The storage and handling of organic peroxides

Guidance Note CS21

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ISBN 978 0 7176 2403 4
Price £5.00

This guidance sets a standard for safe handling and storage of organic peroxides at customer or user sites.

The storage of arrangements prescribed here are for commercially available organic peroxides, packaged in accordance with the *Approved Code of Practice Approved requirements and test methods for the classification and packaging of dangerous goods for carriage* and *the Approved guide to the classification and labelling of substances and preparations dangerous for supply.*

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First published 1991
Reprinted (with amendments) 1998

ISBN 978 0 7176 2403 4

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Introduction

1 This Guidance Note sets a standard for safe handling and storage of organic peroxides at customer or user sites. The storage arrangements prescribed here are for commercially available organic peroxides, packaged in accordance with the Approved Code of Practice *Approved requirements and test methods for the classification and packaging of dangerous goods for carriage* (see reference 1) and the *Approved guide to the classification and labelling of substances and preparations dangerous for supply* (see reference 2).

2 The guidance does not cover storage in either tank or intermediate bulk containers, nor does it cover formulations which have a peroxide concentration of less than 10%.

3 Industrially, organic peroxides are used widely in both solid and liquid forms as initiators in polymerisation reactions for the manufacture of resins, plastics and elastomers, and for curing glass reinforced plastic products such as boats and silos.

Properties and Hazards

4 Organic peroxides are organic chemicals which contain the unstable -O-O- peroxy linkage in their molecular structure. They are highly reactive, combustible and thermally unstable substances which may undergo self-accelerating decomposition. They also possess oxidising characteristics and will react, often violently, with organic matter and chemical reducing agents. A limited number of liquid compositions are low flash point, highly flammable liquids.

5 In the pure state some are detonable and easily initiated. These properties are suppressed or removed by dilution or phlegmatisation (desensitisation) with liquids such as water and phthalates. Even so, commercially available organic peroxides are capable of self heating and runaway decomposition. Initiation is by heating or contamination with, for example, transition metal compounds (particularly those of vanadium, chromium, manganese, iron and cobalt) amines, strong acids and alkalis. Contamination of a container of organic peroxide with parts per million of a resin accelerator is likely to result in an exothermic runaway reaction. The conclusion to a runaway reaction may be a violent pressure burst of the container together with a sudden release of hot flammable vapours which might be toxic and ignite spontaneously. If the container provides significant confinement, an explosion of the peroxide may occur. Peroxides spilled onto combustible materials eg wood, paper, cotton, may result in a fire.

6 Every packaged organic peroxide has a characteristic temperature at and above which exothermic runaway decomposition takes place, known as the self accelerating decomposition temperature (SADT). For a particular peroxide this generally decreases with increasing packaging size and varies with the stacking arrangement of the packaged product. SADT values and recommended storage temperatures for packaged peroxide products should be provided by the supplier. The recommended maximum storage temperature, known as the 'control' temperature, and the temperature at which emergency procedures should be implemented, the 'emergency' temperature, are related to the SADT as follows:

SADT	*Control temperature*	*Emergency temperature*
20°C or less	20°C below SADT	10°C below SADT
Over 20°C to 35°C	15°C below SADT	10°C below SADT
Over 35°C	10°C below SADT	5°C below SADT

7 Some organic peroxides can separate out of solution if they become too cool, resulting in a concentrated peroxide which may be explosive and sensitive to shock. The advice of the supplier should be sought concerning the minimum temperature at which formulations can be stored and, if appropriate, the necessary storage conditions.

8 Organic peroxides include a variety of substances of variable toxicity. Those that are corrosive can be expected to damage eyes, skin and all mucous membranes (ie mouth, throat, gullet, stomach, nose, etc). If a spray or cloud occurs for any reason, or if the peroxide has a high vapour pressure, it is possible that any corrosive droplets reaching the smaller air passages may cause asthma (ie difficulty in breathing) particularly in people prone to asthmatic attacks. However no reports are available to suggest that this has occurred. Due regard should be paid to the advice given by the supplier regarding procedures for dealing with accidental ingestion or eye and skin contact.

Storage

9 The principal storage recommendations are:

(a) keep in original containers;
(b) hold within the predetermined temperature limits;
(c) keep in dedicated stores;
(d) prevent contact/contamination with other materials such as acids, alkalis, amines, accelerators, combustible materials, metals, reducing agents etc (see paragraph 5);
(e) minimise the quantity at the workplace so that no more is present than is necessary for the job in hand.

Flammability types

10 For the purpose of providing guidance on storage, packaged peroxides have been divided into four flammability types as given below. Assignments for packaged peroxides known to be in use in the UK are given in the Appendix (substances that have not been assigned a flammability type are shown with an asterisk in the Appendix). Advice on the flammability types of new substances can be obtained from the Health and Safety Executive (HSE).

11 (a) *Type 1* - This contains both 'Explosive' labelled packaged peroxides and packaged peroxides which burn *very intensely*.
(b) *Type 2* - This contains packaged peroxides which burn in a way which is intermediate between Types 1 and 3.
(c) *Type 3* - This contains packaged peroxides which burn in the range 'gently' up to something akin to solvents and hydrocarbons.
(d) *Type 4* - This contains packaged peroxides which are noncombustible and from which the available oxygen is not more than 5%.

Quantities up to 5 kg (Types 1 and 2) and up to 10 kg (Type 3)

12 Where small quantities are required for experiment, test, or control purposes, they should be kept in a dedicated fire-resisting metal cupboard or lidded bin, designed to retain any spillages. It should be of robust construction which will withstand high temperatures (in excess of 750°C) and prevent or retard the passage of flame and hot gases.

13 If refrigeration is required, a suitably designed commercial refrigerator/freezer should be used. The form of construction required will depend upon the hazards of the individual peroxides concerned (see paragraphs 16 (f) to (i)) and advice should be sought from the peroxide and equipment suppliers. It is likely to include protected/separated electrical equipment, a lid or door which opens easily to relieve any internal pressure, and a high temperature alarm device which, if the resulting hazard is high, gives warning at a permanently manned location. It should be noted that some refrigerated peroxides are sensitive to very low energy sources - ie even heat from a light bulb may be enough to initiate decomposition in some cases.

14 The cupboard/refrigerator should be carefully sited so as not to prejudice the means of escape eg not in corridors or on staircases. For refrigerators holding these quantities on a regular basis, a temperature monitoring device should be fitted which gives a clear indication outside the fridge of the temperature inside.

