		OP5			3102	3)
2	„	≤ 52 as a paste with silicon oil					OP7			3106	
2	DI-(2-ETHYLHEXYL) PEROXY-DICARBONATE	> 77 - 100					OP5	– 20	– 10	3113	
2	„	≤ 77					OP7	– 15	– 5	3115	
3	„	≤ 52 as stable dispersion in water					OP8	– 15	– 5	3117	
4	„	≤ 42 as stable dispersion in water (frozen)					OP8	– 15	– 5	3118	
2	DIETHYL PEROXYDICARBONATE	≤ 27		≥ 73			OP7	– 10	0	3115	
1	2,2-DIHYDROPEROXYPROPANE	≤ 27			≥ 73		OP5			3102	3)
2	DI-(1-HYDROXYCYOLOHEXYL) PEROXIDE	≤ 100					OP7			3106	
1	DI-1SOBUTYRYL PEROXIDE	> 32 - 52		≥ 48			OP5	– 20	– 10	3111	3)
2	„	≤ 32		≥ 68			OP7	– 20	– 10	3115	
2	DI-ISOPROPYLBENZENE DIHYDROPEROXIDE	≤ 82	≥ 5			≥ 5	OP7			3106	24)
1	DI-ISOPROPYL PEROXYDICARBONATE	> 52 - 1000					OP2	– 15	– 5	3112	3)
2	„	≤ 52		≥ 48			OP7	– 10	0	3115	
2	DIISOTRIDECYL PEROXYDICARBONATE	≤ 100					OP7	– 10	0	3115	

Storage group	Organic peroxide	Concentration (%)	Diluent type A (%)	Diluent type B (%)	Inerte solid (%)	Water	Packing Method	Control Temperature (°C)	Emergency Temperature (°C)	Number Generic entry	Subsidiary risk and remarks
2	DILAUROYL PEROXIDE	≤ 100					OP7			3106	
4	„	≤ 42 as stable dispersion in water					OP8,N			3109	
1	DI-(2-METHYLBENZOYL) PEROXIDE	≤ 87				≥ 13	OP5	+ 30	+ 35	3112	3)
2	DI-(4-METHYLBENZOYL) PEROXIDE	≤ 52 as a paste with silicon oil					OP7			3106	
1	2,5-DIMETHYL-2,5-DI-(BENZOYLPEROXY)HEXANE	> 82 - 100					OP5			3102	3)
2	„	≤ 82			≥ 18		OP7			3106	
2	„	≤ 82				≥ 18	OP5			3104	
2	2,5-DIMETHYL-2,5-DI-(tert-BUTYLPEROXY)HEXANE	> 52 - 100					OP7			3105	
3	„	≤ 52			≥ 48		OP7			3106	
2	„	≤ 47 as a paste					OP8			3108	
3	„	≤ 52	≥ 48				OP8			3109	
2	2,5-DIMETHYL-2,5-DI-(tert-BUTYLPEROXIDE)HEXYNE-3	> 52 - 86	≥ 14				OP5			3103	26)
3	„	≤ 52			≥ 48		OP7			3106	
2	2,5-DIMETHYL-2,5-DI-(2-ETHYL-HEXANOYLPEROXY)HEXANE	≤ 100					OP7	+ 20	+ 25	3115	
1	2,5-DIMETHYL-2,5-DIHYDRO-PEROXYHEXANE	≤ 82				≥ 18	OP6			3104	
2	2,5-DIMETHYL-2,5-DI-(3,5,5-TRIMETHYL-HEXANOYLPEROXY)HEXANE	≤ 77	≥ 23				OP7			3105	
2	1,1-DIMETHYL-3-HYDROXYBUTYL PEROXYNEOHEPTANOATE	≤ 52	≥ 48				OP8	0	+ 10	3117	
2	DIMYRISTYL PEROXYDICARBONATE	≤ 100					OP7	+ 20	+ 25	3116	
4	„	≤ 42 as stable dispersion in water					OP8	+ 20	+ 25	3119	
4	„ (in IBC's)	≤ 42 as stable dispersion in water					N	+ 15	+ 25	3119	
2	DI-(2-NEODECANOYLPER-OXYISOPROPYL)BENZENE	≤ 52	≥ 48				OP7	– 10	0	3115	
2	DI-n-NONANOYL PEROXIDE	≤ 100					OP7	0	+ 10	3116	
2	DI-n-OCTANOYL PEROXIDE	≤ 100					OP5	+ 10	+ 15	3114	
3	DIPEROXY AZELAIC ACID	≤ 27			≥ 73		OP7	+ 35	+ 40	3116	
2	DIPEROXY DODECANE DIACID	> 13 - 42			≥ 58		OP7	+ 40	+ 45	3116	
5	„	≤ 13			≥ 87					Exempt	
1	DI-(2-PHENOXYETHYL) PEROXYDICARBONATE	> 85 - 100					OP5			3102	3)
2	„	≤ 85				≥ 15	OP7			3106	
3	DI-PROPIONYL PEROXIDE	≤ 27		≥ 73			OP8	+ 15	+ 20	3117	
1	DI-n-PROPYL PEROXYDICARBONATE	≤ 100					OP4	– 25	– 15	3113	
2	DISTEARYL PEROXYDICARBONATE	≤ 87			≥ 13		OP7			3106	
1	DISUCCINIC ACID PEROXIDE	> 72 - 100					OP4			3102	3), -17)
2	„	≤ 72				≥ 28	OP7	+ 10	+ 15	3116	

