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THE CONDITIONS OF THE ROAD TRANSPORT AND STORAGE OF ORGANIC PEROXIDES IN THE CASE OF BENZOYL PEROXIDE

Summary. Organic peroxides are materials that belong to one of the 13 classes of dangerous goods, i.e., class 5.2. They are characterized by specific hazards and, due to that fact, require strictly determined conditions of storage and transport. Regulations that govern the issue of the road transport of dangerous goods and the storage of organic peroxides are separately contained in various legal acts. Storage conditions of organic peroxides are determined in the legal regulations in the form of general guidelines, which need to be described in detail, based on expert knowledge from the entities engaged in this process. This article attempts to provide details regarding the conditions of the road transport and storage of C-type organic peroxides using the example of benzoyl peroxide (concentration 75%).

Keywords: dangerous goods; regulations; organic peroxides; type C; storage

1. INTRODUCTION

The term ‘organic peroxides’ refers to peroxides in pure as well as dissolved form. Organic peroxides occur in solid, liquid or paste form. The structure of these chemical compounds includes at least two oxygen atoms -O-O- linked together with the use of a chemical bond. These substances may be treated as derivatives of the most popular inorganic peroxide, hydrogen peroxide (H_2O_2), in which one or two hydrogen atoms have been replaced by

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organic radicals. The peroxide group -O-O-, which is an integral structural element of every organic peroxide, is chemically unstable. It may be subject to quick exothermic decomposition, both at normal temperature and at elevated temperature. Moreover, a very large number of organic peroxides decomposes along with the release of harmful or flammable gases or vapours, which creates a fire risk as a result of mixing with the air. It should be emphasized that the rate of decomposition of these substances increases along with the temperature, depending on the formulation of organic peroxide. Decomposition of the peroxide is the result of the rupture of the oxygen-oxygen bond, which causes the creation of two radicals (Fig. 1). The created radical constitutes a reactive molecular entity. Decomposition can be initiated by various external factors. The most common include: elevated temperature, activity of another chemical substance, contact with contaminants, ultraviolet radiation and mechanical stimuli such as friction or impact.

Fig. 1. Decomposition scheme of the organic peroxide

Organic peroxides are flammable products that exhibit a high probability of explosion. Dangerous properties of these substances are the result of the chemical structure of their particles. It should also be emphasized that the burning process of organic peroxides occurs in a quick and intensive manner. This results from the fact that organic peroxides contain both fuel (organic part, i.e., carbon) and oxygen in one particle. In addition, part of the substances belonging to this group may decay in an explosive manner, particularly in closed conditions. Flammability and explosiveness are the main types of dangers related to organic peroxides. A certain part of organic peroxides may exhibit toxic and corrosive properties. Despite strong properties, the toxic effect very often causes symptoms that occur with delay. Some of them may cause serious damage to the cornea, even in the case of brief contact. Moreover, they may exhibit a corrosive effect on the skin. Organic peroxides that belong to this group may also exhibit a corrosive effect on metals. The literature includes a number of studies regarding the characteristic of properties and hazards created by organic peroxides. [1,2,3].

The conditions for road transport and associated activities related to organic peroxides have been regulated by appropriate provisions of the law: ADR Agreement [4] and the Act of 19 August 2011 on the Transport of Dangerous Goods, as Amended [5]. Guidelines regarding the conditions of the in-house transport and storage of organic peroxides are contained in the Regulation of the Minister of Industry and Commerce of 1 March 1995 on Occupational Safety and Health in the Production, Use, Storage and In-house Transport of Organic Peroxides [6].

2. TEMPERATURE CONTROL REQUIREMENTS

2.1. Road transport

As substances of class 5.2, organic peroxides have been divided into two groups:

- P1 - organic peroxides that do not require temperature control
- P2 - organic peroxides that require temperature control

The criterion for the above-mentioned division into groups, that is, whether to use temperature controls, is dictated by the need to maintain an appropriate level of safety during transportation and associated activities. Controlled temperature means the highest temperature at which organic peroxides may be transported in a sufficiently safe manner. Certain organic peroxides may be transported only under conditions of controlled temperature. The basis for the designation of controlled temperature is the self-accelerating decomposition temperature (SADT) and the method of road transportation for organic peroxide, i.e., packaging or tankers (Table 1). The SADT is the lowest temperature at which the self-accelerating decomposition of organic peroxides, located in the packaging used for transport, may occur. The determination of the SADT and the consequences of heating the material, in order to carry out the appropriate classification, is made on the basis of Part II of the *Manual of Tests and Criteria*. The literature includes a series of studies on SADT prediction, involving the use of various methods [7,8]. In order to ensure the maximum level of safety during transportation, the emergency temperature has also been determined. The emergency temperature is the temperature that constitutes a threshold and, after reaching it, in cases where there is a possible loss of control over the temperature, it is necessary to undertake pre-established emergency procedures.