Quantities up to 150 kg (Types 1 to 3)

15 For *outdoors*, a secure store is needed. The walls and floor should be constructed from non-combustible materials and the store provided with weather protection, particularly against direct sunlight (eg the roof should be opaque). The store should preferably be located at least five metres from boundaries and buildings. Alternatively it may be against the outside wall of a building providing that:

(a) the wall, preferably of concrete, masonry or brick construction, is capable of providing a minimum of one half-hour fire resistance in accordance with BS 476 Part 8 for existing structures, or Parts 20 to 23, as appropriate, for new structures (references 3 to 7);
(b) there are no openings in the wall for at least two metres horizontally from the store; and
(c) the store is not beneath any openings which might be affected by a fire in the store.

16 For *indoors* a dedicated storeroom is recommended with the following features:

(a) the walls, floor and any internal ceiling should be of non-combustible construction. All structural elements of the store that form internal partitions with adjoining rooms (such as walls, floors, ceilings and doors) should be of at least half-hour fire resistance (see paragraph 15 (a));
(b) the floor should be impervious eg concrete;
(c) precautions should be made to shield organic peroxides from direct sunlight (eg the roof should be opaque);
(d) access to the room should preferably be via door(s) in the outside wall. Alternatively, doors inside should be provided with strong fastenings and hinges;
(e) if the storeroom is located in a single storey building the roof should be of lightweight construction, to act as explosion relief. Alternatively, relief panels, which vent to a safe place, may be provided in one or more external walls;

(f) where practicable, electrical equipment should be excluded from the storage area. Switches should be external and there should be no socket outlets in the store;
(g) where electrical equipment has to be installed inside the store, care should be taken to protect it against the effects of any corrosive vapours/dusts (see paragraph 28);
(h) where organic peroxides capable of giving off flammable vapours (ie by decomposition) are stored, electrical equipment should be suitable for use in a Zone 2 area and constructed to a recognised standard eg BS EN 50014 - BS EN 50020 (reference 8). A Zone 2 area is one in which an explosive vapour/air mixture is not likely to occur in normal operation, and if it does occur, will exist only for a short time. The surface temperature of the equipment should be below the ignition temperature of the vapour. General guidance on this matter can be found in BS 5345 (reference 9);
(i) if accumulations of combustible dusts are possible, electrical equipment should be provided to BS 6467 (references 10 and 11) which makes recommendations for electrical equipment based on the maximum surface temperature and on the restriction of dust ingress into the enclosure. (Note: Zone 2 equipment is not suitable for protection against ingress of dust and, equally, dust-proof equipment is not suitable for use in a Zone 2 area);
(j) the installation of smoke or heat detectors connected to an alarm system and/or sprinklers, is recommended;
(k) for *liquid* organic peroxides, the door opening should be provided with a raised threshold to contain the ENTIRE liquid contents of the store. This is to restrict the size of a peroxide fire and minimise the potential thermal radiation effects;
(l) for liquid organic peroxides which are highly flammable liquids, as defined in references 12 and 13, store rooms should be adequately ventilated at high and low level to disperse vapour from any leak or spill. A standard of at least five air changes per hour is recommended, using air bricks or louvres in at least one, and preferably more, external walls. To provide this, these openings should normally have a total area of at least 2½% of the total area of the walls and roof. Care should be taken to ensure that they are not obstructed;
(m) refrigerated organic peroxides can be held in either refrigerators/freezers (constructed as outlined earlier in paragraph 13), or in a refrigerated room. For the latter the refrigeration unit should be positioned outside the room and the store provided with a high temperature alarm which gives warning at a permanently manned location;
(n) some form of heating may be necessary for some organic peroxides in certain circumstances, to maintain the temperature of the store above a minimum. Acceptable forms of heating include thermostatically-controlled warm air (indirectly heated) and water radiators; containers of organic peroxides must be kept at least 0.5 metres away from water radiators (fixed barriers are recommended) and the temperature of the surfaces of these radiators must be controlled via thermostatically controlled valves to a maximum of 60°C. If the room can overheat above the control temperature then an automatic high temperature cut out and alarm should be provided.

Quantities over 150 kg

17 Quantities in excess of 150 kg should be held in a dedicated separate storage building.

18 For *ambient* storage the following features are recommended:

(a) the walls of the store should be of non-combustible construction, preferably concrete, masonry or brick;
(b) the floor should be concrete and sloped to allow both the detection and

accumulation (for subsequent removal and dispersal) of spillages at the entrance to the store;

(c) where practicable, doorways should not face boundaries or windows and exits of adjacent buildings. For liquid organic peroxides the doorways should also be provided with spillage retention facilities capable of containing the entire liquid organic peroxide contents of the store. This is to minimise the size of the fire and the associated thermal radiation effects. The separation distances given in paragraph 20 have been derived assuming no spread of fire outside of the peroxide store;

(d) the roof must be opaque (to exclude direct sunlight). Normally the roof should provide explosion relief for the building, ie be lightweight and fixed so that it easily blows off in an explosion. Alternatively, relief panels, which vent to a safe place, may be provided in one or more external walls;

(e) the store design and layout should include consideration of water supplies, fire protection equipment, fire fighting, means of escape, means of access for fire brigade appliances, protection of fire fighters and arrangements to ensure an early call out of the fire brigade in the event of fire. The fire authority should be consulted on these matters, at the planning stage in the case of new or altered facilities;

(f) consideration is also needed of the consequences that fire water run-off might have on the environment and local water courses. Consultation with the Environment Agency may be appropriate. Guidance can be found in *The control of fire water run-off from CIMAH sites to prevent environmental damage* (see reference 14) and *Design of containment systems for the prevention of water pollution from industrial incidents* (see reference 15).

(g) stores holding Type 1 organic peroxides (see paragraph 11) should be provided with an automatic water sprinkler deluge system. This should be designed, installed and maintained to an appropriate standard such as BS 5306: Part 2 1996 *Fire extinguishing installations and equipment on premises Part 2 Specification for sprinkler systems*. Advice on the required water delivery rate should be sought from the peroxide supplier. It is recommended that this should be in the form of fine droplets ie a fog. Such sprinkler systems are also strongly recommended for Type 2 organic peroxides. Stores equipped with sprinklers should also have 'bund' overfiow facilities which are channelled to a place of containment (to prevent serious damage to the environment) and which is located so that burning liquid is kept away from other buildings and the boundary;

(h) for liquid organic peroxides which are highly flammable liquids, as defined in references 12 and 13, store rooms should be adequately ventilated to disperse vapour from any leak or spill. A standard of at least five air changes per hour is recommended, using air bricks, louvres etc in at least one, and preferably more, external walls. To provide this, these openings should normally have a total area of at least 2½% of the total area of the walls and roof and should be all high and low level;

(i) if electrical equipment has to be installed inside the store, it should be suitably protected for use in potentially flammable atmospheres as described in paragraphs 16(g) to (i);

(j) if heating is required, then the requirements of paragraph 16(n) must be followed.

