Chapter 39: Organic Peroxides

General Comments

This chapter addresses the hazards associated with the storage, handling and use of organic peroxides. These chemicals possess the characteristics of flammable or combustible liquids and are also strong oxidizers. Class V organic peroxides pose little fire hazard; therefore, these materials are not regulated by specific storage or use requirements. Some organic peroxides are unstable and become increasingly reactive with age or heating.

Organic peroxides pose the dual hazard of being both oxidizers and flammable or explosive compounds. This unusual combination of properties requires special storage and handling precautions to prevent uncontrolled release, contamination, hazardous chemical reactions, fires or explosions. In addition to these properties, organic peroxides are unusually sensitive to temperature. Heat, whether by fire exposure or environmental, is a major factor in the decomposition of peroxide compounds. Some organic peroxides will decompose uneventfully when subject to a gradual temperature increase but may explode if they undergo the thermal shock of a rapid, uncontrolled temperature rise.

J.S. Townsend (1993) notes that some organic peroxides are just as dangerous when they become too cold as when they are too hot. For example, acetyl peroxide becomes unstable above 122°F (50°C)—its self-accelerating decomposition temperature (SADT). When cooled below 17°F (-8.3°F), acetyl peroxide forms crystals that are shock sensitive. Consequently, special precautions must be taken to transport and store acetyl peroxide between 32°F (0°C) and 90°F (32°C).

Organic peroxides are commonly used in the plastics industry to initiate polymerization. Although the requirements of this chapter pertain to industrial applications in which significant quantities of organic peroxides are stored or used, smaller quantities of organic peroxides still pose a significant hazard. These materials, therefore, must be stored and used in accordance with the applicable provisions of this chapter and Chapter 27.

Purpose

The provisions of this chapter are intended to manage the fire and oxidation hazards of organic peroxides by preventing their uncontrolled release.

SECTION 3901

GENERAL

3901.1 Scope. The storage and use of organic peroxides shall be in accordance with this chapter and Chapter 27. Unclassified detonable organic peroxides that are capable of detonation in their normal shipping containers under conditions of fire exposure shall be stored in accordance...
The specific requirements for the storage, handling and use of organic peroxides in this chapter are intended to complement the general hazardous materials requirements of Chapter 27. Because of the hazards to people and property, organic peroxides capable of being detonated in their usual shipping containers or packages under fire conditions must be stored in accordance with the provisions of Chapter 33 for explosives. Examples of unclassified detonable (UD) materials are organic peroxides classified as Type A by DOT 49 CFR 173.128(b)(1) and materials classified as explosives by DOT 49 CFR 173, Subpart C. DOT Type A organic peroxides have an SADT of 122°F (50°C) or less.

3901.2 Permits. Permits shall be required for organic peroxides as set forth in Section 105.6.

The process of issuing permits gives the fire code official an opportunity to carefully evaluate and regulate hazardous operations. Permit applicants should be required to demonstrate that their operations comply with the intent of the code before the permit is issued. See the commentary to Section 105.6 for a general discussion of operations requiring an operational permit and Section 105.7 for a general discussion of activities requiring a construction permit. The permit process also notifies the fire department of the need for pre-fire planning for hazardous property.

SECTION 3902 DEFINITIONS

3902.1 Definition. The following word and term shall, for the purposes of this chapter and as used elsewhere in this code, have the meanings shown herein.

Definitions of terms can help in the understanding and application of the code requirements. The purpose for including here those definitions that are most closely associated with the subject matter of this chapter is to provide more convenient access to them without having to refer back to Chapter 2. For convenience, these terms are also listed in Chapter 2 with a cross reference to this section. The use and application of all defined terms, including those defined in this section, are set forth in Section 201.

ORGANIC PEROXIDE. An organic compound that contains the bivalent -O-O- structure and which may be considered to be a structural derivative of hydrogen peroxide where one or both of the hydrogen atoms have been replaced by an organic radical. Organic peroxides can present an explosion hazard (detonation or deflagration) or they can be shock sensitive. They can also decompose into various unstable compounds over an extended period of time.

Class I. Describes those formulations that are capable of deflagration but not detonation.

Class II. Describes those formulations that burn very rapidly and that pose a moderate reactivity hazard.