Tab. 1

Derivation of control and emergency temperatures [4]

Type of receptacle	SADT	Control temperature	Emergency temperature
Single packaging and IBCs	20°C or less	20°C below SADT	10°C below SADT
	Over 20°C and up to 35°C	15°C below SADT	10°C below SADT
	Over 35°C	10°C below SADT	5°C below SADT
Tanks	Not greater than 50°C	10°C below SADT	5°C below SADT

2.2. Storage

Working temperature and alarm temperature are determined on the basis of the SADT. Their maximum levels during the storage of peroxides are also precisely determined. In order to understand the significance of these parameters, it is necessary to refer to the definition of the indicated terms. Working temperature is the maximum temperature at which the organic peroxide may be safely stored. Alarm temperature is the maximum temperature at which rescue actions should be undertaken in order to eliminate the risk of the SADT being reached by the organic peroxide. Both parameters are determined on the basis of the SADT (Table 2).

Tab. 2

Derivation of control and emergency temperatures [6]

SADT	Working temperature	Alarm temperature
20°C or less	20°C below SADT	10°C below SADT
20°C to 35°C	15°C below SADT	10°C below SADT
over 35°C	10°C below SADT	5°C below SADT

3. CHARACTERISTICS OF ORGANIC PEROXIDES

3.1. Types of organic peroxides

Organic peroxides should be stored in accordance with the applicable rules of safety, health and fire protection. Storage rooms should meet the conditions determined in the Regulation of the Minister of Industry and Commerce of 1 March 1995 on Occupational Safety and Health in the Production, Use, Storage and In-house Transport of Organic Peroxides. Considering the various explosion hazards created by these substances, organic peroxides have been divided into seven types [6]:

- **Type A -** All formulations of the organic peroxides that may be subject to detonation or quick deflagration.
- **Type B** - All formulations of organic peroxides that are characterized by explosive properties. Substances classified according to this type do not undergo detonation, nor quick deflagration in packaging; however, they exhibit susceptibility to thermal explosion.
- **Type C** - All formulations of the organic peroxides that are characterized by explosive properties, but are not susceptible to detonation, quick deflagration and thermal explosion, when located in the packaging.
- **Type D** - Three types of formulations of organic peroxides, which, under laboratory test conditions:
  - partially detonate; however they do not undergo quick deflagration and, during heating in closed conditions, do not exhibit rapid signs of occurring reaction
  - do not detonate, but undergo slow deflagration; during heating in closed conditions, they do not exhibit rapid signs of reaction
  - do not detonate and do not undergo deflagration; however, they exhibit mild signs of reaction during heating in closed conditions
- **Type E** - All peroxide formulations that do not detonate and do not undergo deflagration during laboratory tests. Moreover, during heating in closed conditions, they exhibit weak or no signs of reaction.
- **Type F** - All peroxide formulations that do not undergo detonation in the fragmented state, nor deflagration during laboratory tests. They exhibit either no or only weak signs of reaction during heating in closed conditions. Formulations of organic peroxides belonging to this type contain an agent desensitizing the diluents, other than A-type diluents. Moreover, the formulations of this type are not thermally stable.
- **Type G** - All formulations of organic peroxides that do not undergo detonation in the fragmented state, nor deflagration during laboratory tests. During the test for heating in closed conditions, there are no signs of reaction, nor do they have a tendency to explode. Peroxide formulations belonging to this type contain an A-type diluent, which fulfils the role of a desensitizing agent. Moreover, they are thermally stable because their SADT is above 50 °C.

The degree of hazard created by them is contained in international regulations regarding the road transport of dangerous goods, the ADR Agreement and the criteria for classification of organic peroxides into seven types. Peroxides belonging to type A are not allowed to be transported in packaging in which they are tested. Peroxides classified as type G are not subject to the provisions of class 5.2. Grading of peroxides from types B to F is associated with the maximum quantity of material allowed per a single item of packaging [4].