19 For *refrigerated* storage the recommendations as per paragraphs 18 (a) to (d) and (i) are appropriate together with:

(a) location of the refrigeration equipment outside the storeroom. Sufficient space should be left between the stacks to allow air circulation:

(b) careful consideration of the cooling arrangements to ensure that there is uniform cooling of all parts of the storeroom. Where a supplementary air circulation fan is required this should be dealt with in accordance with paragraphs 16(f) to (i);

(c) provision of a fixed automatic fire-fighting system for Type 1 organic peroxides and possibly for Type 2 organic peroxides. Account should be taken of the low temperature in the design of water spray systems (see reference 16);
(d) a 'high' temperature alarm giving warning at a permanently manned location (set to give an early detection of cooling failure in advance of pending instability of the products stored);
(e) effective arrangements for dealing with refrigeration failure, eg use of solid carbon dioxide, transfer to other store(s), back-up refrigeration unit

Minimum separation distances for detached stores holding more than 150kg of peroxides (Types 1 to 3)

20 Recommended minimum separation distances from organic peroxides stores of Types 1, 2 and 3 packaged organic peroxides to boundaries and 'sensitive facilities' are shown in Figure 1.

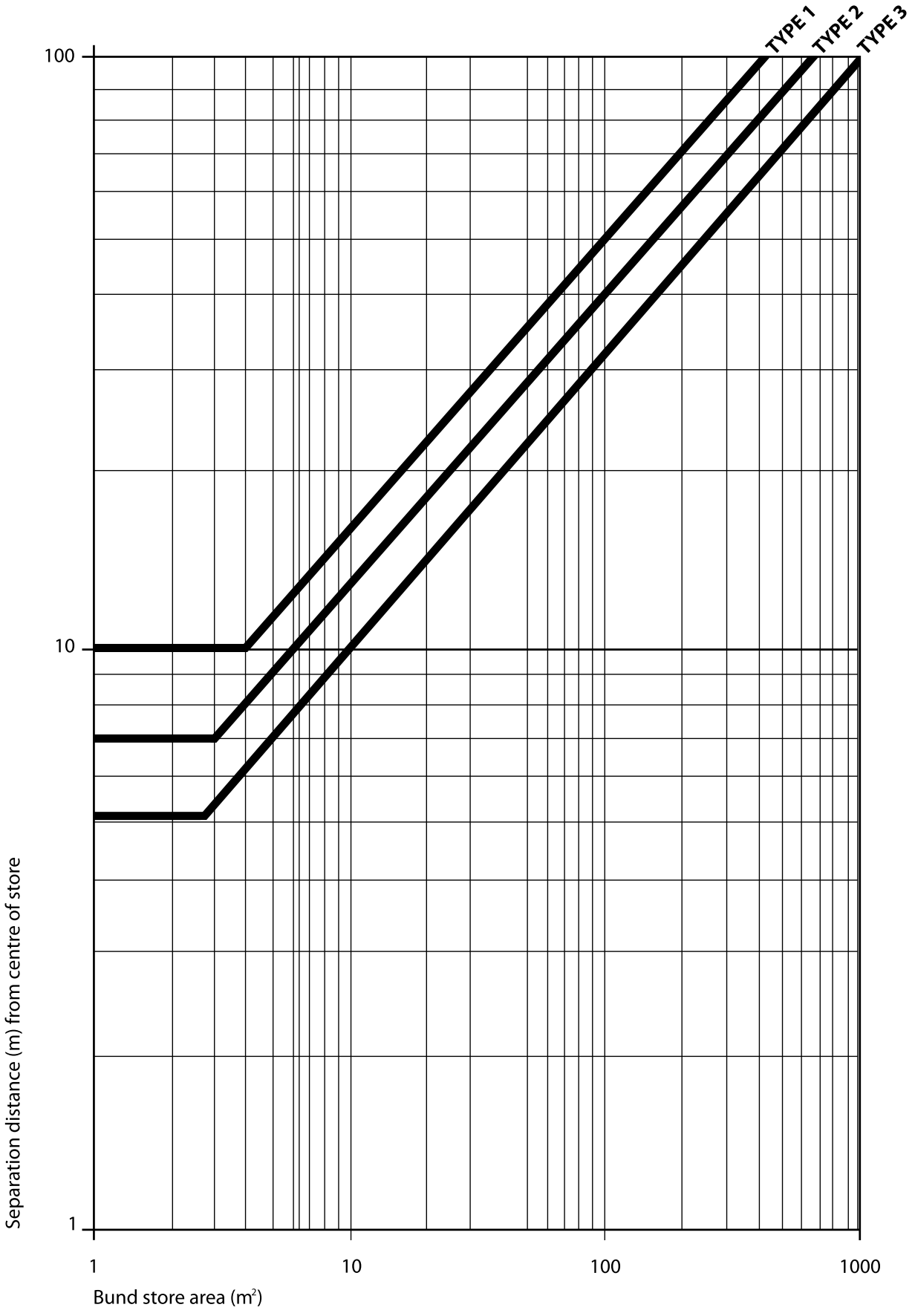

Figure 1 Separation distances to boundaries/buildings from organic peroxide stores

Notes:

(a) These separation distances correspond to the thermal radiation of 12.6 kw/m^2, ie the level for piloted ignition of dry wood, and minimise the risk of fire spreading from the store to other buildings. If there are vulnerable populations in the vicinity whose escape to a place of safety might be delayed, further consideration could well be needed of the stores' location and protective measures to ensure that the resultant level of thermal radiation will not cause ignition. For more details see *Thermal radiation: physiological and pathological effects* (reference 17).

(b) For determination of separation distances for liquid organic peroxides, the 'store area' is the surface area (m^2) of the floor or bunded area over which spilled burning liquid organic peroxide can spread.

(c) If the recommended safety distances cannot be achieved they may be reduced, in appropriate cases, by the provision of fire walls* and other protective measures such as fixed water-spray cooling systems. The walls of the store may serve as fire walls if of appropriate construction. Advice may be sought from the enforcing authority.

(d) 'Sensitive facilities' include the following:

  (i) occupied buildings and facilities which, if they caught fire, could threaten people's lives (eg offices, stores, houses, process plant etc); and

  (ii) facilities (eg stores and plant) which, if they caught fire, could present a serious threat to either the environment or people nearby (eg by release from a toxic store; by fire/explosion from a flammable store). In certain cases, eg storage of liquefied petroleum gases, other guidance will also apply, which may specify larger separation distances which will override the requirements of this Guidance Note.

(e) For stores holding mixed types of organic peroxides, separation distances for the highest flammability type present must be selected.

(f) The flammability types of packaged organic peroxides, known to be in use in the UK, are given in the Appendix (see also paragraphs 10 and 11).

