

Guideline rules for the transport classification of PAA based products

Object: peroxyacetic acid and
ADR Classification



**Peracetic
Acid
Association**
A SECTOR GROUP OF CEFIC

As peroxyacetic acid is an organic peroxide, the various formulations have to be considered first for transport classification in Division 5.2 as organic peroxide.

To arrive at a full transport classification of a new organic peroxide formulation, the United Nations Recommendations on the Transport of Dangerous Goods, Model Regulations, twenty-first revised edition, present a classification procedure. This classification procedure is condensed in a flowchart and comprises a number of small-scale tests and tests on the packaged material. The flowchart and the tests to be carried out are outlined in the United Nations Manual of Tests and Criteria, seventh revised edition ([1915377_E_ST_SG_AC.10_11_Rev.7.pdf](#) (unece.org)).

Basically, the classification procedure comprises the determination of the following properties:

- ▶ the ability to propagate a detonation
- ▶ the ability to propagate a deflagration
- ▶ the sensitivity to heating under confinement
- ▶ the explosive power

In principle, it is necessary to carry out the following tests, in accordance with the United Nations Manual of Tests and Criteria, seventh revised edition:

the UN detonation test (A.6)

the time/pressure test (C.1)

the deflagration test (C.2)

the Koenen test (E.1)

the Dutch pressure vessel test (E.2)

the modified Trauzl test (F.4). (the German BAM is using the Trauzl-test (F.3) instead of the “modified Trauzl test” (F.4)) - This is used in different ways by different test institutes

Test A.6 is used to determine the detonative properties. The deflagrative properties are judged on basis of a combination of tests C.1 and C.2. The combination of tests E.1 and E.2 determines the sensitivity to heating under confinement. Using test F.4, the explosive power is determined. The latter test is only applicable for organic peroxides that are to be transported in tanks or intermediate bulk containers or it can be used in some cases for the screening for detonative properties.

Depending on the results of the series A, C and E tests, also tests on the packaged material have to be carried out according to test series B, D and/or G. Within the framework of the current study, tests on the packaged material were not relevant.

Apart from the tests included in the flowchart, the self-accelerating decomposition temperature (SADT) needs to be determined in accordance with one of the test methods that are included in test series H. The result of this test determines whether the material should be transported at a controlled temperature.

The provisions for classification and labelling under Regulation (EC) No 1272/2008 (i.e. the European CLP Regulation) are similar to the provisions for transport classification.

According the ADR tests we can confirm that:

▶ Peracetic Acid with > 5% in Peracetic acid may/must be classified:

- Division 5.2, UN 3105 (PEROXYACETIC ACID, TYPE D, stabilized, ≤43%) - OP7
- Division 5.2, UN 3107 (PEROXYACETIC ACID, TYPE E, stabilized, ≤43%) - OP8
- Division 5.2, UN 3109 (PEROXYACETIC ACID, TYPE F, stabilized, ≤43%) - OP8

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ORGANIC PEROXIDE	Concentration (%)	Diluent type A (%)	Diluent type B ¹ (%)	Inert solid (%)	Water (%)	Packing Method	Control temperature (°C)	Emergency temperature (°C)	Number (Generic entry)	Subsidiary hazards and remarks
PEROXYACETIC ACID, TYPE D, stabilized	≤ 43					OP7			3105	13) 14) 19)
PEROXYACETIC ACID, TYPE E, stabilized	≤ 43					OP8			3107	13) 15) 19)
PEROXYACETIC ACID, TYPE F, stabilized	≤ 43					OP8			3109	13) 16) 19)

- 13) *“CORROSIVE” subsidiary hazard label required (Model No 8, see 5.2.2.2.2).*
- 14) *Peroxyacetic acid formulations which fulfil the criteria of 2.5.3.3.2 (d).*
- 15) *Peroxyacetic acid formulations which fulfil the criteria of 2.5.3.3.2 (e).*
- 16) *Peroxyacetic acid formulations which fulfil the criteria of 2.5.3.3.2 (f).*
- 19) *Mixtures with hydrogen peroxide, water and acid(s).*