2	DI-(3,5,5-TRIMETHYLHEXANOYL) PEROXIDE	> 38 - 82	≥ 18		OP7	0	+ 10	3115	
3	„	≤ 52 as stable dispersion in water			OP8	+ 10	+ 15	3117	
3	„	≤ 38	≥ 62		OP8	+ 20	+ 25	3119	
3	„ (in IBC's)	≤ 38	≥ 62		N	+ 10	+ 15	3119	
3	„ (in tanks)	≤ 38	≥ 62		M	– 10	0	3119	
2	DI-(3,5,5-TRIMETHYL-1,2-DIOXOLANYL-3) PEROXIDE	≤ 52 as a paste			OP7	+ 30	+ 35	3116	20)
2	ETHYL 3,3-DI-(tert-AMYLPEROXY)-BUTYRATE	≤ 67	≥ 33		OP7			3105	
1	ETHYL 3,3-DI-(tert-BUTYLPEROXY)-BUTYRATE	> 77 - 100			OP5			3103	
2	„	≤ 77	≥ 23		OP7			3105	
2	„	≤ 52		≥ 48	OP7			3106	
1	3,3,6,6,9,9-HEXAMETHYL-1,2,4,5-TETRAOXACYCLONONANE	> 52 - 100			OP4			3102	3)
2	„	≤ 52	≥ 48		OP7			3105	
2	„	≤ 52		≥ 48	OP7			3106	
1	ISOPROPYL sec-BUTYLPEROXYDICARBONATE + DI-sec-BUTYL PEROXYDICARBONATE + DI-ISOPROPYL PEROXYDICARBONATE	≤ 52 + ≤ 28 + ≤ 22			OP5	– 20	– 10	3111	3)
3	ISOPROPYLCUMYL HYDROPEROXIDE	≤ 72	≥ 28		OP8,M			3109	13)
2	p-MENTHYL HYDROPEROXIDE	> 72 - 100			OP7			3105	13)
3	„	≤ 72	> 28		OP8,M			3109	27)
2	METHYLCYCLOHEXANONE PEROXIDE(S)	≤ 67		≥ 33	OP7	+ 35	+ 40	3115	
1	METHYL ETHYL KETONE PEROXIDE(S)	≤ 52	≥ 48		OP5			3101	3), 8), 13)
2	„	≤ 45	≥ 55		OP7			3105	9)
2	„	≤ 40	≥ 50		OP8			3107	10)
2	METHYL ISOBUTYL KETONE PEROXIDE(S)	≤ 62	≥ 19		OP7			3105	22)
2	ORGANIC PEROXIDE, LIQUID, SAMPLE				OP2			3103	11)
2	ORGANIC PEROXIDE, LIQUID, SAMPLE, TEMPERATURE CONTROLLED				OP2			3113	11)
2	ORGANIC PEROXIDE, SOLID, SAMPLE				OP2			3104	11)
2	ORGANIC PEROXIDE, SOLID, SAMPLE, TEMPERATURE CONTROLLED				OP2			3114	11)
2	PEROXYACETIC ACID, TYPE D, stabilized	≤ 43			OP7			3105	13), 14), 19)
3	PEROXYACETIC ACID, TYPE E, stabilized	≤ 43			OP8			3107	13), 15), 19)
4	PEROXYACETIC ACID, TYPE F, stabilized	≤ 43			OP8,N			3109	13), 16), 19)
2	PINANYL HYDROPEROXIDE	56 - 100			OP7			3105	13)
3	„	< 56	> 44		OP8,M			3106	
2	TETRAHYDRONAPHTHYL HYDROPEROXIDE	≤ 100			OP7			3109	
2	1,1,3,3-TETRAMETHYLBUTYL HYDROPEROXIDE	≤ 100			OP7			3105	
2	1,1,3,3-TETRAMETHYLBUTYL PEROXY-2 ETHYLHEXANOATE	≤ 100			OP7	+ 20	+ 25	3115	