Marking and labelling

21 Sites storing more than 25 tonnes of dangerous substances, as defined by the CHIP Regulations (see reference 13), should be marked in accordance with The Dangerous Substances (Notification and Marking of Sites) Regulations 1990 (see reference 18).

22 Storerooms, cupboards and bins must be marked to indicate their contents. Where direct marking is not reasonably practicable the marking should be displayed close to the store. 'No smoking' signs should also be displayed.

23 Individual containers should be clearly marked to indicate their contents, principal hazard and basic safety precautions. In most cases this will be dealt with by the Carriage of Dangerous Goods (Classification, Packaging and Labelling) and Use of Transportable Pressure Receptacles Regulations 1996 (see reference 19). Organic peroxides which are designated as presenting a significant hazard from explosion must bear a subsidiary explosion risk label when kept or conveyed

* An imperforate wall, screen or separating partition of substantial construction, of concrete, masonry or brick, designed to reduce the effects from radiated heat from an organic peroxide fire. The fire wall should not reduce the ventilation of the store below acceptable levels (see paragraphs 16(l) and 18(h).

in accordance with paragraphs 9 to 11 of Schedule 3 of the Classification and Labelling of Explosives Regulations 1983 (SI 1983/1140).

Store management

Keeping of peroxides

24 Access to the storage area should be restricted to authorised personnel. Organic peroxides should be kept in their original packages. They should be used on a stock rotation basis and not held longer than specified by the manufacturers. The stocks should be stable and stored not more than two packages high, unless stored on pallets when they can be four high. The containers should have an air gap around them to allow air circulation. It should be ensured that packages do not obstruct the means of escape.

25 Peroxides should not be decanted in the store (see paragraph 29). Stores should be kept free of all incompatible and combustible materials (see paragraphs 5 and 9(d)), other than the packaging materials and pallets as supplied or in use. Even then, if the outer packaging material becomes contaminated with organic peroxide, this should be removed and disposed of in accordance with the advice given by the manufacturer/supplier. Spillages of peroxides should be dealt with immediately (see paragraph 5). There should be no smoking in the stores and signs should be displayed accordingly.

26 The high/low temperature alarms required for refrigerated storage should be tested monthly and the results of such tests recorded and kept available for inspection by the enforcing authority for a period of 12 months. Similarly the automatic fire protection systems should be tested at regular intervals in accordance with Loss Prevention Council rules (reference 16).

Handling

27 Whenever organic peroxides are handled, chemical goggles and suitable protective gloves should be worn as a minimum. Only the minimum amount of organic peroxide should be held at the workplace. It should be used as soon as possible and in any event should not exceed the requirement of a shift.

28 All containers and equipment which come into contact with peroxides must be compatible. Suitable materials include glass, porcelain, polyethylene and 316 grade stainless steel.

Dispensing

29 If a process batch requirement is less than the supplied container size, then a separate, designated dispensing area/room should be provided and kept free of all incompatible materials and combustibles. Dispensing of liquid peroxides should be carried out over a suitable clean spillage retention tray which is capable of holding the entire contents of the peroxide container. The receptacles used should not introduce confinement over and above that provided by the container as supplied .

Transfer

30 The transfer of liquid peroxides should be performed using dedicated clean dispensers/syphons or pumps. The advice of the supplier should be sought on suitable equipment and materials. Particular care should be taken in the design of pumped systems where frictional heating, overpressurisation or static generation may be a problem.

Empty and partially empty containers

31 If unused material has to be returned to the original containers, then extreme care must be taken to avoid contamination. Original containers should be resealed immediately after use, using only the original cap.

Spillages and disposal

32 A supply of a suitable inert material such as vermiculite, kieselguhr or sand should be kept readily available for absorption of any spillages which should be cleared immediately. Incompatible materials such as rags, sawdust or paper should not be used. The peroxide soaked absorbent must not be confined and spillage should not be allowed to contaminate drainage and other water systems. Contaminated areas should be soaked with water where necessary. The correct disposal procedures for waste materials should be considered carefully and advice should be sought from the supplier.

Fork lift trucks

33 Where appropriate, fork lift trucks and other vehicles used within the hazardous areas associated with container storage and handling areas should be protected against igniting flammable vapour or dusts. General guidance on the standards for diesel vehicles in hazardous areas is contained in *Lift trucks in potentially flammable atmospheres* (reference 20). For other vehicles, specialist advice should be obtained. Battery charging should not be carried out in hazardous areas and vehicles should not be parked in such areas.

Emergency procedures/ Training

34 People involved in organic peroxide storage and handling should be given adequate instruction and training, both in safe 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.

First aid

35 For any significant exposure an ambulance should be called.

36 Where organic peroxides are stored and handled, facilities should be provided and maintained to allow emergency washing of skin and eyes in the event of contact with peroxides. The procedures laid down by the peroxide supplier should be followed rigorously and people rendering first aid should take precautions to avoid contaminating their own skin.

37 Contaminated clothing should be rapidly removed and placed in water to prevent spontaneous ignition. Should organic peroxide enter the eyes, thorough irrigation with water for 15 minutes at least, with eyelids apart, should be started as soon as possible. If skin contact occurs immediate copious washing with cold water should be carried out. If skin burns develop, irrigate continuously with cold water for 15 minutes then cover the burn with a first aid dressing.

38 After accidental ingestion of a corrosive peroxide, no attempt should be made to induce vomiting. As ingested peroxides may be corrosive, fluids must be withheld. Perforation of the gullet or stomach may have already occurred. Ingestion of fluids may extend the area of corrosion in both the chest and abdominal cavity.

Fire fighting

39 Sufficient and suitable portable first aid fire-fighting equipment should be provided. Advice on both the type and adequacy of equipment should be sought from the fire authority.

40 Extinguishers which depend upon suffocation (eg carbon dioxide) are ineffective, because the peroxides contain their own oxygen for combustion.

Major hazards

41 The Notification of Installations Handling Hazardous Substances (NIHHS) Regulations 1982 (SI 1982/1357) require a person who stores, manufactures, processes, or uses five tonnes or more of specified organic peroxides to supply information about the activity to the Health and Safety Executive (HSE). New installations or proposals to increase the notified capacity to more than three times the original capacity must be notified at least three months in advance. Changes in the activity, including cessation, must be notified immediately. The particulars to be notified are in Schedule 2 of the Regulations.

