

SAFE STORAGE OF ORGANIC PEROXIDES

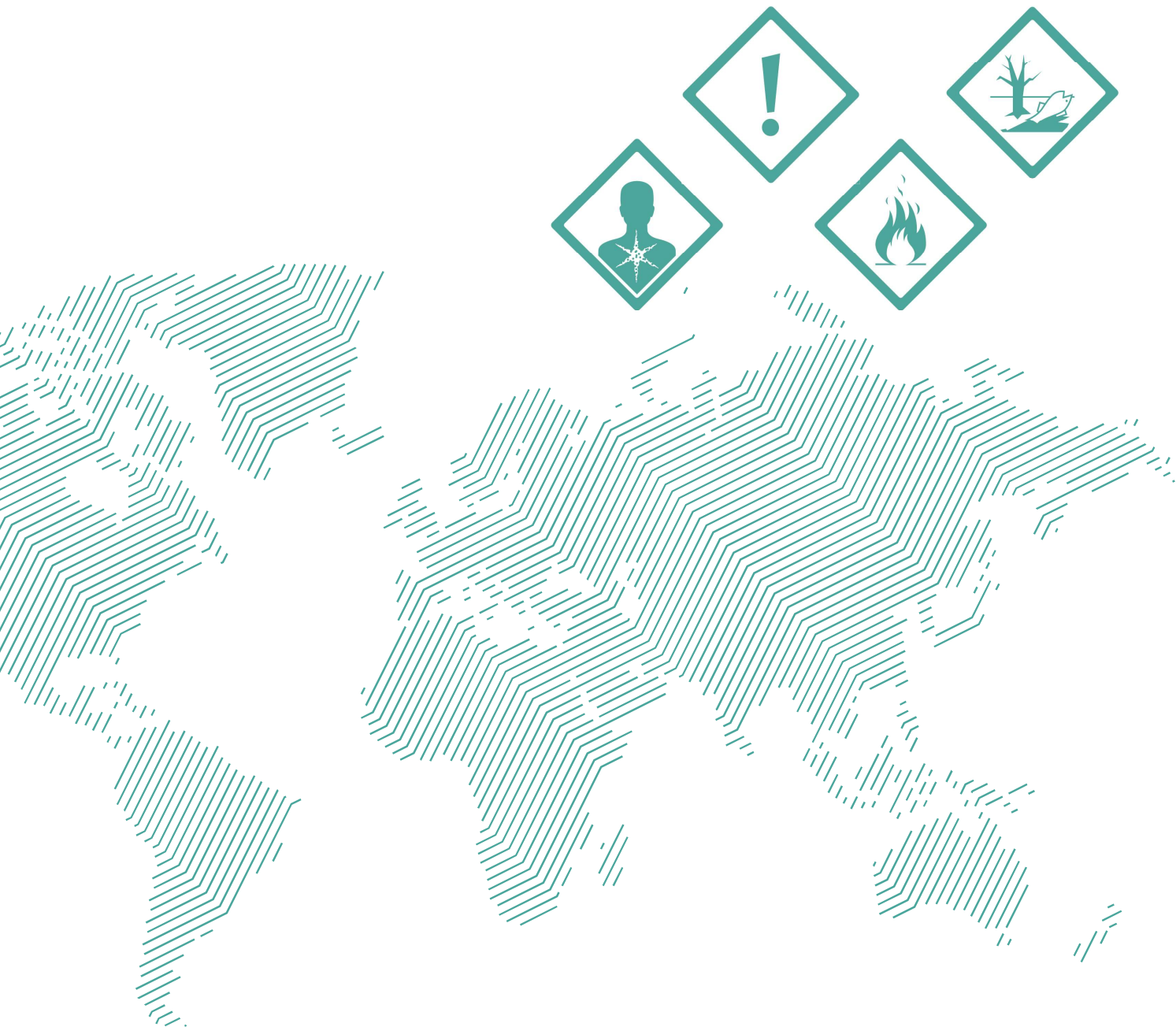
BEST PRACTICES

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European Organic Peroxide Safety Group

A sector group of  **cefic**





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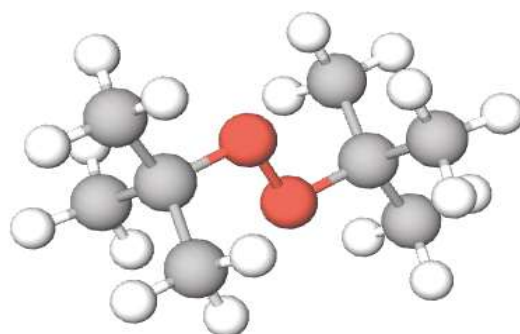


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NOTE: As general advise please always seek for more information from your organic peroxides supplier.