- ▶ Peracetic Acid with less than 5% in Peracetic acid may/must be classified after tests: Division 5.1, UN 3149, PG II (HYDROGEN PEROXIDE AND PEROXYACETIC ACID MIXTURE with acid(s), water and not more than 5 % peroxyacetic acid, STABILIZED) For < 5% PAA formulations, classification as UN 3149 is possible, provided that you meet the requirements of Special Provision 196, which means that all classification test results shall be "No". In the flowchart for classification of organic peroxide, such formulation will end up as Type G, which means that it is exempted from class 5.2 and thus allowed for transport in class 5.1.
- ▶ PEROXYACETIC ACID, TYPE G, Does not exist in ADR for Peracetic Acid; (TYPE G : Any organic peroxide which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows no effect when heated under confinement nor any explosive power, provided that it is thermally stable (self-accelerating decomposition temperature is 60°C (140°F) or higher for a 50 kg (110 lb) package), and, for liquid mixtures, a diluent having a boiling point of not less than 150°C (302°F) is used for desensitization. If the organic peroxide is not thermally stable or a diluent having a boiling point less than 150 °C (302 °F) is used for DESENSITIZATION, the chemical must be classified as Type F. So, due to the fact that for many Peracetic acid solutions water is included, water cannot be considered as Desensitization Agent (boiling point less than 150 °C (302 °F)) and consequently for ADR PEROXYACETIC ACID, TYPE G classification cannot be applied. PEROXYACETIC ACID can be classified as organic peroxide, TYPE G if it can be justified that the classification is validated by a competent Authority in accordance with 2021 2.2.52.1.8).

- DESENSITIZATION in order to ensure safety during carriage, self-reactive substances are in many cases desensitized by use of a diluent. Where a percentage of a substance is stipulated, this refers to the percentage by mass, rounded to the nearest whole number. If a diluent is used, the self-reactive substance shall be tested with the diluent present in the concentration and form used in carriage. Diluents which may allow a self-reactive substance to concentrate to a dangerous extent in the event of leakage from a packaging shall not be used. Any diluent shall be compatible with the self-reactive substance. In this regard, compatible diluents are those solids or liquids which have no detrimental influence on the thermal stability and hazard type of the self-reactive substance. Liquid diluents in formulations requiring temperature control (see 2.2.41.1.14) shall have a boiling point of at least 60 °C and a flash-point not less than 5 °C. The boiling point of the liquid shall be at least 50 °C higher than the control temperature of the self-reactive substance. (ADR 2017 2.2.41.1.16 Desensitization)
- The UN Recommendations on the Transport of Dangerous Goods specify in Section 2.5.3.2.1 that any organic peroxide shall be considered for classification in Division 5.2, unless the organic peroxide formulation contains:

a) not more than 1.0% available oxygen from the organic peroxides when containing not more than 1.0% hydrogen peroxide; or

b) not more than 0.5% available oxygen from the organic peroxides when containing more than 1.0% but not more than 7.0% hydrogen peroxide.

- Formulation of a stabilized distilled PeroxyAcetic acid that is derived from **distillation of PeroxyAcetic acid** originating from PeroxyAcetic acid in concentration of not more than 41% with water, total active oxygen (PeroxyAcetic acid+H₂O₂) ≤ 9.5%, which fulfills the criteria of 2.5.3.3.2 (f) is an organic peroxide of Division 5.2 with a subsidiary risk of Class 8 (corrosive). It is assigned to UN 3119.

UN no.	Name and description	Class and Div.	Subsidiary risk	UN pack. group	Special provision	LQ /EQ	Packagings and IBCs		Portable tanks and bulk containers	
							Packing inst.	Special pack. provision	Instruction	Special provision
3119	ORGANIC PEROXIDE TYPE F, LIQUID, TEMP. CONTROLLED	5.2			122 274 323	0 / E0	P520 IBC520			T23

3. With regard to subsidiary risks of UN 3119, only 2.5.3.2.4 list of organic peroxides is referred to in special provision 122:

122 The subsidiary risks, control and emergency temperatures if any, and the generic entry number for each of the currently assigned organic peroxide formulations are given in 2.5.3.2.4.