42 The intention to have more than five tonnes of specified organic peroxides on site requires the operator to apply for permission under the Planning (Hazardous Substance) Regulations 1992 (PHS) (SI 1992/656) or The Town and Country Planning (Hazardous Substances) (Scotland) Regulations 1993 (SI 1993/323(S.31). The list of substances is given in Schedule 1, part B of these regulations and is based on Schedule 1 of the NIHHS Regulations but includes some additional named organic peroxides. Consent applications are made to the Hazardous Substance Authority, usually the planning authority, who will consult HSE before making a decision. HSE will take into account the quantities of hazardous substance that will be present and the risks to the surrounding population. Under these regulations the planning authorities will also consult the HSE about developments near to existing sites storing organic peroxides above the PHS threshold.

43 It should be noted that compliance with the Health and Safety at Work etc Act 1974, for example, basing hazardous substance consent proposals on the minimum separation distances set out in this Guidance Note, does not imply that hazardous substance consent will be automatically granted. In reaching their decision the LPA not only consider existing developments but also future developments which may involve a high density population or the introduction of other potential hazards in the adjacent area. Consequently, after consultation with HSE, the LPA may decide that more stringent criteria should be applied for

land-use planning control. It is recommended therefore that consultation with HSE and the LPA is undertaken as early as possible whenever it is intended to introduce a notifiable quantity of organic peroxide on to a site.

44 The Control of Industrial Major Accident Hazards Regulations 1984 (CIMAH) and subsequent amendments apply to sites where organic peroxides are present above certain thresholds. The regulations apply at two levels:

(a) bottom-tier duties, which apply where the quantity exceeds the lower of two thresholds, require the operator to demonstrate, if requested, that all major accident hazards have been identified and adequate steps have been taken to prevent major accidents and minimise the consequences of any that do occur.
(b) top-tier duties, which apply where the quantity exceeds the upper threshold, require the operator to prepare:

    (i) a written safety report;
    (ii) an on-site emergency plan;

and provide:

    (i) information to the local authority for the preparation of an off-site emergency plan;
    (ii) specified information to the public who might be affected by a major incident.

45 The thresholds are different for substances that are involved in a process activity and those that are in storage. Further details can be found in the regulations or the guide to the regulations, HSR21 (see reference 22).

46 The more specific requirements apply to 'process activities' using at least 50 tonnes of a specified organic peroxide. The second amendment of the CIMAH Regulations (1990) extends the scope of the requirements to any storage (including warehouses) handling 'oxidising' substances and preparations as defined in the Chemicals (Hazard Information and Packaging for Supply) Regulations 1994. The inventory for application of the more general and specific requirements to these newly covered installations is 10 and 200 tonnes respectively, but it is also necessary to include any other substances or preparations classified as 'very toxic', 'toxic' or 'explosive' under CPLR when calculating the quantity present against the given thresholds.

47 A fundamental review of the EC directive that underpins the CIMAH Regulations will be implemented in the UK in February 1999 by the Control of Major Accident Hazard (COMAH) Regulations. The new regulations follow the same basic principles as the CIMAH Regulations and will replace them. The major changes to CIMAH will be as follows:

(a) The qualification criteria will no longer be based on a list of named organic peroxides. Instead the generic qualification criterion of oxidising substance as classified under the CHIP Regulations will be used. An aggregation of all such substances will be made and the general requirements will apply for aggregated quantities above 50 tonnes and the specific requirements will apply above 200 tonnes.
(b) The distinction between process and storage will be removed.
(c) The general requirements will include the preparation of a major accident prevention policy.
(d) The specific requirements will require the testing of emergency plans.
(e) Where several establishments are located close to one another and there is the potential for knock-on effects then these establishments will be required to share information, especially on emergency planning.

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22 *Guide to the Control of Industrial Major Accident Hazards Regulations* 1984 HSR21 HSE Books 1990 ISBN 0 11 885579 4

The future availability and accuracy of the references listed in this publication cannot be guaranteed.

Appendix Assignments of packaged organic peroxides to flammability types

Organic peroxide	Concentration (%)	Diluent type A (%)	Diluent type B (%) 1)	Inert solid (%)	Water (%)	Packing method	Control temperature (°C)	Emergency temperature (°C)	Subsidiary risks and remarks	Previous UN number	UN No (generic entry)	Flammability type (see paragraph 10)
ACETYL ACETONE PEROXIDE	≤ 42	≥ 48			≥ 8	OP7A			2	2080	3105	2
	≤ 32 as a paste					OP7B			21	3061	3106	3
ACETYL BENZOYL PEROXIDE	≤ 45	≥ 55				OP7A				2081	3105	*
ACETYL CYCLOHEXANESULPHONYL PEROXIDE	≤ 82				≥ 12	OP4B	- 10	0	3	2082	3112	1
	≤ 32		≥ 68			OP7A	- 10	0		2083	3115	3
tert-AMYL HYDROPEROXIDE	≤ 88	≥ 6			≥ 6	OP8A				3067	3107	1
tert-AMYL PEROXYBENZOATE	≤ 96	≥ 4				OP7A				3044	3105	*
tert-AMYL PEROXY-2-ETHYLHEXANOATE	≤ 100					OP7A	+ 20	+ 25		2898	3115	1
tert-AMYL PEROXYNEODECANOATE	≤ 77		≥ 23			OP7A	0	+ 10		2891	3115	1
tert-AMYLPEROXYPIVALATE	≤ 77		≥ 23			OP5A	+10	+ 15		2957	3113	1
tert-AMYLPEROXY-3,5,5-TRIMETHYLHEXANOATE	≤ 100					OP5A			3		3101	*
tert-BUTYL CUMYLPEROXIDE	≤ 100					OP7A				2091	3105	1
n-BUYL-4,4-DI-(tert-BUTYLPEROXY)VALERATE	53-100					OP5A				2140	3103	*
	≤ 52			≥ 48		OP7B				2141	3106	3
tert-BUTYL HYDROPEROXIDE	73-90				≥ 10	OP5A			14	2094	3103	*
	≤ 80	≥ 20				OP7A			4,14	2092	3105	*
	≤ 72				≥ 28	OP8A, M			14	2093	3109	2
tert-BUTYL HYDROPEROXIDE + DI-tert-BUTYLPEROXIDE	≤ 82 + ≤ 9				≥ 7	OP5A			14	3075	3103	*
tert-BUTYL MONOPEROXYMALEATE	53-100					OP5B			3	2099	3102	*
	≤ 52	≥ 48				OP6A				2100	3103	2
	≤ 42 as a paste					OP8B			21	2101	3108	2
tert-BUTYL MONOPEROXYPHTHALATE	≤ 100					OP5B			3	2105	3102	*
tert-BUTYL PEROXYACETATE	53-77	≥ 23				OP5A			3	2095	3101	*
	≤ 52	≥ 48				OP6A				2096	3103	2
tert-BUTYL PEROXYBENZOATE	78-100	≥ 22				OP5A				2097	3103	1
	53-77	≥ 23				OP7A				2095	3105	*
	≤ 52			≥ 48		OP7B				2890	3106	2
tert-BUTYL PEROXYCROTONATE	≤ 77	≥ 23				OP7A				2183	3105	*
tert-BUTYL PEROXYDIETHYLACETATE	≤ 100					OP5A	+ 20	+ 25		2144	3113	*
tert-BUTYL PEROXYDIETHYLACETATE + tert-BUTYL PEROXYBENZOATE	≤ 33 + ≤ 33	≥ 33				OP7A				2511	3105	*
tert-BUTYL PEROXY-2-ETHYLHEXANOATE	53-100					OP6A	+ 20	+ 25		2143	3113	1