Class III. Describes those formulations that burn rapidly and that pose a moderate reactivity hazard.

Class IV. Describes those formulations that burn in the same manner as ordinary combustibles and that pose a minimal reactivity hazard.

Class V. Describes those formulations that burn with less intensity than ordinary combustibles or do not sustain combustion and that pose no reactivity hazard.

Unclassified detonable. Organic peroxides that are capable of detonation. These peroxides pose an extremely high-explosion hazard through rapid explosive decomposition.

The chemical structure of organic peroxides differs from that of hydrogen peroxide (an oxidizer) in that an organic radical replaces the hydrogen atoms. Figure 3902.1 shows an example of this chemical structure in which a benzoyl radical (C6H5CO) in the widely used Class I organic peroxide benzoyl peroxide replaces the hydrogen atoms in hydrogen peroxide (H2O2). Organic chemicals are all carbon based. As a result, organic peroxides pose varying degrees of...
fire or explosion hazards in addition to their oxidizing properties. The classification system in this chapter (see Table 3902.1) is derived from a system developed by the Society of the Plastics Industry (Bulletin 19A).

SECTION 3903
GENERAL REQUIREMENTS

3903.1 Quantities not exceeding the maximum allowable quantity per control area. The storage and use of organic peroxides in amounts not exceeding the maximum allowable quantity per control area indicated in Section 2703.1 shall be in accordance with Sections 2701, 2703, 3901 and 3903.

The provisions of this section complement the requirements of Chapter 27 in structures occupied for the storage, handling or use of organic peroxides. The regulations contained in Sections 3903.1.1 through 3903.1.1.4 assume that the quantity of organic peroxides in a given building is limited to the maximum allowable quantities (MAQs) per control area as established in Section 2703.1; thus, the building is not classified in Occupancy Group H. The general requirements of Sections 2701 and 2703 are fully applicable to the storage and use of organic peroxides, in addition to the provisions of this chapter.

3903.1.1 Special limitations for indoor storage and use by occupancy. The indoor storage and use of organic peroxides shall be in accordance with Sections 3903.1.1 through 3903.1.1.4.

Because certain occupancies may need to have organic peroxides on hand, Sections 3903.1.1 through 3903.1.1.4 provide regulations that are specific to occupancy group classifications and that recognize the relative hazards of both the occupancy and the organic peroxide.

3903.1.1.1 Group A, E, I or U occupancies. In Group A, E, I or U occupancies, any amount of unclassified detonable and Class I organic peroxides shall be stored in accordance with the following:
1. Unclassified detonable and Class I organic peroxides shall be stored in hazardous materials storage cabinets complying with Section 2703.8.7.
2. The hazardous materials storage cabinets shall not contain other storage.

Because of their respective explosive or higher deflagration hazard characteristics, even the smallest quantity of UD or Class I organic peroxides present in Group A, E, I or U occupancies must be stored in an approved hazardous materials storage cabinet constructed and placarded in accordance with Section 2703.8.7 to reduce the exposure of the materials to hazards from the surrounding environment.

In accordance with Table 2703.1.1(1), Note g, storage of UD organic peroxide in any amount is allowed only in buildings equipped throughout with an approved automatic sprinkler system, in accordance with Section 903.3.1. Also, based on Table 2703.1.1(1), Note e, where an approved storage cabinet is used, the MAQ that could be kept in the occupancies can be doubled. To reduce the likelihood of contamination of the organic peroxide materials or damage to their packaging, Item 2 prohibits the storage of other materials in the approved organic peroxide storage cabinet.

In accordance with Section 3901.1, storage of UD organic peroxides must also comply with the applicable provisions of Chapter 33 for explosives.

3903.1.1.2 Group R occupancies. Unclassified detona-
ble and Class I organic peroxides shall not be stored or used within Group R occupancies.

Because of their explosive or higher deflagration hazard characteristics, UD and Class I organic peroxide cannot be stored in any residential occupancy within the scope of the code’s regulations. Storage would result in an increased danger to the occupants, as well as exposure of the peroxides to the otherwise unregulated environment.