Storage group	Organic peroxide	Concentration (%)	Diluent type A (%)	Diluent type B (%)	Inerte solid (%)	Water	Packing Method	Control Temperature (°C)	Emergency Temperature (°C)	Number Generic entry	Subsidiary risk and remarks
2	2,4,4-TRIMETHYLPENTYL-2-PEROXY-NEODECANOATE	≤ 72		≥ 28			OP7	– 5	+ 5	3115	
3	„	≤ 52 as stable dispersion in water					OP8	– 5	+ 5	3119	
2	2,4,4-TRIMETHYLPENTYL-2-PEROXY PHENOXYACETATE	≤ 37		≥ 63			OP7	– 10	0	3115	

Explanatory notes on Subsidiary Risks and remarks

1 Diluent type B may always be replaced by diluent type A.Verdunningsmiddel type B mag altijd worden vervangen door type A.
2 Available oxygen ≤ 4.7%.
3 “EXPLOSIVE” subsidiary risk label required (model No. 01, see 13.5 of reference 1).
4 Diluent may be replaced by di-tert-butyl peroxide.
5 Available oxygen ≤ 9%.
6 With ≤ 9% hydrogen peroxide; available oxygen ≤ 10%.
7 Only non-metallic packagings allowed.
8 Available oxygen > 10%.
9 Available oxygen ≤ 10%.
10 Available oxygen ≤ 8.2%.
11 See 11.3.2.6 of reference 1.
12 Up to 2000 kg per receptacle assigned to ORGANIC PEROXIDE TYPE F on the basis of large scale trials.
13 “CORROSIVE” subsidiary risk label required (Model No. 08, see 13.5 of reference 1).
14 Peroxyacetic acid formulations which fulfil the criteria of 11.3.3.3 (d) of reference 1
15 Peroxyacetic acid formulations which fulfil the criteria of 11.3.3.3 (e) of reference 1
16 Peroxyacetic acid formulations which fulfil the criteria of 11.3.3.3 (f) of reference 1
17 Addition of water to this organic peroxide will decrease its thermal stability.Toevoeging van water aan dit organisch peroxide zal de thermische stabiliteit doen afnemen.
18 No “CORROSIVE” subsidiary risk label required for concentrations below 80%.
19 Mixtures with hydrogen peroxide, water and acid(s).
20 With diluent type A, with or without water.
21 With ≥ 36%, by mass, ethylbenzene in addition to diluent type A.
22 With ≥ 19%, by mass, methyl isobutyl ketone in addition to diluent type A.
23 With < 6 % di-tert-butyl peroxide.
24 With ≤ 8 % 1-isopropylhydroperoxy-4-isopropylhydroxybenzene.
25 diluent type B with boiling point > 110°C.
26 with < 0.5 % hydroperoxide content
27 for concentrations more than 56% “CORROSIVE” subsidiary risk label required (model No. 8, 13.5 of reference 1)

ANNEX 3: Labels

Internation Transport Labels:

organic peroxide label

explosive subsidiary risk label

corrosive subsidiary risk label

Labels according to 'Wet Milieugevaarlijke Stoffen'

O: oxidizing

E: explosive

C: corrosive

Xi: irritant

Xn: harmful

T: toxic

ANNEX 4: Risk- and Safety Sentences

According to the respective EC-Directives Organic Peroxides are to be labelled according to their particular hazards, i.e. the labels O(xidizing), and possibly F+ (Highly flammable), F(lammable), E(xplosive), T+ (Very toxic), T(oxic), C(orrosive), Xn (Harmful) or Xi (Irritant).