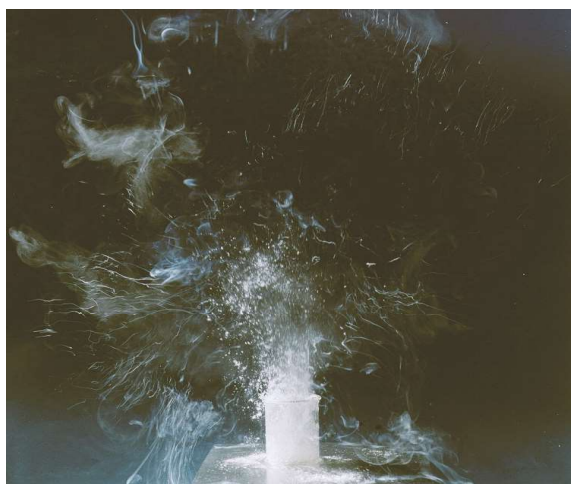
PROPERTIES AND SAFETY ASPECTS

FOR SAFE STORAGE IT IS NECESSARY TO TAKE PRECAUTIONS WITH REGARD TO THE FOLLOWING PROPERTIES ASSOCIATED WITH ORGANIC PEROXIDES.

THERMAL STABILITY

Organic peroxides are thermally unstable due to the relatively weak O-O bond in the molecular structure. As a result of this property organic peroxides are sensitive to heat and will decompose significantly above a certain temperature.

During decomposition heat is released (as reaction is exothermic) and the rate of this decomposition increases exponentially with temperature.



If the heat cannot be transferred to the environment because of tight-packed stacking or high ambient temperatures, self-heating will then accelerate and lead to a violent combustion and/or thermal explosion.

Every packaged organic peroxide has a characteristic temperature at which the self-heating accelerates. This temperature is designated as the **Self Accelerating Decomposition Temperature (SADT)**.

At or above this temperature a runaway reaction will take place. For this reason, strict temperature control and high temperature alarms are required for the storage of organic peroxides.

For many organic peroxides refrigerated facilities will be necessary.

CONTAMINATION

Contamination may accelerate the decomposition of organic peroxides. For instance, most heavy metal compounds have an accelerating effect on decomposition.

Acids, bases and accelerators based on e.g. cobalt or copper, and amines may also cause decompositions to occur at temperatures significantly lower than the recommended storage temperature. Other chemicals or impurities, like dust or rust, may have the same effect/impact.

Therefore, organic peroxides must be stored separately from other chemical compounds, unless compatibility has been proven.

BURNING PROPERTIES

Most organic peroxides should be considered highly combustible. Once ignited many organic peroxides burn vigorously. When heated to their decomposition temperature, organic peroxides will generate vapors.

Many of these decomposition vapors are flammable.

Therefore, the presence of potential ignition sources must be avoided.

Electrical equipment installed should be explosion-proof to avoid sparks.

Nevertheless, auto-ignition of the vapors may still occur. Consequently,

fire-fighting equipment or, even better, (automated) fire extinguishing systems should be present in all storage rooms.



PRESSURE BUILD-UP

As organic peroxides produce vapors during decomposition, pressure build-up in the package occurs. To prevent excessive pressure rise inside storage rooms due to prolonged decomposition and bursting of the packages, storage rooms should be provided with adequate pressure relief panels.

STORAGE GROUPS CLASSIFICATION

The burning properties and the severity of decomposition of the various organic peroxides may differ considerably. These differences should be considered for storage of organic peroxides.

Therefore, organic peroxides are classified into storage groups.