3.2. Sensitivity modification methods for organic peroxides

Modifying the sensitivity of organic peroxides is achieved by the desensitization of these materials. This process consists of the introduction of liquid organic diluents (alcohols, certain phthalic esters), solid organic materials or water into them. This action is undertaken in order to reduce the concentration of organic peroxide. Certain compounds that do not react with organic peroxides are used to dissolve them. Those that are obtained using this method are characterized by increased resistance to mechanical factors and exhibit lower susceptibility to explosion [4]. Thanks to the used treatment, both transport and associated activities - loading, unloading, cargo handling, storage - guarantee the optimum level of safety during the implemented operations. Due to the hazards created by organic peroxides, their characteristics are modified by the addition of the previously mentioned diluents. A type A diluent is a liquid organic material, which is compliant with a liquid organic peroxide with a boiling point amounting to at least 150°C.

Moreover, the modifications associated with the reduction in sensitivity to explosion may be implemented through the use of appropriate packaging and temperature control. Therefore, some of these substances should be stored in cold storage in order to eliminate the risk of decomposition. As a result, it is necessary to obtain information from the product's safety data sheet or technical data sheet regarding the temperature range, in which the peroxide can be safely stored or information regarding the SADT. In the case of a temperature below the determined minimum temperature for the given organic peroxide, there is a risk of the organic peroxide crystals falling out of the initiator solution. The process of crystallization for organic peroxides may be a source of a potential explosion hazard under the influence of mechanical factors, such as friction and impact, or other factors occurring in the environment. In the case of the occurrence of an ambient temperature above the maximum storage temperature, the initiator may be subject to much faster processes, leading to decomposition and causing the loss of original parameters.

4. CONDITIONS OF ROAD TRANSPORT AND STORAGE OF BENZOYL PEROXIDE

Benzoyl peroxide is an organic chemical compound that belongs to the group of organic peroxides. On a laboratory scale, it is obtained as a result of the reaction of benzoyl chloride with hydrogen peroxide in an alkaline environment. It is characterized by flammable and explosive properties. This compound is widely used in the chemical industry as the initiator of radical reactions and, in the pharmaceutical industry, as an ingredient in medications and anti-acne agents. The use of benzoyl peroxide in the pharmaceutical sector is possible due to its strong oxidizing, antibacterial and keratolytic properties.

At a commercial level, it is available in the form of products that contain several dozen percent of water. Water in this system fulfils the function of a stabilizing additive. The most common form in commerce is a product containing 25% water. Therefore, the conditions of road transport and storage will be discussed in reference to the above-mentioned product.

The literature includes a series of studies regarding the conditions in which the handling and storage of organic peroxides should be carried out [9,10,12].

4.1 Conditions of road transport for benzoyl peroxide (25% water)

The legal basis for the determination of the safe conditions for transport and associated activities in relation to benzoyl peroxide is the European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR Agreement, Journal of Laws 2017, Item 1119).

Dibenzoyl peroxide (with 25% water) is classified as dangerous product of class 5.2, with the number UN 3104 Organic Peroxide Type C, Solid (≤77% concentration, ≥23% of water, packing method OP6). No controlled temperature is required during its transport. This material also does not pose a threat to the environment. Classification code P1 was assigned to this material, i.e., organic peroxides that do not require temperature control. UN 3104 may only be transported in appropriate packaging with proper labels. This product should be packed in accordance with the P520 manual. The material should be packed in accordance with the OP6 method, which allows for packaging goods up to a maximum quantity of 50 kg per single item of packaging (maximum quantity - maximum mass (kg)) for solid materials and for combination packaging (liquid and solid materials). The following forms of packaging are allowed for the transport of UN 3104:

- Combination packaging for which the outer packaging comprises: crates (made from steel, aluminium, metal other than steel or aluminium, natural wood (ordinary or with siftproof walls), plywood, reconstituted wood, fibreboard, plastics (expanded or solid)); drums (made from steel, aluminium, fibreboard, plastics, plywood); and jerrycans (made from steel, aluminium, plastics)
- Single packaging: drums (made from steel, aluminium, fibreboard, plastics, plywood) and jerrycans (made from steel, aluminium, plastics)
- Composite packaging with plastic inner receptacles

Glass containers may be also used as the inner packaging of the combination packaging, provided the maximum content does not exceed 0.5 kg. Materials that fulfil the padding function in combination packaging should have non-inflammable properties.