Organic peroxide	Concentration (%)	Diluent type A (%)	Diluent type B (%) 1)	Inert solid (%)	Water (%)	Packing method	Control temperature (°C)	Emergency temperature (°C)	Subsidiary risks and remarks	Previous UN number	UN No (generic entry)	Flammability type (see paragraph 10)
	≤ 52		≥ 48			OP8A	+ 20	+ 25		2888	3117	2
tert-BUTYL PEROXY-2-ETHYLHEXANOATE + 2,2-DI-(tert-BUTYLPEROXY)BUTANE	≤ 31 + ≤ 36		≥ 33			OP7A	+ 35	+ 40		2886	3115	1
	≤ 12 + ≤ 14	≥ 14		≥ 60		OP7B					3106	*
tert-BUTYL PEROXYISOBUTYRATE	53-77		≥ 23			OP5A	+ 15	+ 20	3	2142	3111	1
	≤ 52		≥ 48			OP7A	+ 15	+ 20		2562	3115	1
tert-BUTYLPEROXY ISOPROPYLCARBONATE	≤ 77	≥ 23				OP5A				2103	3103	1
tert-BUTYL PEROXYNEODECANOATE	78-100					OP7A	- 5	+ 5		2594	3115	1
	≤ 77		≥ 23			OP7A	0	+ 10		2177	3115	2
3-tert-BUTYLPEROXY-3-PHENYLPHTHALIDE	≤ 100					OP7B				2596	3106	2
tert-BUTYL PEROXYPIVALATE	68-77	≥ 23				OP5A	0	+ 10		2110	3113	1
	≤ 67		≥ 33			OP7A	0	+ 10		3047	3115	1
tert-BUTYLPEROXY STEARYLCARBONATE	≤ 100					OP7B				3062	3106	*
tert-BUTYL PEROXY-3,5,5-TRIMETHYLHEXANOATE	≤ 100					OP7A				2104	3105	1
3-CHLOROPEROXYBENZOIC ACID	58-86			≥ 14		OP1B			3	2755	3102	*
	≤ 57			≥ 3	≥ 40	OP7B				3081	3106	*
CUMYL HYDROPEROXIDE	≤ 90	≥ 10				OP8A, M			14, 19	2116	3109	2
CUMYL PEROXYNEODECANOATE	≤ 77		≥ 23			OP7A	- 10	0		2963	3115	1
CUMYL PEROXYPIVALATE	≤ 77		≥ 23			OP7A	- 5	+ 5		2964	3115	1
CYCLOHEXANONE PEROXIDE(S)	≤ 91				≥ 9	OP6B			14	2119	3104	1
	≤ 72 as a paste					OP7B			5, 21	2896	3106	2
	≤ 72	≥ 28				OP7A			5	2118	3105	2
	≤ 32			≥ 68						Exempt	Exempt	4
DIACETONE ALCOHOL PEROXIDES	≤ 57		≥ 26		≥ 8	OP7A	+ 30	+ 35	7	2163	3115	2
DIACETYL PEROXIDE	≤ 27		≥ 73			OP7A	+ 20	+ 25	8, 14	2084	3115	2
DI-tert-AMYL PEROXIDE	≤ 100					OP8A					3107	*
DIBENZOYL PEROXIDE	52-100			≥ 48		OP2B			3	2085	3102	*
	78-94				≥ 6	OP4B			3	2088	3102	*
	≤ 77				≥ 23	OP6B				2090	3104	2
	≤ 62			≥ 28	≥ 10	OP7B				3074	3106	2
	53-62 as a paste					OP7B			21		3106	*
	≤ 52 as a paste					OP8B			21	2089	3108	2
	36-52			≥ 48		OP7B					3106	*
	≤ 35			≥ 65						Exempt	Exempt	4

Organic peroxide	Concentration (%)	Diluent type A (%)	Diluent type B (%) 1)	Inert solid (%)	Water (%)	Packing method	Control temperature (°C)	Emergency temperature (°C)	Subsidiary risks and remarks	Previous UN number	UN No (generic entry)	Flammability type (see paragraph 10)
DIBENZYL PEROXYDICARBONATE	≤ 87				≥ 13	OP5B	+ 25	+ 30	3	2149	3112	*
DI-(4-tert-BUTYLCYCLOHEXYL) PEROXYDICARBONATE	≤ 100					OP6B	+ 30	+ 35		2154	3114	1
	≤ 42 as a stable dispersion in water					OP8A, N	+ 30	+ 35		2894	3119	4
DI-tert-BUTYL PEROXIDE	≤ 100					OP8A				2102	3107	1
2,2-DI-tert-BUTYLPEROXY)BUTANE	≤ 52					OP6A				2111	3103	2
1,1-DI-(tert-BUTYLPEROXY)CYCLOHEXANE	81-100					OP5A			3	2179	3101	*
	53-80	≥ 20				OP5A				2180	3103	*
	52	≥ 48				OP7A				2897	3105	2
	≤ 42	≥ 13		≥ 45		OP7B				2885	3106	4
	≤ 27	≥ 36				OP8A			22	3069	3107	3
2,2-DI-(4,4-tert-BUTYLPEROXYCYCLOHEXYL)PROPANE	≤ 42			58		OP7B				2168	3106	3
DI-n-BUTYL PEROXYDICARBONATE	28-52		48			OP7A	- 15	- 5		2169	3115	2
	≤ 27		≥ 73			OP8A	- 10	0		2170	3117	3
DI-sec-BUTYL PEROXYDICARBONATE	53-100					OP4A	- 20	- 10		2150	3113	*
	≤ 52		≥ 48			OP7A	- 15	- 5		2151	3115	2
DI-(2-tert-BUTYLPEROXYISOPROPYL)BENZENE(S)	43-100			≥ 57		OP7B				2112	3106	2
	≤ 42			≥ 58						Exempt	Exempt	4
DI-(tert-BUTYLPEROXY)PHTHALATE	43-52	≥48				OP7A				2107	3105	2
	≤ 52 as a paste					OP7B			21	2108	3106	2
	≤ 42	≥58				OP8A					3107	*
2,2-DI-(tert-BUTYLPEROXY)PROPANE	≤ 52	≥ 48				OP7A				2883	3105	2
	≤ 42	≥ 13		≥ 45		OP7B				2884	3106	2
1,1-DI-(tert-BUTYLPEROXY)-3,3,5-TRIMETHYL-CYCLOHEXANE	58-100					OP5A			3	2145	3101	*
	≤ 57			≥ 43		OP7B				2147	3106	2
	≤ 57	≥ 43				OP8A				2146	3107	3
DICETYL PEROXYDICARBONATE	≤ 100					OP7B	+ 20	+ 25		2164	3116	2
	≤ 42 as a stable dispersion in water					OP8A, N	+ 30	+ 35		2895	3119	4
DI-4-CHLOROBENZOYL PEROXIDE	≤ 77				≥ 23	OP5B			3	2113	3102	*
	≤ 52 as a paste					OP7B			21	2114	3106	3
	≤ 32			≥ 68						Exempt	Exempt	4
DICUMYL PEROXIDE	43-100			≥ 57		OP7B, M			13	2121	3110	2
	≤ 42			≥ 58						Exempt	Exempt	4