This classification is mainly based on the burning rate of the organic peroxide. The burning rate determines the heat radiation of an organic peroxide fire in the storage facility and the resulting heat load to its surroundings.

An organic peroxide with a high burning rate requires stricter measures for a storage facility than an organic peroxide with a low burning rate.

There are only a few countries in the world that have a specific regulation for storage of organic peroxides.

Appendix is showing the list of the European countries and their regulations.

For most of the mentioned regulations, the classification into storage groups (and associated storage requirements) is based on the burning rate of the organic peroxide, sometimes in combination with the transport classification. However, for Czech Republic and Poland the storage classification is only based on the transport classification and the burning rate is not taken into account at all.



STORAGE TEMPERATURE CONTROL

When storing organic peroxides, a distinction is made between maximum, minimum and recommended storage temperatures.

- › **Maximum Storage Temperature:** This is the maximum storage temperature for safety reasons. For "temperature-controlled" organic peroxides (UN3111 to UN3120) it is equal to the control temperature, as defined in the transport regulations. For "non-temperature controlled" organic peroxides (UN3101 to UN3110), it is recommended to take a value of 40°C. Storage at the maximum storage temperature means that the organic peroxide content may decrease if stored for long period, but uncontrolled decomposition will not occur.
- › **Minimum Storage Temperature:** A minimum storage temperature is only specified for products that show freezing, crystallization or phase separation at low temperatures. For some products this could lead to critical safety issues (e.g. friction sensitivity of crystals).
- › **Recommended Storage Temperature:** The recommended storage temperature is often lower than the maximum storage temperature (determined for safety reasons) and prevents any significant quality degradation (e.g. loss of assay, change in colour) during the period of use specified by the manufacturer.

PRODUCT SPECIFIC TEMPERATURE DATA CAN BE FOUND
ON THE PRODUCT LABEL
& ON SAFETY DATA SHEET (CHAPTERS 7, 9 OR 14).

To avoid exceeding the control temperature, active cooling is usually recommended.

However passive cooling can be acceptable for non-temperature controlled organic peroxides (i.e. with a maximum storage temperature of +30°C), provided that the control temperature is never exceeded.

PASSIVE COOLING

For the non-controlled temperature organic peroxides passive cooling may be required to avoid reaching the maximum storage temperature during storage.

Passive cooling may consist of a sunroof, a double roof, insulation walls, earth walls or a water sprinkler system on the roof.

The input of heat by direct sunlight must be avoided (no windows or roof domes).

It is recommended to monitor the temperature inside any storage room.



ACTIVE COOLING

For storage of organic peroxides with a maximum storage temperature $< 30^{\circ}\text{C}$, an effective active cooling system is strongly recommended. To prevent freezing of the door, special cold room doors with a frame heater in explosion-proof design are recommended.

The required cooling machine shall always be placed outside the storage room because of the hot compressor part of the cooling machine.

This is safer and allows easier explosion protection.

The evaporator and fan should be installed close to the ceiling of the storage room, so that the cold air falls down and is evenly distributed throughout the room. If necessary, the cold air must be supplied from two sides to avoid blind spots. The organic peroxide pallets should not be tightly packed, but stored with small gaps (typically 10 to 15cm) between them so that cold air circulation is ensured.

The maximum storage temperature should be indicated on the outside of the storage room.

The storage temperature must be monitored in each actively cooled room by a sufficient number of temperature sensors at suitable locations. It must be possible to read the actual temperature from the outside of the storage room.

A visual/acoustic alarm must be triggered and forwarded to a permanently manned location if the alarm temperature (usually 5°C above the set temperature of the storage room) is exceeded or in case of failure of the cooling equipment.

The set temperature of the storage room is usually the recommended storage temperature but can also be the maximum storage temperature.

An emergency power supply is required for the cooling unit in case of a power failure. In the event of a total loss of the cooling system, back-up or emergency refrigeration shall be available, for instance a back-up cooling unit, a Reefer container or another cold storage room. For smaller quantities a spare refrigerator/freezer or (dry) ice is often sufficient.

If the temperature rise cannot be prevented and it is not possible to move the organic peroxides to another refrigerated area, the storage area has to be evacuated immediately and facility emergency response plan has to be implemented.