UN 3104 should not be packed together with goods that belong to other classes or with goods that are not subject to the provisions of the ADR Agreement. Nevertheless, if the given material is a hardener for materials of class 3 (flammable liquids) or an element of a set of class 3 material, then it is permissible to pack this peroxide with other materials.

Ready pieces of shipment should be loaded onto closed vehicles or containers, or vehicles or containers covered with tarpaulin, in order to minimize the impact of atmospheric factors. In addition, the ready pieces of shipment should be loaded in a manner allowing for the free circulation of air in the cargo area, which maintains the cargo at a constant temperature. If the cargo located in the large container of vehicle contains more than 5,000 kg of material, then the cargo should be divided into parts containing no more than 5,000 kg each. Moreover, the parts should be separated from each other by a distance of not less than 5 cm. The maximum quantity of this peroxide should be limited to 20,000 kg per transport unit.

Before commencement of the loading of the vehicle or container, it is necessary to ensure that these units are properly cleaned and contain no combustible waste.

UN 3104 may also be transported as a dangerous good packed in limited quantities; however, the maximum allowed quantity per one inner packaging is only 100 g.

4.2 Storage conditions for benzoyl peroxide (25% water)

The legal basis for the determination of safe storage conditions in relation to benzoyl peroxide is the Regulation of the Minister of Industry and Commerce of 1 March 1995 on Occupational Safety and Health in the Production, Use, Storage and In-house Transport of Organic Peroxides (Journal of Laws 1995, No. 37, Item 181).

Benzoyl peroxide (with 25% water) should be stored in the original undamaged packaging. The material should not be repacked because this activity may cause a hazard resulting from the incompatibility of the used packaging or possible contaminants that may be located in it. Packaging containing the material should be tightly closed, except in cases when the safety data sheet indicates a different method. This aspect is extremely important because the storage of benzoyl peroxide in opened or partially opened packaging may cause evaporation. The undesired effect of this phenomenon may be inflammation of the material as a result of the appearance of pure peroxide or so-called dry peroxide. The recommended storage temperature for benzoyl peroxide (25% water) is 15-25°C.

As type C peroxide, the material has been classified according to the I hazard group. Hazard groups have been identified in order to indicate the minimum safety distances in warehouses with organic peroxides in relation to other objects (Table 3).

Tab. 3

Minimum safety distance in warehouses with organic peroxides in relation to other objects (m) [6]

Load (kg)	**Object**	**I hazard group**	
		Not embanked	Embanked or with additional protective wall
1,000	External fence	43	34
	Production halls and buildings	30	23
	Tank farms and free-standing installations	32	25
	Administrative and social buildings	40	31
	Public railways and roads	45	35
	Housing estates	65	50
	Single residential buildings	55	43
5,000	External fence	70	51
	Production halls and buildings	50	39
	Tank farms and free-standing installations	53	42
	Administrative and social buildings	60	47
	Public railways and roads	73	59
	Housing estates	109	86
	Single residential buildings	85	66

10,000	External fence	89	63
	Production halls and buildings	64	51
	Tank farms and free-standing installations	65	51
	Administrative and social buildings	77	55
	Production halls and buildings	92	72
	Tank farms and free-standing installations	138	110
	Administrative and social buildings	100	78
50,000	External fence		
	Production halls and buildings		
	Tank farms and free-standing installations		
	Administrative and social buildings		
	Production halls and buildings		
	Tank farms and free-standing installations		
	Administrative and social buildings		

Objects in which organic peroxides are stored should be classified into the appropriate category of explosion hazard. Such classification depends on the hazard group of the organic peroxide; this has resulted in the classification of benzoyl peroxide (with 25% water) into the category of explosion hazard MW1. The obligation to classify objects into the explosion hazard category of MW1 or MW2 rests with the plant manager. It should be noted here that the entire object, part of it or certain parts of it may be classified according to the specific category of explosion hazard. The plant manager is also obliged to designate a protection zone in the area belonging to the plant around each object classified according to the explosion hazard category of MW1 or MW2.

Taking into account the properties of the material, it should be stored in a manner that will protect it against direct impact from sunlight and heat sources, which are stimuli that may initiate its decomposition. Moreover, the rooms intended for storage of this material should be ventilated.