Next to labelling the EC-Directives introduce the use of R(isk)- and S(afety) phrases, the most common of which for peroxides are:

R2	Risk of explosion by shock, friction, fire or other sources of ignition
R3	Extreme risk of explosion by shock, friction, fire or other sources of ignition
R7	May cause fire
R20	Harmful by inhalation
R21	Harmful in contact with skin
R22	Harmful if swallowed
R23	Toxic by inhalation
R24	Toxic in contact with skin
R25	Toxic if swallowed
R34	Causes burns
R35	Causes severe burns
R36	Irritating to eyes
R37	Irritating to respiratory system
R38	Irritating to skin
R40	Possible risks of irreversible effects
R41	Risk of serious damage to eyes
R42	May cause sensitization by inhalation
R44	Risk of explosion if heated under confinement
R20/21	Harmful by inhalation and in contact with skin
R20/21/22	Harmful by inhalation, in contact with skin and if swallowed
R20/22	Harmful by inhalation and if swallowed
R21/22	Harmful in contact with skin and if swallowed
R36/37	Irritating to eyes and respiratory system
R36/37/38	Irritating to eyes, respiratory system and skin
R36/38	Irritating to eyes and skin
R37/38	Irritating to respiratory system and skin
S14	Keep away from ..... (peroxides)
S22	Do not breath dust
S34	Avoid shock and friction
S47	Keep at temperature not exceeding ...
S50	Do not mix with ..... (peroxide-accelerator)
S3/7	7Keep container tightly closed in a cool, well-ventilated place
S36/37/39	Wear suitable protective clothing, gloves and eye/face protection

ANNEX 5: Burning tests

TEST METHODS FOR THE CLASSIFICATION IN STORAGE GROUPS

The test methods to be used for the determination of the burning rate at 10000 kg scale are described in the next sections. In section 1 the “large-scale tests” are described. The large-scale tests are used to determine the burning rate of all peroxide(-formulations). In section 2 a “small-scale” laboratory test for liquids is described. Except for boundary cases the 10000 kg-scale burning rate can be calculated in good approximation from the small scale test. Either test can be used for the classification into storage groups, where the large-scale test is decisive in case of conflict. However, only the large-scale test shall be used for peroxides “type C” of storage group 1 when a burning rate lower than 1200 kg/min is used to calculate safety distances.

1. Determination of burning rate by large scale testing

1.1 Test procedure

1.1.1 Introduction
The burning rate as used in chapter 2 is defined as the burning rate of a mass of 10000 kg. In practice, this burning rate is determined using a stack of packagings with a total mass of approximately 500 kg. The tests shall be performed with the organic peroxides in the packagings as applied in storage. The organic peroxide and the organic peroxide in its packaging shall further be referred to as “the organic peroxide” and “the packaging”, respectively.

The test may only be performed if the organic peroxide can neither detonate in its packaging nor in a stack of packagings. The test is performed to determine
- the way in which the packagings react to a fire,
- the effect of the total quantity of available organic peroxide on the burning rate of the packagings,
- the extent to which the surrounding environment is endangered.

The test performance shall be arranged in such a way that the most unfavourable results will be obtained. Tests shall be performed in singular with
- 1, 6 and 10 packagings, up to a maximum total weight of 500 kg with packagings up to a weight of 25 kg,
- 1, 3 and 6 packagings, up to a maximum total weight of 500 kg with packagings with a weight between 25 and 50 kg,
- 1 or more packagings, up to a maximum total weight of 500 kg with packagings with a weight over 50 kg.