It may be practical to divide a large storage room into several smaller cold compartments, each with its own cooling system. In this way, different organic peroxides can be stored at different temperatures if necessary.

Organic peroxides with different storage temperatures can be stored together as long as the lowest maximum storage temperature is taken into consideration, and there is no conflict with the individual minimum storage temperatures.





LOCATION STORAGE FACILITY AND SAFETY DISTANCES

- › Local regulations must always be followed.
- › Safety distances are distances that must be maintained within a plant between dangerous and endangered objects, measured as the shortest distance between each other. It depends on the storage group respectively heat radiation and the quantity of the organic peroxides.
- › The location on site should be chosen by considering e.g., distances to social and office buildings, production facilities, public roads, railroads, waterways and essential equipment.
- › Additional safety distances to protect the neighborhood, in particular residential areas as well as public roads, railways, waterways might have to be applied.
- › Constructional (e.g. fire-resistant walls) or technical (e.g. adequately dimensioned fire-fighting systems, fire alarm systems...) measures, as well as dividing large storage buildings over multiple smaller storage compartments, might help reducing the safety distance.
- › No definite distances can be stated as generally applicable.

DESIGN OF STORAGE BUILDING

CONSTRUCTION

- › Storage facility must comply to local regulations.
- › Organic peroxides should be stored in dedicated storage buildings only.
- › Material of choice for construction is concrete. Alternatively, other non-combustible materials can be used, please consult your organic peroxide supplier.
- › Storage floor must be made of non-combustible material, liquid-tight, seamless and easy to clean and should have a slope to an adequate drain system.
- › Implement an organic peroxide specific spillage retention facility (see below for more information).
- › Storage should be closed on at least three sides by walls constructed of non-combustible materials.
- › Pressure relief areas (venting capacity) must comply to regulations.
- › Only one-floor storage building should be constructed.
- › Doors should also be functional from inside the building.
- › Sufficient area for handling of material should be available.
- › For cold storage: All doors, walls and roofs should be insulated with non-flammable material.
- › It is recommended to have temperature sensors and fire detectors for all storage rooms (cooled or non-cooled).
- › To reduce the minimum required safety distances, automatic fire-fighting system (e.g. deluge or sprinklers system) may be necessary.
- › Instead of building a storage room, it is also possible to consider mobile storage units, which comply with the above recommendations.

FIRE RESISTANCE

- › Must comply to local regulations, typically 30 to 90 minutes fire resistance (depending on the local regulations)



RETENTION FACILITY FOR LEAKING PRODUCT AND FOR FIRE-FIGHTING WATER

- › Storage building should have an adequate drain system from the inside to the outside.
- › The drain system must be designed with extreme caution to exclude any potential organic peroxide accumulation.
- › The volume of a dedicated retention basin must be adequate (please contact your organic peroxide supplier).
- › Fire-fighting water should be directed to safe location (retention facility) to avoid spreading of the fire.
- › Safety distances for the retention facility must be considered

FIRE-FIGHTING

- › Automatic water sprinkler/deluge system is preferred to help controlling fire, but will most likely not extinguish an organic peroxide fire. It may stop initial fire and reduces the fire spread.
- › Due to low heat capacity CO_2 is typically not sufficient for fire-fighting.
- › The automatic water sprinkler/deluge system would have a typical capacity of 5 to 20 (L/min)/m², depending on the storage classification and local regulation.
- › Fire-fighting water may carry burning organic peroxide and must therefore be caught e.g. in a dedicated retention pit (see retention facility for leaking product and for fire-fighting water).
- › Hand extinguisher for small fires or small storage facilities.
- › Be aware that for refrigerated organic peroxides, fire-fighting water and sprinkler water may initiate undesired decomposition due to unintended heating of the organic peroxide.
- › It might be sometimes safer to let the organic peroxide burn in a controlled way. For more information please contact your organic peroxide supplier.



REQUIREMENTS FOR ELECTRICAL EQUIPMENT

- › All electrical equipment in storages, drain system, retention pit, etc. should be explosion-proof.



LIGHTNING PROTECTION

- › Must be designed according to local requirements.

