Recommendations

RC43

for fire safety in the storage and use of oxidising materials

FPA

InFiReS

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SCOPE

These recommendations present fire safety measures relating to the storage and use of inorganic and organic oxidising chemicals, other than military or civilian explosives.

In chemical terms, oxidation reactions are not confined to chemicals containing oxygen, as other substances may also undergo this process. This document therefore does not specifically confine itself to oxidising materials that incorporate oxygen into their molecular structure.

The storage, use and provision of oxygen from cylinders or pipelines is outside the scope of these recommendations.

Legislation may impose requirements additional to the provisions contained in this document (see section 2 and refs 1-5). Due regard should also be given to considerations of environmental protection. For example, the Landfill (England and Wales) Regulations (ref. 6) ban the landfill of explosive, corrosive and oxidising materials, as well as flammable, highly flammable liquids, hospital waste and clinical wastes at hazardous waste sites.

SYNOPSIS

These recommendations set out precautions that should be observed to ensure the safe handling, storage, use and disposal of oxidising substances and organic peroxides in the workplace. Guidance is also given regarding suitable fire prevention and fire protection measures, how to avoid hazards in processes and how to handle emergencies.

DEFINITIONS

Auto-ignition temperature

The minimum temperature at which a material will ignite spontaneously under specified test conditions.

Classification of hazardous areas (DSEAR (ref. 3) and BS EN 60079-10: 2003 (ref. 7))

This classification refers to areas in which open processes are carried out; areas in which closed processes are undertaken should be subject to a risk assessment.

- Zone 0: an area in which an explosive gas atmosphere is present continuously or for long periods;
- Zone 1: an area in which an explosive gas atmosphere is likely to occur in normal operation; and
- Zone 2: an area in which an explosive gas atmosphere is not likely to occur in normal operation and, if it does occur will persist for a short period only.

Exothermic reaction

A chemical reaction involving the generation of heat.

Oxidising substances

Substances which react with other materials, either at room temperature or with the application of heat, to cause a type of chemical reaction often involving the bonding of oxygen atoms. Oxidation reactions may be exothermic, proceeding sufficiently vigorously to cause explosions. Oxidising materials, however, are not necessarily themselves combustible.

Organic peroxides

Substances which contain carbon, hydrogen and oxygen may be considered to be derivatives of hydrogen peroxide. Organic peroxides are thermally unstable substances which may exhibit exothermic decomposition (see Table 1). Organic peroxides tend to:

- be liable to explosive decomposition;
- burn rapidly;
- be sensitive to impact or friction;
- react dangerously with other substances; and
- cause damage to the eyes.

The properties of some oxides and peroxides in solution can vary markedly at different concentrations, especially, for example, hydrogen peroxide.

INTRODUCTION

Oxidation is one of the most basic chemical reactions and has a profound effect on our everyday lives. Many proprietary products contain oxides or peroxides, these range from washing powders and ear drops to hardeners for fillers used in the building industry. In industry, oxidising agents are used in the production of resins and polymers among many other processes.

In its simplest form, oxidation involves the addition of oxygen to an element or compound. Thus the burning of carbon involves the production of carbon dioxide and is an oxidation reaction which may be expressed in chemical terms as:

$$C + O_2 \rightarrow CO_2 + \text{heat}$$

The chemical equation shows clearly that the reaction has involved the addition of an oxygen molecule to a carbon atom to form a molecule of carbon dioxide and energy is released in the form of heat. Not all oxidation reactions are this simple but they are encountered more frequently than may be expected. Thus the hardening of paints containing linseed oil, the rusting of iron and the part played by oxygen in the respiration process are all oxidation reactions, but these occur relatively slowly and the heat that is produced can be safely dissipated at a rate faster than it is produced.

In some cases – such as when rags have been used to apply linseed oil – the production of heat from the oxidation reaction may not be able to escape as fast as it is produced. In the case of linseed oil, the insulating qualities of the screwed up cloth may cause the heat to build up. The increasing temperature results in the rate of

reaction accelerating until a sufficiently high temperature has been reached to ignite the materials. In this way, the heat produced by a relatively slow reaction can result in fires in certain circumstances.

Some other oxidation reactions, however, are highly exothermic and extremely rapid, producing large quantities of heat and gas which may expand with explosive force. This is the case, for example, when petrol is ignited in an internal combustion engine or gunpowder (a mixture of carbon, sulphur and potassium nitrate) is set alight. Oxidation is also the basis of the reaction of powerful explosions such as those involving trinitrotoluene (TNT).

The principal oxidising agents encountered in commerce and industry tend to be chemical compounds containing relatively large quantities of oxygen, including peroxides, superoxides, nitrates, chlorates, dichromates, permanganates and persulphates. Inorganic, rather than organic oxidising agents, tend to be more commonly encountered in industrial undertakings. This includes many of the relevant barium, lithium, magnesium, potassium, sodium, strontium, calcium, lead and zinc salts. These recommendations, however, concern the safe storage and use of both organic and inorganic materials.

For an oxidation reaction to take place a second substance must be present. In some instances, however, this may not seem to be the case. But in the example of linseed oil on rags referred to above, the oxygen in the air is the oxidising agent. In industry it is generally important, therefore, to keep different types of materials (for example oxidising agents and flammable liquids) isolated and this forms the basis of many of the recommendations set out in this document. Care should be taken particularly to avoid oxidising agents coming into contact with reducing agents (another powerful class of chemicals) and information and advice should always be sought from a competent source regarding the potential incompatibility of various materials before storing them together.