The number of tests and, whereas necessary, the total test mass shall be increased, if the test results and the corresponding hazards cannot be adequately evaluated.

1.1.2 Test description
The packagings shall be placed on wooden and levelled pallets in accordance with DIN 15146. The pallets shall be placed in one (or two, if necessary) catch-trays. A catch-tray must comprise at least one complete pallet including a 10 cm open space all around the pallet. The volume of the catch-tray shall further enable containment of all leaking organic peroxide.

An adequate and stabile windscreen with a height of about 1.6 m is surrected at three sides of the seat of fire.Flammable material is placed under and around the packagings in such a way that an optimum ignition of the organic peroxide is guaranteed. The quantity and type of flammable material shall be selected such that
- the ignition of the tested organic peroxide is guaranteed,
- the burning of the tested organic peroxide is not hardly amplified[1)].

[1)] A quantity of about 10 kg dry wood-wool is usually sufficient in case of 200 kg highly flammable organic peroxide. In case of badly ignitable organic peroxides thin wooden boards can be suitable that may either or not be soaked with a liquid mixture of light heating oil (90%) and light petrol (10%). The packagings may be sprayed with the flammable liquid as well.

The heat of radiation is to be measured during the test by suitable equipment at, at least, three locations with different distances from the seat of fire. The distances shall
- be sufficiently large on the one hand,
- enable detection of sufficiently large signals with respect to the resolution of the equipment on the other hand.

Suitable equipment to measure the radiation, for instance, are calibrated thermocolumns that determine absolute signals and that have
- in good approximation a linear sensitivity between 0.5 and 0.9 mm,
- radiation properties close to those of a “black body”,
- an active surface area of, at least, 0.25 cm^2,
- an angle of incidence enabling complete capture of the flame size of the tested organic peroxide at the distance of detection,
- a high insensitivity to temperature exposure, i.e. are compensated in such a way that the signal level is not affected by changes in the surrounding temperature,
- a detection capacity of radiation levels between 100 and 3000 W/m^2, i.e. a sensitivity of, at least, 1 V/W,
- an adequate response time, i.e. the response time (time-to-63.2% level of the final signal value) should be less than 1000 ms.

The signals shall be continuously recorded. The startingpoint of the fire outbreak is defined as the moment at which the test organic peroxide starts reacting detectably. The end of the fire is determined from the registered radiation curves: this point is characterized by a decrease in radiation level *I* (as caused by the fire) to less than 5% of the detected maximum level (I_{max}). The effect of neither remainders nor burning flammable materials, if present, shall be taken into account in the evaluation. The burning time π is the time span between startingpoint and end-of-fire.

The burning rate *BR* [kg/min] is to be calculated for each tested quantity *m* [kg] and its corresponding burning time π [min] according to the formula

$$BR = \frac{m}{\pi}$$

The percentual average radiating efficiency h at a distance from the seat of fire shall be determined from the measured radiation levels and the theoretical maximum energy.

The theoretical maximum energy is calculated by multiplying the individual mass of tested organic peroxide [kg] with the heat of combustion [kJ/kg]. The amount of energy that in practice appears to be transferred by radiation, is determined by integrating the area below the measured radiation curve after smoothing and being corrected, where and if necessary.

The form factor *f* that must be taken into account during the maximum fire intensity, can be averaged from the formula:

$$f = \frac{I_{relevant}}{I_{calculated}}$$

To this end a graph is made showing the radiation level I [kW/m^2] as a function of time t [min]. The complete radiation dose is calculated by integration of the smoothed and corrected curve down to 1 - 5 % of I_{max} $I_{relevant}$ is obtained from the maximum of the curve I calculated as average value of the radiation by converting the integrated area in a rectangle of equal size during the same time span.

1.1.3 Test report
The test report shall show:
- the composition of the tested organic peroxide,
- the quantities of organic peroxide used in each test,
- the type and construction of each packaging,
- the test set-up and, more in particular, the type, quantities and arrangement of the ignition and initiation materials that are applied,
- the test history, in particular the period of time up to first detected reaction of the organic peroxide (incubation time), the period of time and the burning particulars of the reactions itself (main burning stage and overall burning period of the organic peroxide), as well as the completeness of conversion,
- effect of the reaction on the surroundings,
- the various burning rates BR and their corresponding quantities of organic peroxide m, including graphical representation,
- the weather conditions during testing,
- radiation levels as measured at the various distances,
- percentual average radiating efficiency h and form factor f.