3903.1.1.3 Group B, F, M or S occupancies. Unclassified detonable and Class I organic peroxides shall not be stored or used in offices, or retail sales areas of Group B, F, M or S occupancies.

Because of their explosive or higher deflagration hazard characteristics, UD and Class I organic peroxide cannot be stored in occupancies in Group B, F, M or S. Storage would result in an increased danger to the occupants, as well as exposure of the peroxides to the higher relative fire loads typically encountered in these occupancies.

3903.1.1.4 Classrooms. In classrooms in Group B, F or M occupancies, any amount of unclassified detonable and Class 1 organic peroxides shall be stored in accordance with the following.

1. Unclassified detonable and Class 1 organic peroxides shall be stored in hazardous materials storage cabinets complying with Section 2703.8.7.
2. The hazardous materials storage cabinets shall not contain other storage.

It is the intent of this section to allow for the occasional use of limited amounts of organic peroxides in certain scientific, experimental or demonstration settings; however, this section does not allow storage of any quantity of these materials for any length of time. The fire code official may limit the amount of organic peroxides brought into a structure for these uses. The quantity actually needed for the experiment should determine the amount allowed into a structure. Because of their explosive or higher deflagration hazard characteristics, even the smallest quantity of UD or Class I organic peroxides must be stored in an approved hazardous materials storage cabinet constructed and placarded in accordance with Section 2703.8.7 to reduce the exposure of the materials to hazards from the surrounding environment.

In accordance with Table 2703.1.1(1), Note g, storage of UD organic peroxide in any amount is allowed only in buildings equipped throughout with an approved automatic sprinkler system, in accordance with Section 903.3.1. Also, based on Table 2703.1.1(1), Note e, where an approved storage cabinet is used, the MAQ that could be kept in these occupancies can be doubled.

To reduce the likelihood of contaminating organic peroxide materials or damaging their packaging, Item 2 prohibits the storage of other materials in the approved organic peroxide storage cabinet. Note that in accordance with Section 3901.1, storage of UD organic peroxides must also comply with the applicable provisions of Chapter 33 for explosives.

3903.2 Quantities exceeding the maximum allowable quantity per control area. The storage and use of organic peroxides in amounts exceeding the maximum allowable quantity per control area indicated in Section 2703.1 shall be in accordance with Chapter 27 and this chapter.

The provisions of this section complement the requirements of Chapter 27 in structures occupied for the storage, handling or use of organic peroxides. The regulations in this section assume that the quantity of organic peroxides in a given building is in excess of the MAQ as established in Section 2703.1 and, therefore, that the building is classified in Occupancy Group H. The requirements of Chapter 27 apply to the storage and use of organic peroxides in addition to the provisions of this chapter.

SECTION 3904 STORAGE

3904.1 Indoor storage. Indoor storage of organic peroxides in amounts exceeding the maximum allowable quantity per control area indicated in Table 2703.1.1(1) shall be in accordance with Sections 2701, 2703, 2704 and this chapter. Indoor storage of unclassified detonable organic peroxides that are capable of detonation in their normal shipping containers under conditions of fire exposure shall be stored in accordance with Chapter 33.

This section regulates the indoor storage of organic peroxides when in excess of the MAQ in buildings or portions of buildings classified in Occupancy Group H.
The general and storage provisions of Chapter 27 are applicable in addition to the requirements of this section. Storage of organic peroxides inside of structures must comply with Sections 3904.1.1 through 3904.1.11 to prevent uncontrolled release or exposure to conditions that may result in a fire or explosion. Because of the explosion hazard, UD organic peroxides must be stored in accordance with the provisions of this section and Chapter 33 for explosives.

3904.1.1 Detached storage. Storage of organic peroxides shall be in detached buildings when required by Section 2703.8.2.

Detached structures designed and constructed for the sole purpose of organic peroxide storage provide the best protection for people and property from fire and explosions. Detached storage structures should be constructed of noncombustible materials to prevent them from becoming involved in either an outside fire that may endanger their contents or in a fire themselves, should their contents be ignited. Section 2703.8.2 and Table 2703.8.2 require detached storage when the indoor storage quantities are more than 2 tons (4 metric tons) of Class I, more than 25 tons (50 metric tons) of Class II and more than 50 tons (100 metric tons) of Class III organic peroxides. See the commentary to Section 2703.8.2 and Table 2703.8.2 for further discussion of detached storage requirements. Figure 3904.1.1 shows a cross-sectional diagram of a typical detached storage building.