1. LEGISLATION

There are several items of legislation relating to oxidising substances. These include the:

- Regulatory Reform (Fire Safety) Order 2005 and the equivalent legislation in Scotland and Northern Ireland (refs 8 to 11) which require a suitable and sufficient fire risk assessment of the workplace to be carried out;
- Dangerous Substances and Explosive Atmospheres Regulations 2002 (ref. 3) which require that a risk assessment is carried out of any work activities involving dangerous substances; and
- Classification, Packaging and Labelling Regulations – known as the 'CPL Regulations' – which address health and safety and environmental issues relating to the harmful effects of dangerous chemicals.

There are two main pieces of this legislation, one for dangerous substances and the other for dangerous preparations, namely:

- European Communities (Classification, Packaging, Labelling and Notification of Dangerous Substances) Regulations 2003, SI No 116 (ref. 12); and
- European Communities (Classification, Packaging and Labelling of Dangerous Preparations) Regulations 2004, SI No 62 (ref. 13). (This is shortly to be amended.)

The first of these refers to substances that are chemical compounds, possibly including impurities; the second refers to preparations, deliberate physical mixtures of two or more substances.

The classification of a substance or preparation is based on an evaluation of the hazards that it presents due to its intrinsic properties. These are related to its toxicological, physiochemical, and environmental effects. The classification of a substance is outlined in Schedule 5 of the CPL (Substances) Regulations and a preparation in Schedules 1, 2 and 3 of the CPL (Preparations) Regulations. The hazards are communicated via an appropriate hazard label and safety data sheet.

Oxidising materials are classified as Class 5 materials, which are sub-divided into 5.1, oxidising substances, and 5.2, organic peroxides.

An organic peroxide or preparation containing a peroxide not already classified as explosive is classified as oxidising if the peroxide or its formulation contains:

- more than 5% of organic peroxides; or
- more than 0.5% available oxygen from the organic peroxides, and more than 5% hydrogen peroxide.

Class	Symbol	Examples
Class 5.1 Oxidising agents		• chloric acid • calcium hypochlorite • potassium permanganate • sodium peroxide
Class 5.2 Organic peroxides (liquid or solid)		• benzoyl peroxide • methyl ethyl ketone peroxide • cyclohexanone peroxide • all other organic peroxides

Table 1: Classification of oxidising agents

2. GENERAL CONSIDERATIONS

2.1 When carrying out the fire risk assessment in accordance with the Regulatory Reform (Fire Safety) Order 2005 or the equivalent legislation in Scotland and Northern Ireland (see refs 8 to 11) and the assessment under DSEAR (ref. 3), attention should always be given to eliminating the use of oxidising materials in the workplace wherever possible. Serious consideration should be given to the need for the use of such materials in processes and the possibility of using alternative materials and reactants.

2.2 Although the use of the acronym VICES was introduced in HSE guidance in booklet HS(G)51 (ref. 14) relating to the usage and storage of highly flammable and flammable liquids, it also has application with respect to oxidising materials and thus the recommendations set out below follow this format.

The acronym may be explained as follows:

V Ventilation (see section 4)

- Is there sufficient ventilation to ensure that materials stored are kept cool and self heating is prevented?
- Is the ventilation sufficient to prevent the spread of airborne particles from the immediate work area?

I Ignition (see section 5)

- Have all possible ignition sources been removed?
- Is the temperature of the store being monitored?

C Containment (see section 6)

- Are the materials stored in suitable containers?
- In the event of a spill will the spilled chemical be contained?
- Are there robust procedures in place and suitable equipment provided for clearing up spillages without delay?
- Is it possible to prevent spillages from spreading?
- Are 'empty' containers properly managed?

E Exchange (see section 7)

- Can oxidising materials be eliminated from the workplace?
- Can an oxidising agent be replaced with one that is less hazardous?

S Separation (see section 8)

- Is the storage of oxidising substances separated from other stored materials?
- Are incompatible materials suitably separated?
- Are physical barriers (such as walls, doors and containers) present as required?

2.3 Suitable staff training should be in place to ensure all personnel are aware of the hazards in the workplace and apply VICES to ensure a safer working environment for all.

2.4 Material safety data sheets should be available in the workplace setting out the properties of all hazardous materials, including oxidising agents, with which staff may come into contact.

3. VENTILATION

3.1 Due to the volatility of some organic peroxides, an assessment should be made of the areas where they are stored, handled, used and disposed of to ensure that existing ventilation from the workplace is adequate.

The assessment should consider the properties and quantities of the substances present, the mechanisms for handling and transferring the chemicals and the other processes undertaken in order to determine the level of ventilation that is required. This exercise will normally form part of the COSHH assessment (see ref. 1).

3.2 Where organic peroxides are handled in the workplace a complete system of hoods and ducts may need to be provided to ensure acceptable ventilation. The handling of small quantities, however, may only require a single, well-placed exhaust fan.

3.3 Ventilation systems for organic peroxides should be designed and built so that they do not result in an unintended hazard. Thus the use of organic materials, such as wood, in the construction of these systems should be avoided.

The same principle applies to hoods, fans, shrouds, ductwork and air cleaners, which should also be manufactured from materials compatible with the organic peroxides.

