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COMMITTEE OF EXPERTS ON THE
TRANSPORT OF DANGEROUS GOODS

(Twentieth session,
Geneva, 7-16 December 1998,
agenda item 2 (c) (iii))

WORK OF THE SUB-COMMITTEE OF EXPERTS
ON THE TRANSPORT OF DANGEROUS GOODS

Draft amendment to the Recommendations on the Transport of Dangerous Goods
Manual of Tests and Criteria

Transport of Peroxyacetic acid in IBCs and Tanks

Transmitted by the Observer from Finland

1. Introduction

The carriage of 3109, Peroxyacetic acid, Type F, stabilized, with a peroxyacetic acid concentration equal to or less than 43 % is allowed in accordance with the UN Recommendation, tenth revised edition (the list of peroxides permitted for transport in 2.5.3.2.4). In accordance with the packing instruction 521 (4.1.5.3) the transport of this substance is also permitted in IBCs of the Types 31H1, 31HA1 and 31A, provided that the concentration of the peroxyacetic acid does not exceed 17 %.

In the table "T34 Portable tank instructions" (4.2.4.2.6) many Organic peroxides , Type F liquid, with the UN number 3109 are allowed to be transported in tanks.

Organic peroxide formulations containing almost 40 per cent peroxyacetic acid have in laboratory tests been approved and classified as UN 3109, ORGANIC PEROXIDE, TYPE F, LIQUID (Enclosure 1). Some competent authorities in European countries have issued special licences for both the sea and the land transport of peroxyacetic acid in IBCs and in tanks under the special conditions (Enclosure 2 and 3). Until now no problems have arisen.

Since there is a need for both the sea and the land transport of Organic peroxide Type F, Liquid containing 38 % or less peroxyacetic acid in certain IBCs and in tanks, Finland proposes the following changes to the UN Recommendation:

2. Proposals

2.1 Intermediate Bulk Containers (IBCs)

4.1.5.3 Amend the text at the end of **PACKING INSTRUCTION 521, UN 3109, ORGANIC PEROXIDE, TYPE F, LIQUID:**

UN No	Organic peroxide	Type of IBC 1/	Maximum quantity (litres)	Control temperature 2/	Emergency temperature
3109	**ORGANIC PEROXIDE, TYPE F, LIQUID** Peroxyacetic acid, stabilized, not more than 38 %	31 H1 31 HA1 31A	1500 1500 1500		

1/ See 6.5.3.4, bottom openings allowed.
2/ The temperatures are based on a non-insulated IBC

2.2 Portable tank instructions

4.2.4.2.6 In portable tank instruction T-34, add the following new entry:

T34 PORTABLE TANK INSTRUCTION
This portable tank instruction applies to Division 5.2 organic peroxides. The general provisions of section 4.2.1 and the requirements of section 6.6.2 shall be met. The provisions specific to organic peroxides of Division 5.2 in 4.2.1.13 shall be met

UN No	Substance	Min.test pressure (bar)	Min. shell thickness (mm/ref. Steel)	Bottom opening requirements	Pressure relief requirements	Filling limits	Control temp.	Emerg. temp.
3109	PEROXYACETIC ACID, TYPE F, stabilized ≤ 38 %	4	See 6.6.2.4.2	See 6.6.2.6.3	See 6.6.2.8.2 4.2.1.13.6 4.2.1.13.7 4.2.1.13.8	See 4.2.1.13.13		

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TNO report
PML 1996-C54

Transport classification of a stabilized peroxyacetic acid 38.1% compound

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Assignor	Kemira Chemicals Oy Oulu, Finland
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Abstract	Company Confidential
Report text	Company Confidential
Annexes A - C	Company Confidential

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No. of annexes	3	

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Summary

A composition of peroxyacetic acid (38.1%) was classified by experiments. All the tests required for the classification were performed in conformity with the classification scheme for organic peroxides as represented in the United Nations Recommendations on the Transport of Dangerous Goods.