3904.1.2 Distance from detached storage buildings

The International Building Code® (IBC®) prescribes minimum fire-resistance ratings for exterior walls of buildings based on clearances from adjacent structures and lot lines. The separation distances prescribed by this section are minimums notwithstanding the inherent fire-resistance ratings of the exterior wall assemblies. These clearances are intended to reduce the hazard to nearby structures and people in the event of a fire or explosion in a detached storage structure used for the storage of organic peroxides.
TABLE 3904.1.2.

<table>
<thead>
<tr>
<th>ORGANIC PEROXIDE CLASS</th>
<th>MAXIMUM STORAGE QUANTITY (POUNDS) AT MINIMUM SEPARATION DISTANCE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Distance to buildings, lot lines, public streets, public alleys, public ways or means of egress</td>
</tr>
<tr>
<td></td>
<td>50 feet</td>
</tr>
<tr>
<td>I</td>
<td>2,000</td>
</tr>
<tr>
<td>II</td>
<td>100,000</td>
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<tr>
<td>III</td>
<td>200,000</td>
</tr>
<tr>
<td>IV</td>
<td>No Limit</td>
</tr>
<tr>
<td>V</td>
<td>No Limit</td>
</tr>
</tbody>
</table>

For SI: 1 foot = 304.8 mm, 1 pound = 0.454 kg.
a. When the amount of organic peroxide stored exceeds this amount, the minimum separation shall be 50 feet.

The separation distances specified in the table are intended to reduce the effects of radiant heat exposure in the event of a fire in an adjacent storage structure. Separation distances for UD organic peroxides must conform to the requirements of Table 3304.5.2 (2).

3904.1.3 Liquid-tight floor. In addition to the requirements of Section 2704.12, floors of storage areas shall be of liquid-tight construction.

In addition to the requirement of Section 2704.12 that floors be constructed of noncombustible materials, the requirement for floors to be liquid tight is intended to result in floor construction that has the ability to stop the passage of liquids to adjacent spaces.

3904.1.4 Electrical wiring and equipment. In addition to the requirements of Section 2703.9.4, electrical wiring and equipment in storage areas for Class I or II organic peroxides shall comply with the requirements for electrical Class I, Division 2 locations.

Because of the danger of ignition by arcs or sparks in the event of an accidental spill or leak, electrical equipment and devices in storage areas for organic peroxides must be classified for use in Class I, Division 2, hazardous locations as described in NFPA 70.

3904.1.5 Smoke detection. An approved supervised smoke detection system in accordance with Section 907 shall be provided in rooms or areas where Class I, II or III organic peroxides are stored. Activation of the smoke detection system shall sound a local alarm.

**Exception:** A smoke detection system shall not be required in detached storage buildings equipped throughout with an approved automatic fire-extinguishing system complying with Chapter 9.

An automatic fire detection system with central, remote or proprietary station supervision and a local alarm signal is required to provide early warning of fire to building occupants and fire suppression personnel. Detectors and installation methods in organic peroxide storage areas should be selected for compatibility with the materials stored. Fire alarm equipment and installation methods must comply with Section 907. Materials that give off strong vapors may interfere with fire detection system components or trigger nuisance alarm signals. The required local alarm is intended to alert the occupants in the immediate vicinity of the storage area to a potential hazardous condition. The local alarm is not intended to be part of an evacuation alarm system for the entire structure. The exception indicates that automatic fire detection is not required in detached storage buildings when an automatic fire suppression system is provided. Automatic sprinklers or other approved fire suppression systems reduce the danger to people and property from fire by detecting the fire, sounding an alarm, transmitting the alarm to the fire department and containing or suppressing the fire. Sprinkler systems in detached storage buildings must be supervised by a connection to a central station, a remote supervising station or a proprietary su-
pervising station, or, when approved by the fire code official, be connected to a system that produces an audible and visual signal monitored at a constantly attended on-site location. See the commentary to Section 903.4 for further discussion of sprinkler system supervision and Sections 904.3.5 and 907.7.5 for further discussion of alternative automatic fire-extinguishing system supervision.