3.4 Care should also be taken to avoid the introduction of incompatible and combustible materials when cleaning, servicing and maintaining air cleaning and ventilation systems.

3.5 Air cleaning devices such as dust collectors and the like should be made from non-combustible materials.

3.6 Ventilation systems used for organic peroxides should be kept separate from those exhausting incompatible substances (such as flammable liquids).

3.7 An assessment of the work and storage areas should be carried out and appropriate 'Zones' (see Section 1: Definitions) assigned in accordance with the Dangerous Substances and Explosive Atmospheres Regulations 2002 (DSEAR) (ref. 3) and BS EN 60079-10 (ref. 7). Electrical equipment installed as part of the ventilation system should be suitable for use in the Zone in which it is installed.

3.8 Fan motors should not be positioned within ductwork, and should be suitable for the hazard Zone in which they are installed.

3.9 All mechanical ventilation installations shall comply with BS 5925 (ref. 15).

3.10 Ducting should be constructed of fire resistant material and be routed to a safe place in open air. Care should be taken to keep the ventilation opening clear of obstructions.

3.11 In most cases it should be adequate if the ventilation ductwork is terminated at least 3m above ground level and the same distance from building openings (including the eaves of buildings), boundaries and sources of ignition.

3.12 The location of the exhaust outlet should be subject to a risk assessment in compliance with DSEAR.

3.13 Ducts should be resistant to corrosion – for example, they should be manufactured from metal with a suitable plastic lining.

3.14 Where organic peroxides are stored and no mechanical ventilation is provided, explosion relief should be provided according to the findings of a risk assessment. In such a case, a lightweight roof or relief panels in the walls would serve to vent an explosion, provided that they release the pressure to a safe place so as not to cause injury or damage to property.

3.15 The discharge of dangerous substances into the atmosphere may have an environmental impact and thus expert advice should be sought where necessary.

3.16 No special ventilation system may be needed for work with small amounts of oxidising agents that are not volatile (for example, potassium permanganate, sodium chlorate etc).

4. IGNITION

4.1 One of the major objectives of any fire risk assessment is to identify potential sources of ignition in the workplace. These will include flames, hot surfaces and areas of movement that may lead to the generation of heat by friction or the build up of static charges. All potential sources of ignition should be maintained well below the temperature of self-accelerating decomposition of the most hazardous of any organic peroxides that are present.

4.2 Assessment of the lightning hazard should be undertaken in accordance with BS EN 62305 (or BS 6651, until it is withdrawn) (refs 16, 17 and 18). Further information is set out in FPA Recommendations RC35 (ref. 19).

4.3 Smoking should be prohibited in all areas where oxidising agents are used or stored and suitable notices be prominently displayed.

4.4 All maintenance or contractors' work should be carried out according to a Method Statement (provided by the contractor or the site occupier as necessary) subject to a risk assessment carried out by a competent person and using a 'Permit to Work' system which incorporates a 'Hot Work Permit' scheme. Special precautions are necessary when work may generate heat or sparks and strict safety procedures must be followed in respect of any work involving structures, plant or equipment containing, or used for the handling of oxidising agents.

All hot work necessary in areas in which oxidising agents are stored, dispensed, handled or processed must be controlled by a robust and properly controlled hot work permit scheme (ref. 20).

4.5 Where possible, cold cutting should be used as an alternative to hot work or the equipment should be removed to a safe environment, such as a workshop, for the work to be conducted.

4.6 Heating must be suitable for the Zone in which the work is being carried out. The temperature of the enclosure must be within the safe limits for the most hazardous materials present (see paragraphs 4.8 to 4.13 below).

In the case of large stores, consideration should be given to monitoring the temperature with an alarm being signalled to the monitoring area should the safe limit be exceeded.

4.7 Areas used for the storage of organic peroxides should normally be kept cool and dry. They may be heated only by the following:

4.7.1 A heating system providing ducted warm air or supplying hot water or steam to pipes and radiators should take account of the following:

- the system should incorporate a heat exchanger so as to prevent flammable vapours from coming into contact with an ignition source;
- any furnace or heat exchanger should be segregated and located either outside the Zone or in a separate building of brick or

concrete construction with a self-closing door to each opening. Combustion products should be exhausted to the open, clear of windows or other openings of the Zone in which oxidising materials are being stored or processed; and

- hot water or steam should circulate at a temperature not exceeding 120°C.

4.7.2 Electrical heaters should be of the low temperature flameproof type, certificated for use within the zone. The temperature of the external surface of such heaters should not exceed 120°C.

4.7.3 Electrical under-floor or ceiling heating should have heating elements totally embedded in concrete.

Storage temperature

4.8 The chemical supplier's recommendations will include information regarding the maximum and minimum temperatures for storage and use of oxidising materials and these should be followed. (The upper limit is to prevent, for example, the evaporation of oxidising agents in contact with combustible materials, including elements of the building structure which may result in a fire.)

4.8.1 Higher temperatures than those recommended can be hazardous since they speed up the decomposition rate of organic peroxides. Where appropriate, the maximum storage temperature should be maintained less than 38°C.

4.8.2 Some organic peroxides must be kept at low temperatures in refrigerators or freezers. In these instances only approved or specially modified units (generally known as 'laboratory safe') should be used because standard kitchen refrigerators and freezers contain ignition sources inside the cabinet.

