

Safe transport of organic peroxides

Best practices

EOPSG

European Organic Peroxide Safety Group

A sector group of Cefic





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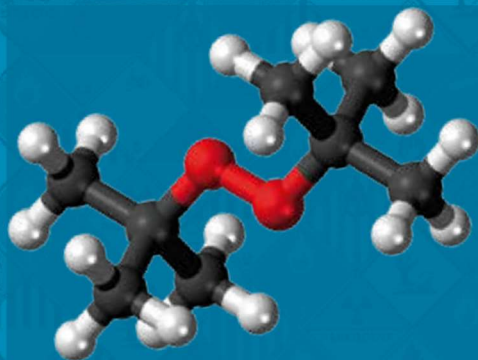
ARKEMA
INNOVATIVE CHEMISTRY

Nouryon

PERGAN
The Peroxide Company

 **UNITED INITIATORS**

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1. Why this brochure?

This brochure is a guide to give a set of recommendations regarding practical safety aspects in handling and transport operations of organic peroxides for road and sea transport.



The existing transport regulations give the general framework for the legal requirements of safe transportation. The details however, regarding technical equipment, procedures for operational issues like pre-loading, truck and/or container preparation, combined loading, instruction manuals, hand- over procedures, emergency procedures, etc., are not fully described in the transport regulations, but are crucial and consequently advisable for safe handling, transport and operation.



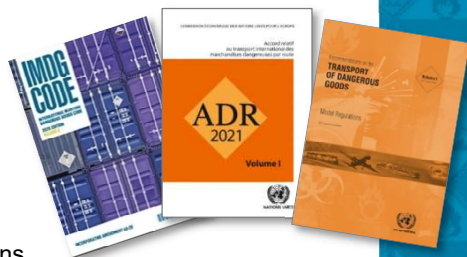
This brochure is drafted by the manufacturers being members of the European Organic Peroxide Safety Group (EOPSG): Arkema, Nouryon, Pergan and United Initiators. Detailed procedures, as laid down in the EOPSG Transport Safety Manual, are used by EOPSG members.

The content of this brochure facilitates safe handling and transport operations of organic peroxides in road and sea transport. The described procedures and equipment, supplementary to the legal requirements, represent the standard practices of the authors of this guide.

2. What are the main transport regulatory aspects?

As organic peroxides are mainly transported by road and sea, the main transport rules for dangerous goods are ADR (road) and IMDG Code (sea).

Organic peroxides are classified in division 5.2 according to the classification principles as laid down in the UN, Recommendations on the Transport of Dangerous Goods, Model regulations (UN-RTDG).



Organic peroxide types are assigned to UN-numbers on the basis of their decomposition properties, their physical state (liquid/solid) and whether or not temperature control is required (Table 1).

Table1

Organic Peroxide Type	UN number			
	not temperature controlled		temperature controlled	
	liquid	solid	liquid	solid
A	*	*	*	*
B	3101	3102	3111	3112
C	3103	3104	3113	3114
D	3105	3106	3115	3116
E	3107	3108	3117	3118
F	3109	3110	3119	3120
G	**	**	**	**

* Organic peroxides of type A are not accepted for carriage.

** Organic peroxides of type G are not subject to the provisions applicable to class 5.2

3. Why is temperature an important aspect?

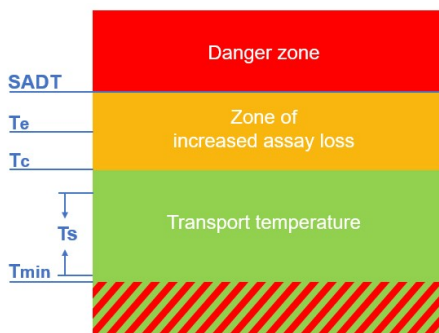
For safety reasons and to preserve quality some organic peroxides must be transported and handled under refrigerated conditions, whereas other peroxides can be shipped and handled at ambient temperature. Improper transport conditions could lead to an uncontrolled decomposition.



Which temperatures are relevant for organic peroxides?

Self-accelerating decomposition temperature (SADT)

The SADT is defined as the lowest temperature at which self-accelerating decomposition may occur in a substance within one week in the packaging as used in transport. If you exceed the SADT thermal decomposition will occur which may result in a fire. This temperature is used to determine the temperatures required to transport organic peroxides. For organic peroxides the following temperatures apply:



For temperature controlled organic peroxides the following temperatures apply:

- **Control temperature (T_C)**

It is the temperature an organic peroxide formulation must be at or below when offered for transport. If the shipped goods exceed this temperature corrective measures must be initiated to avoid reaching the emergency temperature.