3904.1.6 Maximum quantities. Maximum allowable quantities per building in a mixed occupancy building shall not exceed the amounts set forth in Table 2703.8.2. Maximum allowable quantities per building in a detached storage building shall not exceed the amounts specified in Table 3904.1.2.

This section establishes the maximum allowable indoor storage quantities of organic peroxide on a per-building basis, as opposed to a per-control area basis, and regulates both mixed occupancy buildings and detached organic peroxide storage buildings.

3904.1.7 Storage arrangement. Storage arrangements for organic peroxides shall be in accordance with Table 3904.1.7 and shall comply with all of the following:

1. Containers and packages in storage areas shall be closed.
2. Bulk storage shall not be in piles or bins.
3. A minimum 2-foot (610 mm) clear space shall be maintained between storage and un-insulated metal walls.
4. Fifty-five-gallon (208 L) drums shall not be stored more than one drum high.

These provisions detail storage requirements related to the hazards of release or ignition of liquids and vapors of organic peroxide stored in structures. Some of the factors that are considered are as follows:

1. Open containers or packages may permit the release of flammable or oxidizing materials or vapors.
2. Containers in bulk piles or bins may be susceptible to physical damage from stacking or product movement, which could damage the container and lead to an uncontrolled release of product.
3. The required separation distance is intended to minimize the effects of radiant heat exposures to stored materials in the event of a fire outside the structure.
4. The stacking of drums may result in a container being damaged during product movement if a drum is dropped or tipped over.

TABLE 3904.1.7.

3904.1.8 Location in building. The storage of Class I or II organic peroxides shall be on the ground floor. Class III organic peroxides shall not be stored in basements.

Class I and II organic peroxides may not be stored above or below the ground floor because of concerns for fire-fighter access. Because of their lower relative hazard, Class III organic peroxides may be stored on floors above grade; however, they may not be stored on floors below grade because of the difficulty of manual fire suppression operations in below-grade areas.

3904.1.9 Contamination. Organic peroxides shall be stored in their original DOTn shipping containers. Organic peroxides shall be stored in a manner to prevent contamination.
Organic peroxides must be kept in original U.S. Department of Transportation (DOTn)-approved shipping containers to facilitate identification and to minimize the possibility of accidental spills or ignition. The stability of organic peroxides can be markedly reduced through contamination by various materials, such as strong acids or alkalis, sulfur-based compounds or reducing agents of any type. Storage practices must prevent contamination and the hazards associated with it.

3904.1.10 Explosion control. Indoor storage rooms, areas and buildings containing unclassified detonable and Class I organic peroxides shall be provided with explosion control in accordance with Section 911.

Because of the possibility of a deflagration or detonation in the event of ignition of Class I organic peroxides, explosion relief venting must be provided to protect the storage building or structure from collapse. Explosion venting must conform to the requirements in Section 911.

3904.1.11 Standby power. Standby power in accordance with Section 604 shall be provided for storage areas of Class I and unclassified detonable organic peroxide.

A standby power system complying with Section 604 is required as a backup power supply for mechanical and electrical systems, such as refrigeration equipment, neutralizer systems associated with secondary containment and mechanical ventilation equipment for vapor control. These systems may also be connected to an approved emergency power system instead of a separate standby power system. Automatic fire detection systems should also be connected to approved emergency power supplies (also see commentary, Section 604).

3904.2 Outdoor storage. Outdoor storage of organic peroxides in amounts exceeding the maximum allowable quantities per control area indicated in Table 2703.1.1(3) shall be in accordance with Sections 2701, 2703, 2704 and this chapter.

This section regulates the outdoor storage of organic peroxides when in excess of the MAQ per outdoor control area established by Table 2703.1.1(3). The general and storage provisions of Chapter 27 are applicable in addition to the requirements of this section. Storage of organic peroxides in outdoor control areas must comply with Sections 3904.2.1 through 3904.2.5 to prevent uncontrolled release or exposure to conditions that may result in a fire or explosion.

3904.2.1 Distance from storage to exposures. Outdoor storage areas for organic peroxides shall be located in accordance with Table 3904.1.2.