4.9 If the hazard Zone of the storage area requires that resistance to explosion be provided and refrigeration is required, the refrigeration unit and all electrical equipment should be located outside this Zone. Connections between the refrigerator cabinet and the other equipment should be made using tubing that passes through the wall of the storage area.

4.10 Refrigeration equipment should be located in a well-ventilated area to carry away peroxide decomposition products that might result from a refrigeration failure.

4.11 As well as avoiding overheating, it can be hazardous to store some organic peroxides below the minimum recommended temperatures. (For example, acetyl peroxide is usually sold as a 25% solution in dimethyl phthalate to make it less shock sensitive. At temperatures below about –8°C, crystals of pure, shock sensitive, acetyl peroxide form. It is therefore important that organic peroxides which are diluted with water must not be stored at temperatures below 0°C to avoid separating out the pure organic peroxide.)

4.12 Alarms should be installed in storage areas to indicate when storage temperatures are higher or lower than those required.

4.13 Where large volumes of temperature-sensitive oxidising agents are stored, consideration should be given to installing an autostart back-up generator to maintain power to the refrigerators.

4.14 Special care should be taken in the design of laboratory fume cupboards and similar facilities to ensure that the design does not allow the condensation of oxidising materials in the hoods and ducts. Washdown systems should be employed rather than facilities with removable extraction panels.

5. CONTAINMENT

5.1 Material safety data sheets and the supplier's recommendations must be referred to and observed in all cases to ascertain specific storage requirements for each oxidising agent that is held on the premises. The requirements for inorganic oxidising agents (such as potassium permanganate or sodium chlorate), which are normally involatile solids, will be markedly different from those for organic peroxides (such as benzoyl peroxide), some of which are volatile liquids.

5.2 Regular equipment maintenance can prevent leaks or emissions of organic peroxides into the workplace:

Ensure that maintenance personnel know the possible hazards of the materials they may encounter and any special procedures and precautions needed before they begin work.

Prevent leaks of grease or other lubricants from equipment where organic peroxides are used.

Do not allow materials such as cleaning solvents, paints or thinners to contact organic peroxides.

Storage

5.3 Organic peroxides should be stored away from processing and handling areas. They should be kept away from incompatible materials such as strong acids and alkalis, other oxidising materials, highly flammable, flammable and combustible liquids and materials that can be oxidised (often called reducing materials or agents).

Separate storage can reduce personal injury and damage caused in case of fires, spills or leaks. A reduction in such accidents also reduces interruptions to the normal business activities of the site.

5.4 The reactivity data and storage requirements sections of the material safety data sheets should be referred to for details of materials that are incompatible with a specific organic peroxide.

5.5 Walls, floors, shelving and fittings in storage areas for organic peroxides should be constructed of compatible non-combustible materials.

5.6 Floors should be resistant to penetration by the organic peroxides in storage; they should be free of cracks in which chemicals could lodge if spilled.

5.7 Containers should be stored:

- at a convenient height for handling;
- below eye level if possible, to reduce the risk of dropping when handling them; and
- in such a way as to prevent overcrowding.

Containers should not be stored, even temporarily, in out-of-the-way locations where they could be forgotten.

5.8 At the end of the work period any unused quantities of oxidising agents should be returned to the store.

5.9 Containers should be stored away from doors, aisles and other parts of the escape routes from the store.

5.10 Organic peroxides should be stored in areas which are:

- well ventilated;
- dry, cool, out of direct sunlight and away from steam pipes, boilers or other heat sources;
- supplied with adequate firefighting equipment, including sprinklers where possible;
- supplied with suitable spill clean-up equipment and materials;
- free of ignition sources such as open flames, hot surfaces and spark-producing tools and devices;
- accessible at all times; and
- labelled with suitable warning signs.

5.11 In all cases:

- allow only trained, authorised people into storage areas;
- minimise the amounts of oxidising agents, especially organic peroxides, in storage;
- inspect storage areas regularly for any deficiencies including damaged or leaking containers and poor housekeeping; and
- correct all deficiencies as soon as possible.

5.12 Oxidising materials should not be stored or handled in areas that are liable to flooding.

5.13 Oxidising agents should not be allowed to come into contact with hydrocarbon greases.

Spillages

5.14 Any spillages of oxidising materials should be cleared up promptly and safely according to directions in the material safety data sheet.

5.15 Sawdust or other combustible sweeping compounds should not be used to clean up organic peroxide spills.

5.16 Oxidising materials should not be allowed to enter drains. Wherever possible, water used in clearing spillages or for firefighting should be retained on site. The Environment Agency should be consulted regarding the safe disposal of the residues; they should not be allowed to evaporate to dryness.

5.17 A means of spill control, such as floor dishing or ramped sills at door openings should be provided between compartments in which oxidising materials are stored. Small containers should be stored in trays made from compatible materials.

5.18 Spillages can happen at any time. An assessment should be made of the possible location and size of spillage or leakage and an action plan drawn up to include the immediate availability of non-combustible absorbent materials that are compatible with oxidising materials and tools to deal with any incident. Staff should be trained in the correct response to a spillage and rehearse the procedures.

6. EXCHANGE

6.1 The fourth letter of the acronym 'VICES', exchange, refers to the primary need to ensure that oxidising agents are eliminated from the workplace if at all possible. Each reagent and its use should be considered in turn and possible non-combustible or aqueous alternatives be considered.