The test report shall include pictures of a packaging and of the tested stack of packagings as well as copies of the records of measured data. Data relevant for interpreting the measured curves (resolution of instrument, calibration factors, etc.) shall be noted on these records.

1.2 Classification in a storage group
In general, the organic peroxide shall be classified in the storage group that corresponds to the effects shown by the tests with the organic peroxide in its packaging. However, experiences with other tests or, even, incidents can be taken into account as well.

The organic peroxide in its packaging cannot be classified in organic peroxides storage groups if the contents of the packagings do explode almost simultaneously in the course of the burning period (these organic peroxides presumably are organic peroxide type A).

If the packagings don't explode almost simultaneously during the test in the sense described in the previous paragraph, but, in stead, only individual explosions occur the frequency of occurrence of which may increase during a prolonged period of fire, and if the surroundings are endangered by fragments or fire-blasts that are projected around, than the organic peroxide in its standard packaging shall be classified in storage group 1 with an BR_c-value of 1200 kg/min.

The organic peroxide in its packaging can be classified in one of the storage groups 2, 3, 4 or 5 if the packagings neither explode almost simultaneously nor show individual explosions in the course of the burning period as described in the previous two paragraphs, but, in stead, only burn more or less intensively, a process during which individual parts of the package may be projected over a short distance from the seat of fire.

The classification into the storage groups 2, 3, 4 or 5 is based on burning rate. The criterion for classification into either of these storage groups is the burning rate BR_c of a 10 tons quantity of organic peroxide. The burning rate BR_c is determined in the following manner: The measured burning rates *BR* are graphically shown as a logarithmic function of the mass of organic peroxide *m* (ln BR vs. ln *m*). The observed test results are extrapolated by means of this graph to an uncorrected burning rate BR_{10t} for a mass of 10000 kg by application of the formula:

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

The extrapolation is, in general, best performed on basis of the largest test quantities. The value BR_{10t} shall be corrected to the genuine burning rate for a 10 tons mass of organic peroxide (BR_c) by the formula

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

in which H_v is the heat of burning of the organic peroxide [kJ/kg] (i.e. reaction enthalpy of the burning reaction.

BR_c is the burning rate specified in 2.3 and is used for the storage classification as given in table 3.

The classification shall be approved by the competent authority on basis of the reported test results and can ultimately be shown in the annex to the PGS8.
In the Netherlands the competent authority is the Dutch Department of Social Affairs and Employment.

2. Small scale laboratory test

2.1 Test procedure

2.1.1 Introduction
The rate at which a liquid peroxide burns away is tested at laboratory scale. The burning rate is determined by measuring the weight loss of the burning peroxide sample as a function of time. During the measurement the burning surface area is constant. The amount of product burned away per minute, divided by the size of the area of the burning surface, is defined as the burning rate (kg/m^2 min.). In order to simulate the burning of a stack of peroxide packages the burning surface area of the test sample is divided into smaller segments.

2.1.2 Test description
The burning rate test with the peroxide is carried out in a shallow Pyrex or Duran glass beaker. The test beaker has a height of 54 mm, an internal diameter of 87 mm and a wall thickness of 2.5 mm. It is thermally insulated from the surroundings. The insulation is obtained by placing the test beaker concentrically inside a second beaker which has a height of 65 mm and a diameter of 115 mm. The 1 cm space between the bottoms and cylindrical side walls of the two beakers is filled with rockwool. Inside the inner test beaker 14 pyrex glass tubes of 20 mm outside diameter, 29 mm height and 2 mm wall thickness just fit in when placed in upside position. The tubes which are open ended at both sides divide the contents of the test beaker into a number of segments (19 in total) in such a way, that the space between the tubes is not more than 1 mm. A drawing of the experimental set-up is shown in Fig. 1.