From the test results, it is concluded that the formulation containing 38.1% peroxyacetic acid and minor quantities of acetic acid, hydrogen peroxide and stabilizer, can be classified into Division 5.2 as an organic peroxide type F. This implies that the peroxide may be considered for transport in IBCs or tanks.

The minimum conditions for an emergency vent system on transport tanks of 20 m^3 were identified. The venting characteristics were technically determined in a 10 litre test vessel. The information and data obtained by these tests were used in extrapolations to 20 m^3 applying multiphase flow models. The required minimum diameter of a vent system is 129 mm.

According to the tests in the AST applied to the scale of a 20,000 kg payload in a 24 m^3 tank transport, the SADT for this type of transport is 55 °C. This implies that the peroxide formulation can be transported without additional temperature control requirements (i.e. without cooling requirements).

The existing tank vessels admitted for the transport of stabilized hydrogen peroxide solutions (70% at maximum) appear to meet the requirements for the investigated peroxyacetic acid solution. They can be considered for the transport of peroxyacetic acid solution as well.

Annex A Test report on the classification of peroxyacetic acid (38.1%)

Test report
In accordance with Section 20.5 of the United Nations Recommendations on the Transport of Dangerous Goods.

1	*Name of the peroxide*		
	PEROXYACETIC ACID 38.1%		
2	*General data*		
2.1	Composition		
	peroxyacetic acid	38.1%	
	acetic acid	<1%	
	hydrogen peroxide	<1%	
	stabilizer	typical	
2.2	Physical form	freezing-point -18 °C	(38.1%)
		freezing-point -19 °C	(40.9%)
2.3	Colour	colourless	
2.4	Apparent density	1.085	(38.1%)
		1.090	(40.9%)
3	*Detonation (test series A)*		
	Box 1 of the flow chart	Does the peroxide propagate a detonation?	
3.1	Method	UN Detonation test (A.6)	
3.2	Sample conditions	Tested peroxyacetic acid (40.9%) at about 2 °C	
3.3	Observations	Fragmented part of the tubes 19.3 and 17.8 cm (Fragmented part with the blanks 18.4 and 17.3 cm)	
3.4	Result	No	
3.5	Exit	1.3	
4	*Deflagration (test series C)*		
	Box 5 of the flow chart	Does the peroxide propagate a deflagration?	
4.1	Method 1	Time/Pressure test (C.1)	
4.2	Sample conditions	Tested peroxyacetic acid (40.9%) at about 0 °C	
4.3	Observations	Maximum pressure not attained	
4.4	Result	No	
4.5	Method 2	Deflagration test (C.2)	
4.6	Sample conditions	Tested peroxyacetic acid (40.9%) at about 0 °C and 50 °C	
4.7	Observations	No deflagration observed in either case	
4.8	Result	No	
4.9	Overall result	No	
4.10	Exit	5.3	

5	*Heating under confinement (test series E)*	
	Box 9 of the flow chart	What is the effect of heating under confinement?
5.1	Method 1	Koenen test (E.1)
5.2	Sample conditions	Tested peroxyacetic acid (40.9%) mass about 30 g
5.3	Observations	limiting diameter <1 mm fragmentation type O
5.4	Result	No
5.5	Method 2	Dutch Pressure Vessel test (E.2)
5.6	Sample conditions	Tested peroxyacetic acid (38.1%) mass 50 g
5.7	Observations	limiting diameter <1 mm
5.8	Result	No
5.9	Overall result	No
5.10	Exit	9.4

6	*Explosive power (test series F)*	
	Box 12 of the flow chart	What is the explosive power?
6.1	Method 1	Modified Trauzl test (F.1)
6.2	Sample conditions	Tested peroxyacetic acid (40.9%) volume appr. 27.0 ml
6.3	Observations	average net expansion 4.0 ml
6.4	Result	No
6.5	Exit	12.2