6.2 Substitution can be the best way to avoid or reduce a hazard. However, it is not always easy or even possible to find a suitable substitute for a particular task, especially in the case of organic peroxides. Chemical suppliers should be consulted to find out if safer substitutes are available. Material safety data sheets should be obtained for all possible substitutes; an assessment of the possible alternatives should then be undertaken.

All hazards (including toxicity, fire-related properties, corrosivity and chemical reactivity) of these materials should be investigated before making any decision to change. The least hazardous material able to do the job effectively

and safely should be selected. Staff should then receive additional training or briefing as appropriate.

6.3 If materials cannot be substituted, in some cases changing or modifying a process can reduce the hazard of working with oxidising agent. Such modifications could include the installation of alarms or automatic shut-off switches on equipment to warn of equipment failure, high temperatures or high pressures.

6.4 In some instances, it may be possible to reduce the hazard by using oxidising materials in solution rather than as a solid. This also markedly reduces the hazard associated with dusts.

7. SEPARATION

7.1 Wherever oxidising substances are stored or used, a list of the materials present should be maintained, along with details of their quantities and location (see COSHH Regulations, ref. 1). The list should be kept in a place where it is readily available for use by the fire brigade, such as the gatehouse, reception area or security office, together with a plan indicating the location of the storage areas, the firefighting equipment and the position of the controls for any fixed fire suppression systems.

7.2 Oxidising agents should not be stored with highly flammable or flammable liquids but should be stored in separate areas. NFPA 430 (ref. 21) recommends a gap of 8m between stored oxidising materials and flammable liquids.

7.3 Where organic peroxides are handled or stored, attention should be paid to the provision of appropriate physical barriers to restrict the spread of a spillage.

7.4 Where small quantities of oxidising agents are stored in a laboratory, process area or similar workplace suitable cabinets or bins fitted with drip trays should be provided.

7.5 Before storing, all incoming containers should be inspected to ensure that they are undamaged and properly labelled. Deliveries of defective containers should not be accepted.

7.6 To prevent contamination, oxidising agents – and especially organic peroxides – should be stored in the containers in which they are supplied rather than being transferred to alternatives.

7.7 Containers should be suitably labelled and appropriate signs be displayed on the cabinets, bins or stores.

7.8 For organic peroxides requiring temperature control, the recommended storage temperature range should be clearly marked on the container. It is also good practice to mark the date that the container was received and the date it was first opened.

8. HOUSEKEEPING

8.1 Containers should be protected against impact or other physical damage.

8.2 Combustible pallets should not be used for storing organic peroxide containers.

8.3 Containers should be kept tightly closed to avoid contamination in storage, except when the supplier's instructions state otherwise.

8.4 Some liquid organic peroxides, such as methyl ethyl ketone peroxide, and solutions containing more than 8% hydrogen peroxide, gradually decompose giving off gas so these peroxides are shipped in containers with specially vented caps. The following should be observed:

- no other type of cap or sealing should be used for containers of these materials because the vent caps are designed to relieve the normal build up of gas pressure;
- vent caps should be checked regularly to ensure that they are working properly; and
- vented containers must be kept in an upright position and should never be stacked on top of each other.

8.5 Where peroxides are diluted with water or other solvents for use, storing containers that are not properly sealed can lead to evaporation of the solvent. This can, in turn, lead to exposure of the much more hazardous dry peroxide.

8.6 High standards of housekeeping should be maintained to prevent the accumulation of rubbish, particularly combustible materials, in the vicinity of oxidising materials.

8.7 Quantities of organic peroxides held in working areas should be kept to a minimum and be subject to a risk assessment. In all cases the quantities should not exceed the requirements for the day or shift being worked.

8.8 Regular inspections of the workplace can help to spot situations in which oxidising agents and organic peroxides are stored, handled or used in potentially hazardous ways.

8.9 Care must be taken not to contaminate anything that can burn with organic peroxides. For example, serious fires have resulted when the same cotton rag was used to clean up both spilled organic peroxide and accelerator.

8.10 Rags and materials used to mop up spills should be stored in a closed metal container outside the building.

8.11 Any build-up of peroxide dusts on ledges or other surfaces should be avoided.

8.12 Oxidising agents and 'empty' containers should not be accessible to intruders; suitable security measures should be in place.

9. HANDLING

9.1 Containers of organic peroxides should be opened and dispensed in a designated room or area outside the normal storage area. Care should be taken to ensure that organic peroxides do not contact combustible or other incompatible materials during the transfer process.

9.2 Only containers and dispensing equipment – such as drum pumps, scoops or spatulas that the chemical supplier recommends – should be used when dispensing organic peroxides. These items must be made from non-sparking materials compatible with the peroxides being handled. All tools should be kept scrupulously clean to avoid contamination.

9.3 Care should be taken to avoid spilling or contaminating skin or clothing when transferring organic peroxides from one container to another. Spillages from open, unstable or breakable containers during material transfer have caused serious accidents.

9.4 Liquids must not be transferred by pressurising their usual shipping containers with air or inert gas. The pressure may damage drums and barrels and if air is used, it may create a flammable atmosphere inside the container.

9.5 Glass containers with screw caps or glass stoppers are not acceptable for some organic peroxides, especially those sensitive to friction and grinding.