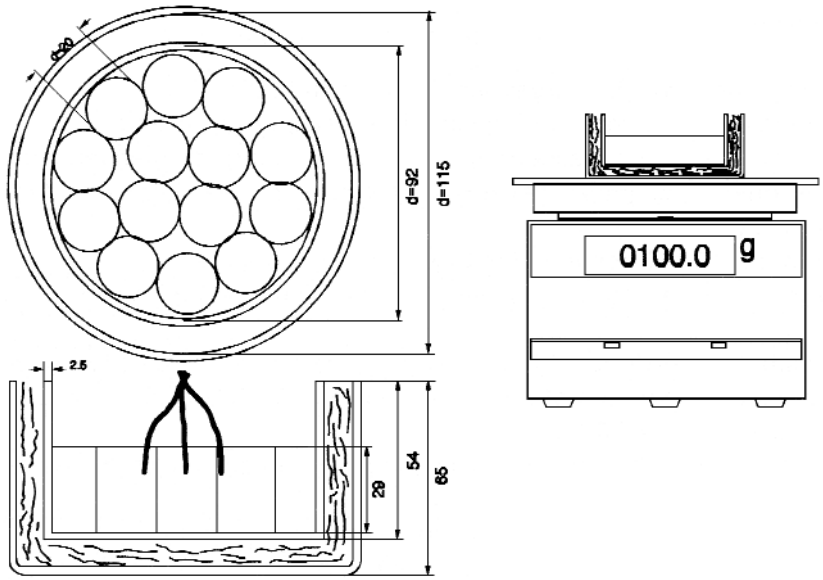


Figure 1: Burning rate test the balance from fire damage

An electrical weighing balance is used to measure the decrease of the sample weight during the burning test. The balance is connected to a chart-recorder provided with a zero point suppression, so that the loss of weight can be registered at a safe distance from the experimental set-up.
The technical specifications of the balance are:
- standard deviation 0.1 g
- linearity 0.15 g
- max. range 1000 g

An aluminum plate of approximately 22 x 36 mm and about 1.5 mm thickness is placed on the balance to protect.

Most peroxides are difficult to ignite and the prolonged use of a gas flame would disturb the temperature of the sample. Therefore, a simple ignition cord is used. The cord which is about 6 cm long and 1 mm thick, is made of 4 glass wool threads. The cord, when soaked with peroxide, can easily be ignited with a match.

The test has to be carried out in a chamber which meets the following requirements:
- fire-proof to prevent extension of the fire,
- shatter-proof to provide personal protection in the unlikely event that the glass beakers are shattered during the test,
- the minimum dimensions of the chamber should measure 2 m high, 0.5 m wide and 0.5 m deep,
- provided with an exhaust fan for the extension of fume and smoke.

The test beaker equipped with the provisions as described above is filled with 100 grams of the peroxide. The sample in the beaker should have a temperature of T_c + 10ºC (see Annex 2) with a maximum of 25ºC.
The test beaker set-up is placed on the aluminum sheet laying on the balance. Balance and recorder are adjusted. Subsequently the ignition cord is partially dipped in the sample and ignited at the other end with a match. The fire quickly spreads over the total surface of the test beaker. The diminishing weight of the burning sample is registered.
The test is carried out in duplicate.

Except for the start and the end of the fire the weight of the sample will decrease almost linearly in time. The time elapsed between 20 % and 80 % weight loss is called burning time. For the evaluation of the test the shorter combustion time is used.

The burning rate (BR) is calculated by use of the equation:

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

where,
sample weight (m) = 0.1 kg
surface area (A) = 0.00545
burning time (t) in min.

2.1.3 Test report
A report is written about the tests, containing at least the following data:
- the description and the chemical composition of the test
- the test temperature
- the recorded burning time
- the calculated burning rate.

A copy of the recorded data shall be attached to the test report, in order to be able to judge if the burning rate responsible for the weight loss between 20 % and 80 % is representative for the substance.

2.2 Classification in a storage group
Organic peroxides type D, E and F are classified in storage group 3 if the burning rate is less than 0.9 kg/min. m^2.

Organic peroxides type C, D and E are classified in storage group 2 if the burning rate does not exceed 9.0 kg/min. m^2.

Type B organic peroxides are classified as storage group 1 peroxides.

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