7	*Thermal stability (test series H)*	
	Derivation of SADT	
7.1	Method:	Adiabatic Storage test (H.2)
7.2	Sample conditions:	Mass tested 831.9 gram
7.3	Observations:	Run-away measured between 22 °C and 75 °C
7.4	Result:	SADT is 55 °C (as determined by tank vessel run-away and heat transfer properties)

8	*Proposed classification*	
	Proper shipping name:	ORGANIC PEROXIDE TYPE F, LIQUID
	UN number:	3109
	Division:	5.2
	Subsidiary Risk:	8
	Technical name:	Peroxyacetic acid, type F, stabilized, less than 1% hydrogen peroxide and less than 1% acetic acid
	Concentration:	38.1%
	Packing method:	M*

* UN packing method code for 'allowed for transport in containers'.

Annex C SADT determination

SADT determination in accordance with Section 28.4 of the United Nations Recommendations on the Transport of Dangerous Goods.

The SADT is defined as the lowest (i.e. critical) temperature of the vessel's surroundings at which a self-accelerating decomposition of a chemical run-away reaction occurs in the vessel (package, container) as transported. The SADT is derived from this critical temperature by rounding to the nearest larger multiple of 5 °C.

The critical temperature, in fact, depends on the balance between the heat generated within and the heat transferred from the vessel. As such it depends on the chemical composition on the one hand, and on the type and size of the vessel on the other hand. From the thermodynamic law on conservation of energy applied to the container it follows that:

$$mc_p\,(dT/dt) = q_{prod} - q_{loss} \qquad (1)$$

From equation (1) it follows that a material with mass (m) and heat capacity (c_p) can only self-heat into a run-away if the heat production (q_{prod}) cannot be balanced by the loss of heat (q_{loss}) at any stage during the self-heating process. This condition implies that the criterion for the self-accelerating decomposition is the highest critical temperature at which q_{prod} still can equal q_{loss} at some stage of the decomposition.

The heat production within the vessel is determined by the reaction rate of the decomposition and as such can be described by an exponential function of temperature in the vessel:

$$q_{prod} = m \cdot HPF \cdot exp.\,(-E_a/RT) \qquad (2)$$

The heat production as well as the heat production factor (HPF) and activation energy (E_a) are determined by the temperature-time curve in the adiabatic experiment in the AST. This measured curve and its simulation by equations (1) and (2) using optimized HPF and E_a values are shown in Figure C.1 as measured points and solid curve, respectively.

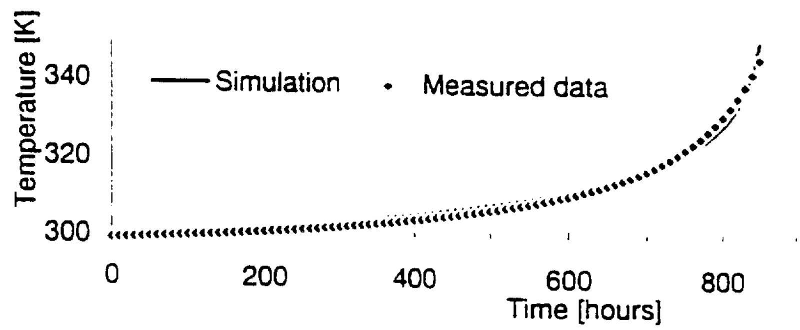

Figure C.1: *Measured and simulated temperature-time curve in the AST experiment. Dots: temperatures as measured; Solid curve: calculated by optimization.*