9.6 Materials stored in vented containers must not be transferred into tightly sealed, non-vented containers as the build up of gas pressure could cause it to rupture.

9.7 Only one container should be open for dispensing at any one time. All the dispensing of one material should be completed before starting to dispense another.

9.8 Dispense only the smallest amount possible, preferably only enough for immediate use.

9.9 Containers should immediately be closed after dispensing to reduce the risk of contaminating their contents.

9.10 When dispensing operations are complete all areas where organic peroxides have been placed must be left clean and free of combustible or incompatible materials and ignition sources.

9.11 Temperatures in areas where peroxides are used should be controlled so as not to become high enough to cause rapid decomposition (see paragraphs 4.8 to 4.14 above).

9.12 Unused material should never be returned to its original container, even if it does not seem to be contaminated.

9.13 If a water-based formulation freezes, the chemical supplier's advice must be followed. The material must not be heated or be chipped or ground to break up the lumps of material.

9.14 Dropping, sliding or skidding heavy metal containers, such as drums or barrels of friction- or shock-sensitive material must be avoided.

10. DISPOSAL

10.1 Waste oxidising materials should be kept in clearly marked, closed containers. Care must be taken not to mix incompatible materials.

10.2 Waste oxidising materials, especially organic peroxide wastes, are hazardous and should be disposed of promptly using suitably experienced waste contractors. (Further guidance is set out in the FPA publication *Fire safety and waste materials,* see ref. 22).

10.3 Organic peroxides accidentally mixed with an unknown or foreign material should be treated as contaminated. Attempts should never be made to salvage spilled or contaminated organic peroxides.

10.4 Unused peroxide-resin mixes should also be disposed of as waste oxidising agents. Partly cured wastes should be allowed to set and cool in safe, open areas before disposal to allow them to cool fully.

10.5 'Empty' drums, bottles, bags and other containers often contain hazardous residues and should never be used for anything else, no matter how clean they seem. Empty containers should thus be treated as hazardous wastes. If not to be disposed of, the chemical supplier's advice must be followed about how safely to handle or decontaminate these 'empty' containers.

10.6 Organic peroxide waste should be stored in the same way as unused organic peroxides. Use only compatible containers for wastes and identify their contents with suitable labels.

10.7 Oxidising materials must never be disposed of with ordinary waste materials or be flushed down sinks, drains or sewers.

11. AVOIDING HAZARDS DURING PROCESSES

11.1 Before undertaking work involving the use of oxidising agents a suitable and sufficient risk assessment should be carried out and recorded in compliance with the DSEAR Regulations (ref. 3).

11.2 It should be ensured that processing equipment is clean, properly designed and made from materials compatible with the organic peroxide being used. Where there is doubt regarding this matter, information should be gathered from the chemical supplier. This is important because copper, brass or lead equipment is dangerous in contact with some organic peroxides at elevated temperatures. Some steels and aluminium alloys, zinc and galvanized metal can also cause rapid decomposition of certain organic peroxides.

11.3 Some jobs require dilution of organic peroxides prior to use. This should be done strictly according to the chemical supplier's advice; using the wrong solvent or a contaminated solvent could cause an explosion. For example, methyl ethyl ketone peroxide and cyclohexanone peroxide may explode if they are mixed with acetone, a common solvent. Using reclaimed solvents of uncertain composition or purity can also be hazardous. They may contain dangerous concentrations of contaminants that are incompatible with the organic peroxide.

11.4 Some operations involving organic peroxides can be especially hazardous. Accidents have occurred during distillation, extraction and crystallisation, because these processes can concentrate organic peroxides.

11.5 Filtering friction- or shock-sensitive chemicals with materials and devices that produce heat, such as sintered glass filters, can be hazardous.

11.6 Before using a new material in an operation, as much information as possible should be gathered about the potential hazards of the particular peroxide and operation.

11.7 Organic peroxides are often used as catalysts to activate resins in plastics production. Organic peroxides should never be mixed directly with any accelerators or promoters; a violent explosion may result. The accelerator or promoter should be thoroughly mixed with the resin mixture before adding the organic peroxide.

11.8 It is dangerous to dissolve peroxides in very small amounts of a monomer (such as styrene) before adding them to a resin mixture. These 'small quantity' mixtures can undergo rapid polymerisation giving off a lot of heat and may result in a fire.

12. FIRE PREVENTION AND FIRE PROTECTION

12.1 Where oxidising materials are used or stored, appropriate portable fire extinguishers – approved and certificated by an independent, third-party certification body – should be provided and maintained in accordance with BS 5306-3 and 8 (see refs 23 and 24).

12.2 Where oxidising agents are stored or used consideration should be given to the installation of an automatic sprinkler installation in compliance with the *LPC Rules for automatic sprinkler installations incorporating BS EN 12845 and Technical Bulletins* (ref. 25).

12.3 Consideration should be given to installing an automatic fire detection and alarm system to comply with BS 5839: Part 1 (ref. 26).

13. HANDLING EMERGENCIES

13.1 It is important that staff react calmly, speedily and effectively in the event of chemical fires, spills and leaks.

13.2 Staff should be aware of the location and mode of use of emergency eyewash stations and safety showers.

13.3 Only specially trained and properly equipped people should handle emergencies. Nobody else should go near the area until it is declared safe.