4. As the above-mentioned formulation of peroxyacetic acid assigned to UN 3119 is allowed to be transported in tanks only, it is not mentioned in 2.5.3.2.4. It is mentioned only in 4.2.5.2.6 tank instruction T23 (footnote d)

T23				PORTABLE TANK INSTRUCTION		T23		
UN No.	Substance	Min. test pressure (bar)	Min. shell thickness (mm-reference steel)	Bottom opening requirements	Pressure-relief requirements	Degree of filling	Control temperature	Emergency temperature
3119	ORGANIC PEROXIDE, TYPE F, LIQUID, TEMPERATURE CONTROLLED	4	See 6.7.2.4.2	See 6.7.2.6.3	See 6.7.2.8.2 4.2.1.13.6 4.2.1.13.7 4.2.1.13.8	See 4.2.1.1 3.13	c	c
	Peroxyacetic acid, distilled, type F, stabilized ^d						+30 °C	+35 °C

c As approved by the competent authority.

d Formulation derived from distillation of peroxyacetic acid originating from peroxyacetic acid in concentration of not more than 41% with water, total active oxygen (peroxyacetic acid+H₂O₂) ≥ 9.5%, which fulfils the criteria of 2.5.3.3.2 (f).

1. During the course of developing the Model Regulations, the information on the corrosive subsidiary risk of that substance has been missed. See annex (Background Information).
2. Finland proposes to add the information on the corrosive subsidiary risk for the above-mentioned formulation of stabilized distilled peroxyacetic acid by adding a requirement to affix a Class 8 placard to transport units carrying that substance.

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This section refers only to those properties of organic peroxides which are decisive for their classification.

A flow chart, presenting the classification principles in the form of a graphically arranged scheme of questions concerning the decisive properties together with the possible answers, is given in Figure 2.5.1.

These properties shall be determined experimentally. Suitable test methods with pertinent evaluation criteria are given in the Manual of Tests and Criteria, Part II.

2.5.3.3.1 An organic peroxide formulation shall be regarded as possessing explosive properties when in laboratory testing the formulation is liable to detonate, to deflagrate rapidly or to show a violent effect when heated under confinement.

2.5.3.3.2 The following principles apply to the classification of organic peroxide formulations not listed

- (a) Any organic peroxide formulation which can detonate or deflagrate rapidly, as packaged for transport, is prohibited from transport in that packaging under Division 5.2 (defined as ORGANIC PEROXIDE TYPE A, exit box A of Figure 2.5.1);
- (b) Any organic peroxide formulation possessing explosive properties and which, as packaged for transport, neither detonates nor deflagrates rapidly, but is liable to undergo a thermal explosion in that package, shall bear an "EXPLOSIVE" subsidiary hazard label (Model No 1, see 5.2.2.2.2). Such an organic peroxide may be packaged in amounts of up to 25 kg unless the maximum quantity has to be limited to a lower amount to preclude detonation or rapid deflagration in the package (defined as ORGANIC PEROXIDE TYPE B, exit box B of Figure 2.5.1);
- (c) Any organic peroxide formulation possessing explosive properties may be transported without an "EXPLOSIVE" subsidiary hazard label when the substance as packaged (maximum 50 kg) for transport cannot detonate or deflagrate rapidly or undergo a thermal explosion (defined as ORGANIC PEROXIDE TYPE C, exit box C of Figure 2.5.1);

(d) Any organic peroxide formulation which in laboratory testing:

- detonates partially, does not deflagrate rapidly and shows no violent effect when heated under confinement; or
- does not detonate at all, deflagrates slowly and shows no violent effect when heated under confinement; or
- does not detonate or deflagrate at all and shows a medium effect when heated under confinement;

is acceptable for transport in packages of not more than 50 kg net mass (defined as ORGANIC PEROXIDE TYPE D, exit box D of Figure 2.5.1);

(e) Any organic peroxide formulation which, in laboratory testing, neither detonates nor deflagrates at all and shows low or no effect when heated under confinement is acceptable for transport in packages of not more than 400 kg/450 litres (defined as ORGANIC PEROXIDE TYPE E, exit box E of Figure 2.5.1);

(f) Any organic peroxide formulation which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows only a low or no effect when heated under confinement as well as low or no explosive power may be considered for transport in IBCs or tanks (defined as ORGANIC PEROXIDE TYPE F, exit box F of Figure 2.5.1); for additional requirements see 4.1.7 and 4.2.1.13;

(g) Any organic peroxide formulation which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows no effect when heated under confinement nor any explosive power shall be exempted from Division 5.2, provided that the formulation is thermally stable (self-accelerating decomposition temperature is 60 °C or higher for a 50 kg package) and for liquid formulations diluent type A is used for desensitization (defined as ORGANIC PEROXIDE TYPE G, exit box G of Figure 2.5.1). If the formulation is not thermally stable or a diluent other than type A is used for desensitization, the formulation shall be defined as ORGANIC PEROXIDE TYPE F.