Organic peroxide	Concentration (%)	Diluent type A (%)	Diluent type B (%) 1)	Inert solid (%)	Water (%)	Packing method	Control temperature (°C)	Emergency temperature (°C)	Subsidiary risks and remarks	Previous UN number	UN No (generic entry)	Flammability type (see paragraph 10)
DICYCLOHEXYL PEROXYDICARBONATE	92-100					OP5B	+ 5	+ 10	3	2152	3112	2
	≤ 91				≥ 9	OP3B	+ 5	+ 10		2153	3114	2
DIDECANOYL PEROXIDE	≤ 100					OP6B	+ 15	+ 20		2120	3114	2
DI-2,4-DICHLOROBENZOYL PEROXIDE	≤ 77				≥ 23	OP5B			3	2137	3102	*
	≤ 52 as a paste with silicon oil					OP7B				2138	3106	3
DI-(2-ETHYLHEXYL) PEROXYDICARBONATE	78-100					OP5A	- 20	- 10		2122	3113	1
	≤ 77					OP7A	- 15	- 5		2123	3115	1
	≤ 42 as a stable dispersion in water					OP8A	- 15	- 5		2960	3117	4
	≤ 42 as a stable dispersion in water (frozen)					OP8B	- 15	- 5		2960	3118	*
DIETHYL PEROXYDICARBONATE	≤ 27		73			OP7A	- 10	0		2175	3115	*
2,2-DIHYDROPEROXYPROPANE	≤ 27			≥73		OP5B			3	2178	3102	*
DI-(1-HYDROXYCYCLOHEXYL) PEROXIDE	≤ 100					OP7B				2148	3106	2
DIISOBUTYRYL PEROXIDE	33-52		≥ 48			OP5A	- 20	- 10	3	2182	3111	*
	≤ 32		≥ 68			OP7A	- 20	- 10			3115	*
DIISOPROPYL PEROXYDICARBONATE	10	90				OP7A	- 10	0		2134	3115	3
	53-100					OP2B	- 15	- 5	3	2133	3112	1
	≤ 52		≥ 48			OP7A	- 10	0		2134	3115	2
DIISOTRIDECYL PEROXYDICARBONATE	≤ 100					OP7A	- 10	0		2889	3115	2
DILAUROYL PEROXIDE	≤ 100					OP7B				2124	3106	2
	≤ 42 as a stable dispersion in water					OP8A, N				2893	3109	4
DI-(2-METHYLBENZOYL) PEROXIDE	≤ 87				≥ 13	OP5B	+ 30	+ 35	3	2593	3112	1
2,5-DIMETHYL-2,5-DI-(BENZOYLPEROXY)HEXANE	83-100					OP5B			3	2172	3102	1
	≤ 82			≥18		OP7B				2959	3106	2
	≤ 82				≥18	OP5B				2173	3104	1
2,5-DIMETHYL-2,5-DI-(tert-BUTYLPEROXY)HEXANE	53-100					OP7A				2155	3105	1
	≤ 52			≥ 48		OP7B				2156	3106	3
2,5-DIMETHYL-2,5-DI-(tert-BUTYLPEROXY)HEXANE-3	53-100					OP5A				2158	3103	1
	≤ 52			≥ 48		OP7B				2159	3106	3
2,5-DIMETHYL-2,5-DI-(2-ETHYLHEXANOYLPEROXY)-HEXANE	≤ 100					OP7A	+ 20	+ 25		2157	3115	*
2,5-DIMETHYL-2,5-DIHYDROPEROXYHEXANE	≤ 82				≥ 18	OP6B				2174	3104	*

Organic peroxide	Concentration (%)	Diluent type A (%)	Diluent type B (%) 1)	Inert solid (%)	Water (%)	Packing method	Control temperature (°C)	Emergency temperature (°C)	Subsidiary risks and remarks	Previous UN number	UN No (generic entry)	Flammability type (see paragraph 10)
2,5-DIMETHYL-2,5,DI-(3,5,5,-TRIMETHYLHEXANOYL-PEROXY)HEXANE	≤ 77	≥ 23				OP7A				3060	3105	*
DIMYRISTYL PEROXYDICARBONATE	100					OP7B	+ 20	+ 25		2595	3116	2
	≤ 42 as a stable dispersion in water					OP8A, N	+ 20	+ 25		2892	3119	4
DI-n-NONANOYL PEROXIDE	≤ 100					OP7B	0	+ 10		2130	3116	1
Di-n-OCTANOYL PEROXIDE	≤ 100					OP5B	+ 10	+ 15		2129	3114	2
DIPEROXY AZELAIC ACID	≤ 27			≥ 73		OP7B	+ 35	+ 40		2958	3116	3
DIPEROXY DODECANE DIACID	14-42			≥ 58		OP7B	+ 40	+ 45		3063	3116	2
	≤ 13			≥ 87						Exempt	Exempt	4
DI-(2-PHENOXYETHYL) PEROXYDICARBONATE	86-100					OP5B			3	3058	3102	*
	≤ 85				≥ 15	OP7B				3059	3106	*
DIPROPIONYL PEROXIDE	≤ 27		≥ 73			OP8A	+15	+ 20		2132	3117	3
DI-n-PROPYL PEROXYDICARBONATE	≤ 100					OP4A	- 25	- 15		2176	3113	*
DISTEARYL PEROXYDICARBONATE	≤ 87			≥ 13		OP7B				2592	3106	2
DISUCCINIC ACID PEROXIDE	73-100					OP4B			3	2135	3102	*
	≤ 72				≥ 28	OP7B	+ 10	+ 15	18	2962	3116	2
DI-(3,5,5-TRIMETHYL-HEXANOYL) PEROXIDE	82	≥ 18				OP7A	0	+ 10		2128	3115	1
DI-(3,5,5-TRIMETHYL-1,2-DIOXOLANYL-3) PEROXIDE	≤ 52 as a paste					OP7B	+ 30	+ 35	21	2597	3116	2
ETHYL 3,3-DI-(tert-AMYLPEROXY)BUTYRATE	≤ 67	≥ 33				OP7A					3105	*
ETHYL 3,3-DI-(tert-BUTYLPEROXY)BUTYRATE	78-100					OP5A				2184	3103	*
	≤ 77	≥ 23				OP7A				2185	3105	1
	52			≥ 48		OP7B				2598	3106	3
3,3,6,6,9,9-HEXAMETHYL-1,2,4,5-TETRAOXACYCLONONANE	53-100					OP4B			3	2165	3102	*
	≤ 52	48				OP7A				2167	3105	*
	≤ 52			≥ 48		OP7B				2166	3106	3
ISOPROPYLCUMYL HYDROPEROXIDE	≤ 72	≥ 28				OP8A, M			14	2171	3109	2
p-MENTHYL HYDROPEROXIDE	56-100					OP7A			14	2125	3105	2
	≤ 55	≥ 45				OP8A, M					3109	*
METHYLCYCLOHEXANONE PEROXIDE(S)	≤ 67		≥ 33			OP7A	+ 35	+ 40		3046	3115	1
METHYL ETHYL KETONE PEROXIDE(S)	52	≥ 48				OP5A			3, 9, 14	2563	3101	*
	≤ 45	≥ 55				OP7A			10	2550	3105	1
	≤ 40	≥ 60				OP8A			23	3068	3107	*
METHYL ISOBUTYL KETONE PEROXIDE(S)	≤ 62	≥ 19				OP7A				2126	3105	1