13.4 Planning, training and practicing for emergencies helps people to know what they must do. A written emergency plan should be prepared and rehearsed. The plan should be updated whenever conditions in the workplace change.

13.5 An information pack should be prepared and made available for the emergency services. This should include:

- a site plan;
- a list of oxidising materials stored on site;
- the location of the stores; and
- the location of the controls for fixed fire suppression systems.

13.6 Staff charged with fighting fires involving organic peroxides should receive appropriate training. This is because the 'built-in' supply of oxygen in organic peroxides makes extinguishing methods based on smothering ineffective (for example, the use of foam or carbon dioxide). Often, cooling with large amounts of water may be the only suitable method.

13.7 Water is the preferred extinguishing medium for fighting fires involving oxidising agents. Dry chemical powders containing ammonium compounds are not recommended for use on oxidising agents that may produce chlorine when subject to a fire.

14. CHECKLIST

14.1	General considerations	Yes	No	N/A	Action required	Due date	Initial on completion
14.1.1	Have suitable and sufficient risk assessments been undertaken in compliance with the Regulatory Reform (Fire Safety) Order 2005 (or the equivalent legislation in Scotland and Northern Ireland) and the Dangerous Substances and Explosives Atmospheres Regulations (DSEAR) 2002?						
14.1.2	Has the use of oxidising agents been eliminated or reduced where possible?						
14.1.3	Have staff been trained in the hazards associated with the materials and processes in use?						
14.1.4	Are material data safety sheets available in the workplace?						
14.2	**Ventilation**	**Yes**	**No**	**N/A**	**Action required**	**Due date**	**Initial on completion**
14.2.1	Have the ventilation of storage and handling areas been assessed to ensure their adequacy?						
14.2.2	Are ventilation systems for areas where oxidising agents are used separate from those exhausting incompatible substances (such as flammable liquids)?						
14.2.3	Have hazard Zones been identified and suitable ventilation and other electrical equipment installed in these areas?						
14.2.4	Is exhaust ducting constructed from non-combustible materials with the outlet assessed and found to be in a safe position?						
14.3	**Ignition**	**Yes**	**No**	**N/A**	**Action required**	**Due date**	**Initial on completion**
14.3.1	Have all potential sources of ignition (including hot surfaces) in the workplace been identified?						
14.3.2	Is the temperature in areas where oxidising agents are stored or in use monitored (to prevent too low, as well as too high, a temperature)?						
14.3.3	Has the method of heating been assessed and found to be suitable?						
14.4	**Containment**	**Yes**	**No**	**N/A**	**Action required**	**Due date**	**Initial on completion**
14.4.1	Are the oxidising agents stored in compliance with the material safety data sheets?						
14.4.2	Are staff aware of the hazards associated with the materials with which they are working?						

		Yes	No	N/A	Action required	Due date	Initial on completion
14.4.3	Are work permits and a hot work permit scheme in operation in areas in which oxidising agents are stored and used?						
14.4.4	Are the storage areas inspected periodically to ensure that the provisions are suitable?						
14.5	**Exchange**	**Yes**	**No**	**N/A**	**Action required**	**Due date**	**Initial on completion**
14.5.1	Wherever possible, have oxidising materials been replaced with less hazardous alternatives?						
14.5.2	Where oxidising agents cannot be substituted, have measures been taken to ensure that the process operates as safely as possible?						
14.6	**Separation**	**Yes**	**No**	**N/A**	**Action required**	**Due date**	**Initial on completion**
14.6.1	Is an inventory of oxidising materials, including the approximate amounts and locations, available for fire brigade reference?						
14.6.2	Are suitable cabinets or bins – fitted with drip trays where applicable – provided in the workplace for the storage of oxidising materials?						
14.7	**Housekeeping**	**Yes**	**No**	**N/A**	**Action required**	**Due date**	**Initial on completion**
14.7.1	Are the quantities of oxidisng agents held in the workplace kept to a minimum and subject to periodic risk assessment?						
14.7.2	Are containers of oxidising agents protected against impact and physical damage?						
14.7.3	Where containers of organic peroxides are fitted with vent caps are these checked regularly to ensure that they are accessible and working properly?						
14.7.4	Are suitable compatible materials immediately available to enable spillages to be cleared up promptly and safely?						
14.8	**Handling**	**Yes**	**No**	**N/A**	**Action required**	**Due date**	**Initial on completion**
14.8.1	Is there a designated area for the opening and dispensing of organic peroxides to ensure that they do not come into contact with combustible or incompatible materials?						
14.8.2	Where small amounts of organic peroxides are used in the workplace, are they held in suitable containers? (Note: Glass containers with screw caps or glass stoppers are not acceptable.)						