Figure 2.5.1: FLOW CHART SCHEME FOR ORGANIC PEROXIDES

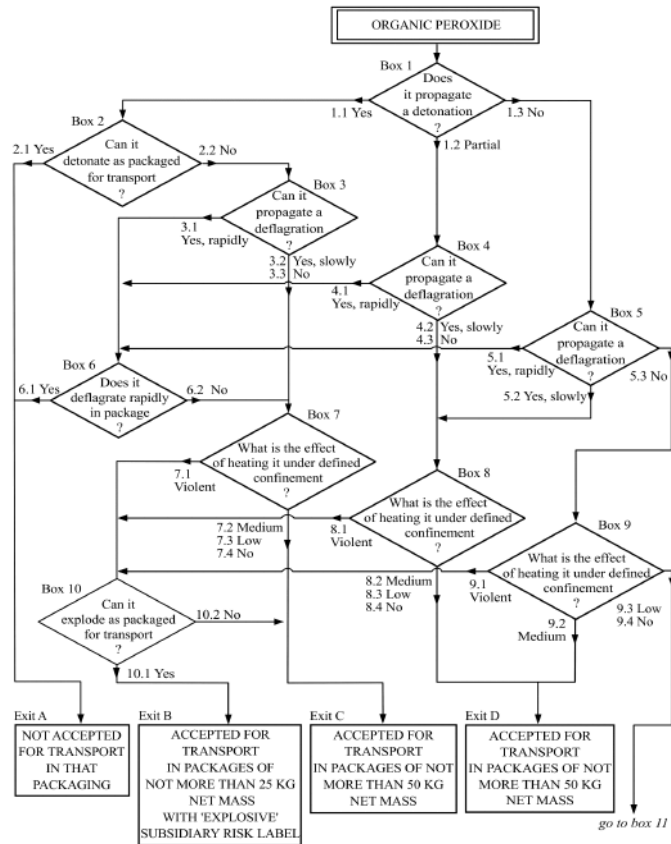


Figure 2.5.1: FLOW CHART SCHEME FOR ORGANIC PEROXIDES

Figure 2.5.1: FLOW CHART SCHEME FOR ORGANIC PEROXIDES (cont'd)

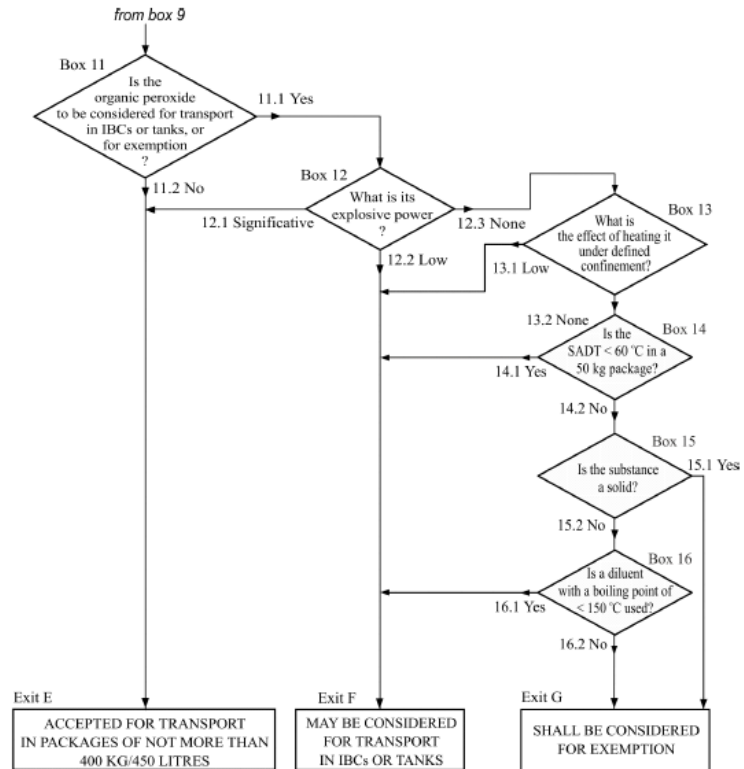


Figure 2.5.1: FLOW CHART SCHEME FOR ORGANIC PEROXIDES (cont'd)