VENTILATION AND AIR CIRCULATION

- › Sufficient air ventilation must be guaranteed to avoid build-up of flammable decomposition vapors.
- › If a heating system is necessary, dedicated precautions must be taken to avoid excess of heating and/or hot surface temperature. The maximum surface temperature, and warm air temperature, should not exceed 60°C.
- › Air circulation is required to prevent self-heating of organic peroxide.
- › Organic peroxide should never be in direct contact with the heating system.



MAIN GENERAL RULES FOR STORAGE

Temperature, Light & Heat control

- › Carefully obey storage temperatures.
- › Organic peroxides should be protected from direct sunlight and all other sources of heat.

Packaging type

- › Organic peroxides should be stored separately from incompatible substances (e.g. accelerators or other reducing agents) according to local storage/separation regulations
- › All organic peroxides, irrespective of their subsidiary hazard label (e.g. corrosive) can be stored together. This includes exempted organic peroxides (type G) being classified as flammable solids.
- › Organic peroxides should be stored only in closed original packaging.
- › Packaging should be stored so that the label and other safety information are visible.
- › Emptied packages must be treated as original full ones.

Packaging arrangement

- › Packaging must be placed or stacked in such a way that they cannot move, they are not deformed by their weight and endangers safety, and the necessary measures can be taken to maintain the stability of the materials.
- › A sufficient distance (typically 10-15 cm) must be taken into account between the pallets to allow maximum air circulation.
- › For storage of liquid organic peroxides, compatible absorbent material should be available.
- › The storage area must be kept clean.

Inventory management

- › First-In-First-Out inventory management is essential.
- › A maximum storage period, specified by the manufacturer, should not be exceeded.



Fire Safety

- › Sources of ignition must be avoided (like smoking, open fire, sparks...) in and near the storage rooms.
- › Packaging must be stored with a distance from partition walls, ceilings, doors or windows to prevent heat transfer and warm up in the event of a fire in a neighboring room.

Personnel and inspections

- › Only regularly trained personnel should have access to the storage building.
- › Regular inspections of the storage building are recommended.
- › Written permission is required for any work that increases the risk, e.g. fire and hot work and the removal of operational faults where there is a risk of ignition of organic peroxides.
- › In warehouses, only the work necessary for their operation may be carried out, e.g. administrative work such as keeping documentation, labeling packages or stowing and holding them ready for dispatch.
- › Any refilling shall be avoided.