The IBC prescribes minimum fire-resistance ratings for exterior walls of buildings based on clearances from adjacent structures and lot lines. The separation distances prescribed by this section are minimums notwithstanding the inherent fire-resistance ratings of the exterior wall assemblies. These clearances are intended to reduce the hazard to nearby structures and people in the event of a fire or explosion in a detached storage structure or outdoor area used for the storage of organic peroxides.

3904.2.2 Electrical wiring and equipment. In addition to the requirements of Section 2703.9.4, electrical wiring and equipment in outdoor storage areas containing unclassified detonable, Class I or II organic peroxides shall comply with the requirements for electrical Class I, Division 2 locations.

Because of the danger of ignition by arcs or sparks in the event of an accidental spill or leak, electrical equipment and devices in outdoor organic peroxide storage areas must be classified for use in Class I, Division 2, hazardous locations as described in NFPA 70.

3904.2.3 Maximum quantities. Maximum quantities of organic peroxides in outdoor storage shall be in accordance with Table 3904.1.2.

Outdoor storage of organic peroxides must comply with the storage requirements specified in Table 3904.1.2, which establishes the minimum separation distances required between the outdoor storage area and exposures, including other outdoor storage areas, and the MAQ of organic peroxides being stored.

3904.2.4 Storage arrangement. Storage arrangements shall be in accordance with Table 3904.1.7.
Similar to Section 3904.1.7 for indoor storage, this section references the provisions of Table 3904.1.7 for organic peroxide storage arrangements. Pile limitations specified in the table are based on the relative hazard of the material when involved in fire. These limits apply to Class I, II, III and IV organic peroxides in combustible and noncombustible containers and packages.

3904.2.5 Separation. In addition to the requirements of Section 2703.9.8, outdoor storage areas for organic peroxides in amounts exceeding those specified in Table 2703.8.2 shall be located a minimum distance of 50 feet (15 240 mm) from other hazardous material storage.

The required minimum 50-foot (15 240 mm) separation distance from other hazardous materials storage is intended to reduce the hazard of dangerous chemical reactions with other incompatible materials in the event of a spill, fire or explosion.

SECTION 3905 USE

3905.1 General. The use of organic peroxides in amounts exceeding the maximum allowable quantity per control area indicated in Table 2703.1.1(1) or 2703.1.1(3) shall be in accordance with Sections 2701, 2703, 2705 and this chapter.

This section applies to indoor and outdoor dispensing, use and handling of organic peroxides when the amounts being dispensed, used or handled are in excess of the MAQ per indoor or outdoor control area indicated in Table 2703.1.1(1) or 2703.1.1(3), respectively. The administrative, general, use, dispensing and handling provisions of Chapter 27 are applicable, in addition to the requirements of this chapter. Once the MAQ of organic peroxide per control area has been exceeded, indoor areas where materials are being dispensed, used or handled must be located in a building or portion of a building complying with the IBC for a Group H occupancy because of the increased hazards associated with quantity.

Although no occupancy group is assigned to them, outside organic peroxide use areas require an increased level of regulation when quantities exceed the MAQs per outdoor control area. The MAQs per control area listed in Tables 2703.1.1(1) and 2703.1.1(3) have been divided into closed-use and open-use systems. Corresponding MAQs recognize that an open-use condition is generally more hazardous than a closed-use condition because the organic peroxide is more directly exposed to the surrounding environment and can become more readily involved in an incident than if it is totally confined. The MAQs for use are based on the aggregate quantity in both use and storage, not exceeding the exempt amount listed for storage.

INTERESTING TWEETS

- Lori Greene at Ingersoll Rand Security Technologies has an interesting blog on Fire Doors. Check it out: http://idighardware.com/2011/01/63k/

- University of California, San Diego has released a new video titled ‘A Day in the Lab (A PIs Perspective)’.

http://www.youtube.com/watch?v=aA8mC5Rlj5k&feature=player_detailpage.

- HCCC students call Frankfort fire station home. New program gives EMTs place to stay while attending classes: For more, visit: http://www.uticaod.com/news/x1791704517/HCCC-students-call-Frankfort-fire-station-home