- **Emergency temperature (T_e)**

It is the temperature at which emergency procedures need to be implemented (see chapter 10). Both temperatures (T_C and T_e) are derived from the SADT. These temperatures, if applicable (i.e. for UN 3111 – 3120), are listed in the organic peroxide tables in the transport regulations and are mentioned in the transport documents.

If the SADT is greater than 50 °C, no explicit temperatures are listed. But in cases where the organic peroxide is being transported or warehoused in hot geographical regions, temperature control should be used, particularly for organic peroxide formulations that have an SADT below 65 °C.

- **Set temperature for transport (T_s)**

For improved safety and quality reasons, the recommended set temperature, T_s is lower than T_C and higher than T_{min} . In some cases, non-temperature controlled organic peroxides will be transported under temperature controlled conditions for quality reasons.

For temperature controlled and non-temperature controlled organic peroxides the following temperature applies:

- **Minimum transport temperature (T_{min})**

The minimum transport temperature (T_{min}) must be followed because in some products dangerous phase separation of the organic peroxide from the diluent, crystal deposits or solidification can occur.

Product specific temperature data can be found on the product label and Safety Data Sheet (e.g. chapters 7, 9 or 14).

4. How do we make sure that organic peroxides are packed safely?

Organic peroxides (Type B to F) are packed in special packaging:

- With UN approval
- With volumes/quantities as given in the packing instructions.
- Made of compatible materials such as HDPE plastics, stainless steel, etc.
- Where necessary some specific products are provided with vented caps.
- With readily visible and legible labels with the correct UN-number and proper shipping name as well as the class 5.2 label and if required any subsidiary hazard labels.



In order to allow a product to be transported in IBCs or tanks, additional tests must prove that adequate emergency pressure relief and/or venting is guaranteed.

Either plastic or wooden pallets may be used during storage or transportation of packaged organic peroxides.

It is important to ensure that:

- The pallets are new, dry and clean.
- The pallets are free of dirt and any materials that may damage the packaging, such as nails sticking out, etc.
- The goods are palletized in a safe and stable manner and secured well with film pallet wrap or other suitable means.

5. What measures are taken for safe preparation, loading, stowage and unloading of containers or trucks?

A number of measures are taken for safe preparation, loading, stowage and unloading of containers or trucks. For organic peroxides, the key elements as described below are of most importance.

General aspects

- All activities must be carried out by well-trained experienced personnel and third-party service providers.
- All temperature controlled organic peroxides are pre-cooled to, or below the set-temperature (T_s).
- If a variety of organic peroxides are transported together, then T_s is always based on the product with the lowest control temperature (T_C), taking also into consideration the minimum transport temperature (T_{min}) if applicable.
- The member companies of EOPSG have stowage plans in place taking into consideration different control temperatures, solid/liquid stowage, etc.

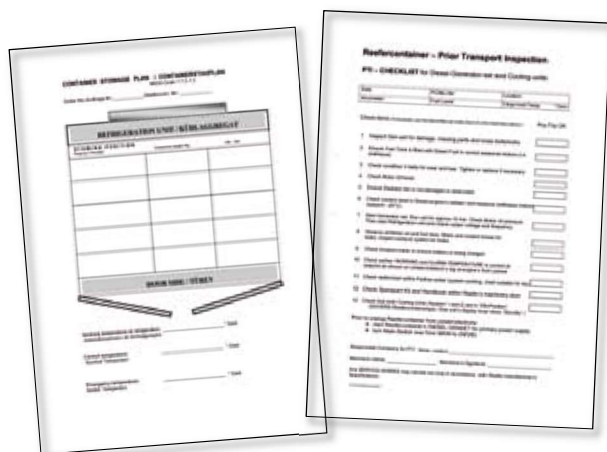
Securing of cargo

- Blocking, bracing, lashing must be done according to applicable standards.
- Suitable stowage and bracing of the cargo with ample air-ventilation must be applied.



Documentation and checklists

- Evidence for correct loading, stowage and temperature along the transport-chain has to be provided. This should include adequate documentation, such as:
 - > Checklists
 - > Illustrated documentation (photo) of loading and stowage
- Pre-Trip Inspections (PTI) and temperature records for temperature controlled organic peroxides have to be arranged and documented. These important documents must be organized by the shipper and/or its third parties.



Stowage-plans

For temperature controlled organic peroxides, the correct order of stowage has to be considered if different organic peroxides are combined inside one reefer container. Therefore, stowage plans must be available.

6. Is special transport equipment necessary?

Non-temperature controlled transport

For non-temperature controlled organic peroxides no specific transport equipment is necessary, however the transport regulations have to be followed (e.g. closed trucks or dry box container).