Organic peroxide	Concentration (%)	Diluent type A (%)	Diluent type B (%) 1)	Inert solid (%)	Water (%)	Packing method	Control temperature (°C)	Emergency temperature (°C)	Subsidiary risks and remarks	Previous UN number	UN No (generic entry)	Flammability type (see paragraph 10)
ORGANIC PEROXIDE, LIQUID, SAMPLE						OP2A			12		3103	*
ORGANIC PEROXIDE, LIQUID, SAMPLE, TEMPERATURE CONTROLLED						OP2A			12		3113	*
ORGANIC PEROXIDE, SOLID, SAMPLE						OP2B			12		3104	*
ORGANIC PEROXIDE, SOLID, SAMPLE, TEMPERATURE CONTROLLED						OP2B			12		3114	*
PEROXYACETIC ACID, TYPE D, stabilised	≤ 43					OP7A			14, 15, 20	2131	3105	3
PEROXYACETIC ACID, TYPE E, stabilised	≤ 43					OP8A			14, 18, 20	2131	3107	3
PEROXYACETIC ACID, TYPE F, stabilised	≤ 43					OP8A			14, 17, 20	2131	3109	3
PINANYL HYDROPEROXIDE	56-100					OP7A			14	2162	3105	2
	≤ 55	≥45				OP8A, M				3109		
TETRAHYDRONAPHTHYL HYDROPEROXIDE	≤ 100					OP7B				2136	3106	*
1,1,3,3-TETRAMETHYLBUTYL HYDROPEROXIDE	≤ 100					OP7A				2160	3105	*
1,1,3,3-TETRAMETHYLBUTYL PEROXY-2-ETHYLHEXANOATE	100					OP7A	+ 20	+ 25		2161	3115	*
2,4,4-TRIMETHYLPENTYL-2-PEROXY PHENOXYACETATE	≤ 37		≥ 63			OP7A	- 10	0		2061	3115	1

See over for key.../

Key to subsidiary risks and remarks

* Substances that have not been assigned to a flammability type

(1) Diluent type B may always be replaced by diluent type A
(2) Available oxygen ≤ 4.7%
(3) 'EXPLOSIVE' subsidiary risk label required
(4) Diluent may be replaced by di-tert-butyl peroxide
(5) Available oxygen ≤ 9%
(6) Available oxygen ≤ 7.5%
(7) With ≥ 9% hydrogen peroxide; available oxygen ≤ 10%
(8) Only non metallic packagings allowed
(9) Available oxygen > 10%
(10) Available oxygen ≤ 10%
(11) Available oxygen ≤ 8.2%, diluent may be replaced by diisobutylnylonate
(12) See 11.3.2.6 of UN Recommendations (ref 18)
(13) Up to 2000 kg per receptacle assigned to ORGANIC PEROXIDES TYPE F on the basis of large scale trials
(14) 'CORROSIVE' subsidiary risk label required
(15) Peroxy acetic acid formulations which fulfil the criteria of 11.3.3.3 (d) of UN Recommendations (ref 18)
(16) Peroxy acetic acid formulations which fulfil the criteria of 11.3.3.3 (e) of UN Recommendations (ref 18)
(17) Peroxy acetic acid formulations which fulfil the criteria of 11.3.3.3 (f) of UN Recommendations (ref 18)
(18) Addition of water to this organic peroxide will decrease its thermal stability
(19) No 'CORROSIVE' subsidiary risk label required for concentrations below 80%
(20) Mixtures with hydrogen peroxide, water and acids
(21) With diluent type A, with or without water
(22) With > 3%, by mass, ethylbenzene
(23) With > 19%, by mass, methyl isobutyl kentone

Notes:

(a) Diluents type A are organic liquids which are compatible with the organic peroxide and which have a boiling point of not less than 150 degrees C. Type A diluents may be used for desensitising all organic peroxides.

(b) Diluents type B are organic liquids which are compatible with the organic peroxide and which have a boiling point of less than 150 degrees C but not less than 60 degrees C and a flash point of not less than 5 degrees C. Type B diluents may only be used for desensitisation of organic peroxides for which temperature control is required. The boiling point of the liquid should be at least 50 degrees C higher than the control temperature of the peroxide.

(c) The 'UN Number (generic entry)' column in the table above relates to the substance/article numbers in the sixth revised edition of the *UN Recommendations on the Transport of Dangerous Goods* (ref 18).

(d) The 'previous UN Number' column in the table above relates to the, out of date, substances/article numbers in the fifth edition of the UN Recommendations referred to above.

(e) The ‘Packaging method’ column in the table above are packagings methods (and associated capacity/mass limitations per package) as given in the UN Recommendations, paragraph 9.4.7 and Tables 11.2(a) and (b)

(f) The subsidiary risks and remarks are those given in table 11.3 of the UN Recommendations.

Further information

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Published by HSE 04/10