Considering the properties of benzoyl peroxide (25% water), this material should be stored in segregated or isolated warehouses. The isolated warehouse should be located in a separate warehouse building and used for the storage of peroxides classified into the I, II and III hazard groups. Unlike the isolated warehouse, the separated warehouse may be located in the warehouse building with various applications; however, it should be separated from the rest of the object by separating elements of a fire protection nature. A warehouse of this type may also be used for the storage of organic peroxides classified in the I, II, III hazard groups, albeit in strictly determined quantities. The maximum quantity of material amounts to 50 kg.

The area where the warehouse dedicated for the storage of organic peroxide is located should be fenced off. Due to its specific properties, the material should not be stored in the same room as other materials. It is also not permissible to store peroxides whose forms of packaging are damaged in any way because this is associated with the risk of leaks or the scattering of the stored material. As such, particular attention should be paid to:

- the tightness of packaging

- the technical condition of packaging (especially the closing elements)
- other defects (cracks and dents)

Packaging that contains these materials should be stored in rows, in one layer. Packaging containing benzoyl peroxide (25% water) should not be stacked because the stacking of packaging is only permitted for solid peroxides in the III hazard group. However, this practice should be carried out in accordance with the manufacturer's manual. The distance between items of packaging depends on the shape of the packaging, i.e.:

- Organic peroxide contained in packaging with a rectangular bottom or a square bottom - minimum 5 cm
- Organic peroxide contained in packaging with a round bottom or an oval bottom - minimum 2 cm

It is permissible to place packaging with peroxide on a rack; however, the following conditions should be met:

- In one vertical section, only packaging containing the same organic peroxide should be placed
- Height of the top shelf - 150 cm
- Shelves of the rack should be in the form of grates
- Placement of plastic trays at a distance of 10 cm under each shelf on which packaging containing organic peroxides in liquid form are located
- Wood should not be the construction material of the racks (the racks should be made of flame-retardant materials in order to eliminate the risk of fire hazard)

Regardless of whether the peroxide is stored in a storage chamber or a warehouse, separate batches of the material should be marked with the date of receipt. The oldest batches should be directed for processing. Packaging containing the material, which is located in the warehouse rooms, may be opened only in the event of sampling for technical inspection. If the organic peroxide is placed in encapsulated packaging, then the possibility, necessity and regularity of their venting are indicated in the storage manual. As in the case of racks, there are also restrictions regarding the construction materials of the pallets, which are intended for storage of organic peroxides. Pallets made of wood should not be used for these purposes.

In-house transport of benzoyl peroxide (with 25% water) should be carried out with the use of devices characterized by explosionproof and sparkproof properties. Moreover, such devices should be adapted to the transport of this type of material. During the performance of such activities as loading, unloading and cargo handling, the engine of the vehicle should be turned off. Due to the high sensitivity of the material towards thermal stimuli, it is necessary to ensure that there will be no contact made by the packaging containing this peroxide with hot surfaces of the vehicle or exhaust gases. The surface of the vehicle should be clean and non-absorbent. Without a doubt, this requirement is dictated by the need to eliminate the risk associated with the possibility of the following:

- Accumulation of material in the slits and on surfaces in the cargo area
- Contact made by organic peroxide with contaminants, which may be a factor initiating the dangerous decomposition of this material

It must be also noted that, according to the Regulation of the Minister of Development of 29 January 2016 Concerning the Types and Quantities of Hazardous Substances Present in Industrial Plants, which determines the recognition of a plant as a plant with an increased or

high risk of serious industrial failure, the threshold quantity of benzoyl peroxide (with 25% water) that determines whether the plant is classified as a plant with increased risk is 50 t, and 200 t for a plant to be considered as being at high risk [11].

4. SUMMARY

The correct conditions for the road transportation and storage of organic peroxides minimize the risk associated with the occurrence of hazards, which may in turn result in the loss of human life, damage to health, destruction of property and destruction of the environment. All safety measures that should be applied in relation to these materials are dictated by the need to eliminate or minimize the risk of decomposition during storage or transport of the moved materials. The use of guidelines contained in the applicable provisions of the law, information contained in complete and well-prepared safety data sheets, and expert knowledge regarding the given material guarantee that the appropriate level of safety during the performance of these activities is maintained.

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