In addition, for non-temperature controlled products where, for safety reasons, the T_{\min} has to be respected, temperature control (i.e. keeping the product above the crystallization temperature) must be applied and the appropriate transport equipment must be selected.

Temperature controlled transport

- **Road transport**

Temperature controlled products are transported in refrigerated trucks, reefer containers or tanks with at least thermal insulation and cooling unit(s). The cooling unit(s) must be capable of working independently from the truck engine. Thermal insulation with coolant system (a “consumable refrigerant” e.g. dry ice) is not used. The trucks have both an optical and acoustic alarm that recognizes and indicates when the alarm temperature is exceeded. The temperature of the cooling compartment should be readable in the truck driver’s cabin at all times. It is the standard practice to use mechanical or digital temperature recorders for monitoring the transport temperature. Spare parts for the refrigeration must be available at roadside service providers or in the truck. Further, transport companies must have lists of service providers for the refrigeration system along the transport route.

- **Sea transport**

Temperature controlled organic peroxides for sea transport are shipped in reefer containers or refrigerated tank containers. These containers are fitted with, double (redundant) cooling system, or in special cases a single unit (only where allowed according to IMDG code). EOPSG members use GPS/CMS for reefers with redundant cooling system in order to receive an early warning regarding temperature deviations.



7. What is escorting and why is it important?

Escorting provides the organized, planned supervision of reefer containers on every transit point in the transport chain. This is done by a qualified escorting person (company's employee or third-party service provider who must have received dedicated training). Escorting is important to make sure that the reefer container is working properly and maintains the correct temperature.



How is escorting and tracking organized?

Important elements of the escorting procedures, as implemented by EOPSG members, for their reefers are:

- Presence of the escorting person during loading procedure of the container on the ship.
- Hand over sea transport instruction, transport emergency card and Dangerous Goods Declaration (DGD), along with the reefer container manual to responsible ship's officer.
- Check of reefer-position on the ship (accessibility of doors and cooling units) and inform the carrier in case of deviations.
- Check of fuel-level of diesel generator whenever the container is loaded on the ship.
- Verification of correct connection with electric power supply of the ship and reefer container settings.
- Explanation of reefer function as well as location of spare parts to responsible ship's officer.
- Availability of escorting person for answering questions.
- Signature of the hand-over protocol by ship's responsible officer.

8. How can we arrange safe intermediate storage in the transport chain?

EOPSG considers direct transfers from vessel to trailer or *vice versa* as preferable.

Intermediate storage e.g. during transshipments should be reduced to a minimum.

In general, reefer containers and dry boxes are inherently not suitable for permanent storage of organic peroxides.

In practice, temporarily storing a container may be unavoidable. For instance, this may occur during the road transport chain until the container reaches the final destination as well as whilst reefer containers are in harbours for transit or for customs clearance and/or inspection.

If intermediate storage is unavoidable respect the following principles:

General

- Take provisions against unauthorized access and theft.
- Prohibit smoking in the area around the peroxide container/tank.
- Avoid heating of containers such as by sunlight or other sources of heating.
- Store in shaded places.
- Make appropriate technical and organizational resources and emergency responders available for emergency situations. (see also chapter 10 of this brochure).



**NO ACCESS
FOR UNAUTHORISED
PERSONS**



NO SMOKING



NO FIRE

For reefers

- Keep doors and machinery accessible.
- Ensure proper electrical connection and operation.
- Keep set temperature for the product stored and secured.
- EOPSG recommends checks and records with **a frequency not longer than 4 hours** to verify that:
 - > the cooling units are working properly.
 - > reefer-container run at the set temperature.



**TEMPERATURE
IS CHECKED**



In addition, EOPSG members use GPS/CMS-monitoring systems to recognize temperature deviations at an early stage.

- A checklist showing that the reefer was in full working order prior to road-transport or at scheduled transit ports is required.

**IN CASE OF ABNORMAL RISE
OF MONITORED
TEMPERATURE, ANY ALARM,
ANY SPILLAGE, SMELL, SMOKE
OR ABNORMAL NOISES OF THE
CONTAINER**

**THE EMERGENCY
RESPONSE NUMBER
(INDICATED ON THE
REEFER CONTAINER)
SHOULD BE CALLED**

9. How to deal with mixed loading and segregation?

As most organic peroxides are of the same chemical family (with the exception of peroxyacetic acid) and consequently have the same properties, they can be stowed together in one container or transport unit. Even in the case where a product has a subsidiary hazard label or mark, e.g. corrosive, explosive, environmentally hazardous, it can be stowed together with any other organic peroxides. Further, some organic peroxides formulations being exempted from class 5.2 classification but classified as flammable solids class 4.1 can be stowed together with other organic peroxides (see Table 2). Statements on this "mixed-loading" are available. Nevertheless, compatibility of other co-loaded goods with organic peroxides has to be taken into consideration as well as transport regulatory segregation rules. Organic peroxides must not be shipped in one container together with food stuff or pharmaceuticals.