HOT WORK PERMIT	
<small>THIS HOT WORK PERMIT IS REQUIRED FOR ANY TEMPORARY OPERATION INVOLVING OPEN FLAMES OR PRODUCING HEAT AND/OR SPARKS. THIS INCLUDES, BUT IS NOT LIMITED TO: CUTTING, GRINDING, WELDING, BURNING, SOLDERING, BRAZING</small>	
<p>INSTRUCTIONS</p> <p>DATE: _____</p> <p>1. HAS EXFLOMETER BEEN BING TESTED? <input type="checkbox"/> YES <input type="checkbox"/> NO</p> <p>2. HAS EXFLOMETER BEEN CALIBRATED IN PAST MONTH? <input type="checkbox"/> YES <input type="checkbox"/> NO</p> <p>3. HOT WORK BEING DONE BY: <input type="checkbox"/> EMPLOYEE <input type="checkbox"/> CONTRACTOR</p> <p>4. NATURE OF JOB: _____</p> <p>5. DESCRIPTION OF WORK: _____</p> <p>6. NAME OF PERSON DOING HOT WORK: _____</p> <p>7. PERMIT VALID FROM _____ AM TO _____ PM</p> <p>8. IF HOT WORK INVOLVES CONFINED SPACE ENTRY, FIREHOLE BREAKING, OR LADDER/Scaffold WORK, RESPECTIVE PROCEDURES MUST BE FOLLOWED.</p> <p>9. EXFLOMETER READING PRIOR TO ISSUING THE PERMIT: _____ % SEE MONITORED BY: _____</p> <p>10. OPERATORS/AREA PERSONNEL NOTIFIED: EMPLOYEE _____ AREA/STATION _____</p> <p>11. FIRE WATCHER ASSIGNED <input type="checkbox"/> YES <input type="checkbox"/> NO</p> <p>12. NAME OF FIRE WATCHER: _____</p> <p>13. OK FOR HOT WORK</p> <p>14. SIGNATURE _____ INITIALS _____</p> <p>15. PRODUCTION MAINTENANCE</p> <p>16. Fire Watcher sign-off 30 Minutes after work completed</p> <p>DATE: _____ SIGNATURE _____</p>	<p>PRECAUTIONS/PREVENTATIVE MEASURES CHECKLIST</p> <p>YES N/A</p> <p><input type="checkbox"/> <input type="checkbox"/> EXTINGUISHING MEDIA (water, fire extinguisher, etc.) ON HAND AND IS IN GOOD WORKING ORDER.</p> <p><input type="checkbox"/> <input type="checkbox"/> SPRINKLER SYSTEMS IN GOOD WORKING ORDER.</p> <p><input type="checkbox"/> <input type="checkbox"/> HOT WORK EQUIPMENT IN GOOD WORKING CONDITION.</p> <p><input type="checkbox"/> <input type="checkbox"/> MOVABLE FLAMMABLE LIQUIDS AND COMBUSTIBLE MATERIALS SECURED AT LEAST 15 FEET OF HOT WORK AREA.</p> <p><input type="checkbox"/> <input type="checkbox"/> FLAMMABLE LIQUIDS, DUST, OR OILY DEPOSITS ON FLOOR REMOVED.</p> <p><input type="checkbox"/> <input type="checkbox"/> IF AN EXPLOSIVE ATMOSPHERE WAS DETECTED, HAS THE SOURCE BEEN CORRECTED AND HAS THE EXPLOSIVE ATMOSPHERE BEEN ELIMINATED?</p> <p><input type="checkbox"/> <input type="checkbox"/> ALL WALL AND FLOOR JOINTS COVERED.</p> <p><input type="checkbox"/> <input type="checkbox"/> GUARDS IN PLACE TO CONTAIN HEAT, SPARKS, AND SLAG. GUARDS REPLACE TO PROTECT IMMEDIATE FIRE HAZARD ZONE AS WELL AS CONTAINING FLAMMABLE OR COMBUSTIBLE WALLS, PARTITIONS, CEILING, ETC.</p> <p><input type="checkbox"/> <input type="checkbox"/> COMBUSTIBLE FLOORS WITH SOAK OR COVERED WITH FIRE-RESISTANT MATERIAL.</p> <p><input type="checkbox"/> <input type="checkbox"/> COMBUSTIBLE MATERIALS ON OTHER SIDE OF A METAL PARTITION, WALL, CEILING, OR FLOOR THAT MAY BE IGNITED BY RADIATION OR CONDUCTOR REMOVED FROM AREA.</p> <p><input type="checkbox"/> <input type="checkbox"/> FIRE WATCHER TRAINED IN EXTINGUISHING EQUIPMENT</p> <p><input type="checkbox"/> <input type="checkbox"/> FIRE WATCHER TRAINED IN FACILITIES FOR SOUNDING ALARM IN THE EVENT OF A FIRE.</p> <p><input type="checkbox"/> <input type="checkbox"/> FIRE WATCHER WILL SMOKE IN AREA FOR ADDITIONAL 10 MINUTES AFTER HOT WORK HAS BEEN COMPLETED TO DETECT AND EXTINGUISH POSSIBLE SMOULDERING FIRES.</p>

APPENDIX

NATIONAL STORAGE REGULATIONS FOR ORGANIC PEROXIDES IN EUROPE

Czech Republic – ČSN 65 0211

France - Arrêté du 6 novembre 2007

Germany – TRGS741

Netherlands – PGS 8

Poland – Regulation 181

Spain – APQ 9

Sweden - SÄIFS 1996:4

UK - Guidance Note CS 21



All information concerning storage of organic peroxides are offered in good faith and believed to be reliable. EOPSG members, however, make no warranty or representation that the information in this brochure is accurate or sufficient for the storage of organic peroxides.

The content of the brochure is for general information only and does not constitute any form of advice or recommendation upon which a specific decision should be made. EOPSG members accept no responsibility for loss or damage that may arise from reliance on information or advice contained in this brochure.

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