		Yes	No	N/A	Action required	Due date	Initial on completion
14.8.3	Have relevant staff been trained in the correct methods of handling and dispensing oxidising agents?						
14.9	**Disposal**	**Yes**	**No**	**N/A**	**Action required**	**Due date**	**Initial on completion**
14.9.1	Are waste oxidising agents kept in clearly marked, closed containers so as not to come into contact with incompatible materials?						
14.9.2	Are empty containers treated as hazardous waste and disposed of safely in accordance with the supplier's guidance?						
14.10	**Avoiding hazards during process**	**Yes**	**No**	**N/A**	**Action required**	**Due date**	**Initial on completion**
14.10.1	Are risk assessments undertaken before using oxidising agents in chemical processes?						
14.10.2	Are all items used in a process properly designed, made of suitable materials and cleaned thoroughly before use?						
14.10.3	Where oxidising agents are to be diluted before use, is this done in accordance with the chemical supplier's advice?						
14.11	**Fire prevention and fire protection**	**Yes**	**No**	**N/A**	**Action required**	**Due date**	**Initial on completion**
14.11.1	Has an automatic fire detection and alarm system been installed in the workplace?						
14.11.2	Is there an appropriate number of suitable fire extinguishers available?						
14.11.3	Have relevant staff been trained in the use of the firefighting equipment?						
14.12	**Handling emergencies**	**Yes**	**No**	**N/A**	**Action required**	**Due date**	**Initial on completion**
14.12.1	Are staff aware of the location and mode of use of emergency eyewash stations and safety showers?						
14.12.2	Has a sufficient number of staff been trained to respond to an emergency and have procedures been rehearsed to ensure a calm, speedy and effective response?						
14.12.3	Has an information pack been provided for the emergency services?						

Staff training

- The workforce should be made aware of the presence and use of oxidising agents, and the hazards involved within the buildings in which they are working.
- All staff should be familiar with the hazards associated with the product(s) used, the necessary precautions and the action to be followed in the event of fire or spillage. These include how to:
  - raise the alarm;
  - ensure all staff evacuate the facility;
  - call the fire brigade;
  - attack the fire if it is safe to do so; and
  - contain spillage and dispose of the spilled or contaminated materials safely.
  - Staff training should emphasise the need, when working with organic peroxides, to:
  - wash hands before eating, drinking, smoking or going to the toilet;
  - remove contaminated clothing and footwear, since they can be a severe fire hazard;
  - wash contaminated items immediately and thoroughly in water before re-wearing or discarding;
  - wash thoroughly at the end of the workday; and
  - not wear or carry items that may be contaminated into areas having ignition sources or where smoking is allowed.
  - A scheme should be established and monitored for the training and refresher training of people who are using or could be using oxidising agents.
  - Staff should be made aware of the hazards of deliberate fire raising, which may be carried out by both colleagues and intruders.
  - Regular checks of the emergency eyewash stations and safety showers should be made wherever accidental exposure to organic peroxides might occur.

15. REFERENCES

1. Control of Substances Hazardous to Health Regulations 2002, SI 2002/2677 (as amended).
2. Chemicals (Hazard Information and Packaging for Supply) Regulations 2002, SI 2002/1689.
3. Dangerous Substances and Explosive Atmospheres Regulations 2002, SI 2002/2776.
4. Health and Safety (Safety Signs and Signals) Regulations 1996, SI 1996/341.
5. Special Waste Regulations 1996, SI 1996/972.
6. Landfill (England and Wales) Regulations 2002, SI 2002/1559.
7. BS EN 60079-10: 2003: Electrical apparatus for explosive gas atmospheres: Classification of hazardous atmospheres, British Standards Institution.

8 Regulatory Reform (Fire Safety) Order 2005, SI 2005/1541.

9. The Fire (Scotland) Act 2005, asp 5.
10. Fire Safety (Scotland) Regulations 2006, Scottish SI 2006/456.
11. Fire and Rescue Services (Northern Ireland) Order 2006, SI 2006/1254 (NI9).
12. European Communities (Classification, Packaging, Labelling and Notification of Dangerous Substances) Regulations 2003, SI116.
13. European communities (Classification, Packaging and Labelling of Dangerous Preparations) Regulations 2004, SI62.
14. Health and safety booklet HS(G) 51: *Storage of flammable liquids in containers,* Health and Safety Executive, 1985.
15. BS 5925: 1991: *Code of practice for ventilation principles and designing for natural ventilation,* British Standards Institution.
16. IEC 62305-2: 2003: P*rotection against lightning. Risk management,* British Standards Institution.
17. IEC 62305-3: 2003: *Protection against lightning. Physical damage to structures and life hazard,* British Standards Institution.
18. BS 6651: 1999: *Code of practice for protection of structures against lightning,* British Standards Institution.
19. RC35: *Recommendations for the protection of buildings against lightning strike,* Fire Protection Association, 2005.
20. RC7: *Recommendations for hot work,* Fire Protection Association 2001.
21. NFPA 430: *Code for the storage of liquid and solid oxidisers,* National Fire Protection Association.
22. *Fire safety and waste materials,* Adair Lewis, Fire Protection Association, 2003.
23. BS 5306-3: 2003: *Fire extinguishing installations and equipment on premises. Code of practice for the inspection and maintenance of portable fire extinguishers,* British Standards Institution.
24. British Standard 5306-8: 2000: *Fire extinguishing installations and equipment on premises. Selection and installation of portable fire extinguishers. Code of practice.* British Standards Institution.
25. *LPC Rules for automatic sprinkler installations incorporating BS EN 12845: 2004: Fixed firefighting systems. Automatic sprinkler systems. Design installation and maintenance* (incorporates Technical Bulletins), Fire Protection Association.
26. BS 5839-1: 2002: *Fire detection and fire alarm systems for buildings. Code of practice for system design, installation, commissioning and maintenance,* British Standards Institution.

16. FURTHER READING

LPC Design guide for the fire protection of buildings 2000, Fire Protection Association, 1999.