Table 2

class	5.2 + 1	5.2 + 8	5.2 + "N"	9	4.1
5.2	✓	✓	✓	✓	✓

5.2 = Organic peroxides

1 = Explosive

8 = Corrosive

"N" = Environmentally hazardous substance

9 = Miscellaneous dangerous goods

4.1 = Organic peroxides exempted from class 5.2 being classified as flammable solids

✓ = Co-loading allowed

10. What to do in case of emergency?

Despite the hazards associated with organic peroxides due to their high reactivity, they can be transported safely if the relevant regulations and adequate precautions are followed.

Deviations

Any deviation of normal transport conditions must be considered potentially dangerous and treated accordingly.

Deviations of normal transport conditions could be for example:

- Abnormal rise of monitored temperature above T_s .
- Any alarm.
- Malfunctioning of cooling units. Any spillages/leakages.
- Odors and smoke coming from the container or fire.
- Traffic accidents

For all cases, call the emergency response number.



Emergency response 24 hours/7days

EOPSG members have an emergency response number available 24 hours a day, indicated on the transport documents, reefer manual, reefer itself and in safety data sheets. Immediate technical assistance in emergency response will be given.

The following information should be kept available in case of emergency calls:

- Your contact details.
- Name of the vessel and position (only for sea transport).
- Carrier.
- Container ID (for reefers).
- Location (for road transport).
- Product type (UN number), product name and quantity.
- Nature of the incident and its development.
- Corrective actions undertaken.
- If available recorded temperature values.
- Current temperature of the cargo.

Actions when deviations occur

Abnormal rise of temperature above T_s , any alarm or malfunctioning cooling units:

- If temperature is checked regularly, deviation will be recognized at an early stage and as a result there will be ample time for emergency measures.
- Always call the emergency response number.

Any spillage/leakages:

- Take care for personal protection.
- Avoid all sources of ignition.
- Stop the leak if possible.
- Use non-combustible absorbent materials (e.g. Vermiculite which has to be wetted after absorption of the organic peroxide to avoid ignition or dangerous decomposition) or clean with plenty of water.

Smell and smoke coming from the container or fire:

- Take care for personal protection.
- Keep safe distance.
- Alert emergency responders.
- Call the fire brigade.
- Avoid all sources of ignition.
- Fire fight from safe distance and cool surroundings and surface of container.
- On ships: alert crew.

Traffic accidents

Check if cargo is affected by the incident and if the cooling system (if applicable) is still working.

In case of traffic deviations see above and inform authority.

For more information contact producer and/or consult available emergency procedures (e.g. EmS, ERI-card).

11. What training, education and training material is available?

EOPSG members all have training material available.

Specialists can provide dedicated transport safety training. This training can give in depth information on organic peroxides as well as their safe transport and safe handling. The content of such training can be tailored to the specific needs of the target group, who can be:

- Employees in logistics.
- External warehouse employees.
- Carriers.
- Agents. Shipping lines.
- Reefer service providers.
- Operators in ports of departure, transit and arrival.
- Customers.
- Authorities.

The content of such transport safety training comprises of:

- Transport regulations, classification and temperature control aspects
- Packaging and related issues.
- Preparation, loading, stowage and unloading of the container or truck.
- Transport equipment and escorting.
- Intermediate storage.
- Documentation, statements and checklists. Incidents and emergency response.

For more information and assistance do not hesitate to contact your supplier.

INFORMATION

training

EDUCATION

12. List of abbreviations

ADR	European agreement concerning the international carriage of dangerous goods by road
DGD	Dangerous Goods Declaration
EmS	Emergency response procedures for ships carrying dangerous goods
EOPSG	European Organic Peroxide Safety Group
ERI-card	Emergency Response Intervention Card
GPS	Global Positioning System
CMS	Control Management System
HDPE	High Density Polyethylene
IBC	Intermediate Bulk Container
IMDG	International Maritime Code for Dangerous Goods
PTI	Pre-Trip Inspection
SADT	Self Accelerating Decomposition Temperature
T_c	Control Temperature
T_e	Emergency Temperature
T_{min}	Minimum Transport Temperature
T_s	Set Temperature
UN-RTDG	United Nations Recommendations on the Transport of Dangerous Goods

All information concerning transport and handling 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 handling and transport 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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