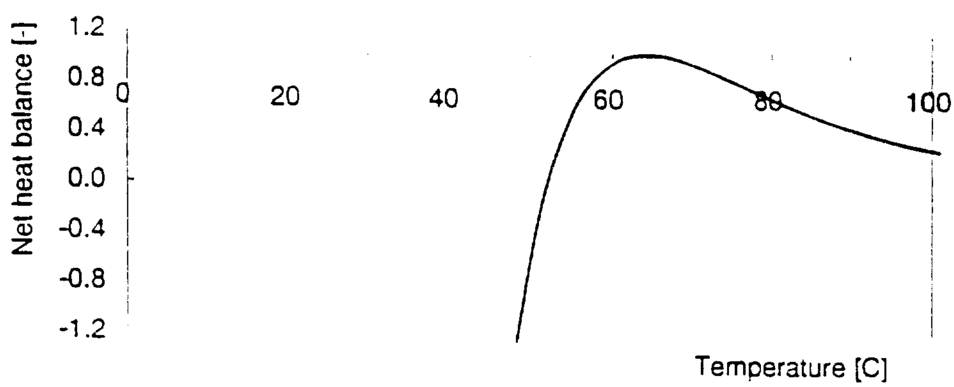

Figure C.2: *The net heat balance as a function of vessel temperature corresponding to the critical temperature of 52.4 °C.*

The heat loss from the vessel is determined by the difference in temperature within the vessel and temperature of the surroundings, and as such is a linear function of the vessel temperature:

$$q_{loss} = hA \cdot (T - T_s) \quad (3)$$

The heat loss, thus, is proportional to the heat transfer coefficient (h) and the heat transfer area (A). The heat transfer coefficient h is based on the heat fluxes within the vessel (determined by the Nusselt number) and outside the vessel (determined by the Grashof number), and on the heat conductivity of the vessel wall. For non-insulated larger metal vessels, the resistivity against heat flow is mainly determined by the heat flux outside the vessel. Therefore, the heat transfer coefficients (h) of larger vessels will be independent of size. The basic consequence is that the ratio between heat loss and heat production for vessels with different sizes will be affected to a major extent by the differences in respective ratios of vessel surface area and vessel mass (A/m). Values of heat loss factors per unit mass (hA/m) are shown in [2] for a variety of vessels and vessel sizes. The heat loss factor as derived for the 24,000 m^3 container from the values of the metal containers in [2] appears to be 0.011 W/kgK.

The net heat balance is the quotient (q_{loss} / q_{prod}). The net heat balance at a vessel temperature (T) equals 1 if the heat transfer capacity equals the heat production capacity at that temperature. The net heat balance is maximum if its derivative with respect to vessel temperature equals 0. Both criteria imply that the critical temperature corresponds to the maximum temperature of the surroundings at which a net heat balance equal to 1 coincides with a derivative equal to 0. The net heat balance has been determined as a function of vessel temperature (T) for a series of surrounding temperatures. Only at a surrounding temperature of 52.4 °C, do the net heat balance and its temperature derivative become 1 and 0, respectively. The critical temperature, thus, becomes 52.4 °C. The net heat balance for this critical temperature is shown as a function of vessel temperature in Figure C.2. The SADT is derived from the critical temperature by rounding this temperature to the nearest larger multiple of 5 °C. The SADT, thus, is 55 °C for the peroxide composition tested.

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RESOLUTION no	9044/370/96
Date	23.1.1997
Applicant	Kemira Chemicals Oy
Address	P.O.Box 171 FIN-90101 OULU
Date of application	23.12.1996
Invoice no	12814

In case of interpretation disputes the Finnish text applies

Subject Approval of organic peroxide preparation to be carried in tanks

Resolution The competent Finnish authority concerning classification of organic peroxides, **Safety Technology Authority** has approved the peroxyacetic acid preparation specified by this resolution and made by Kemira Chemicals Oy to be carried in tanks by road and rail under the following ADR/RID-class 5.2 9°(b) heading:

3109 organic peroxide type F, liquid

Chemical composition of the preparation

The preparation may contain dangerous substances as follows:

- peroxyacetic acid	not more than 38.0%	(± 2.0%)
- hydrogen peroxide	1,0%	(± 1,0%)
- acetic acid	2,0%	

Conditions on the carriage

1. The preparation may be carried in fixed and demountable tanks and tank containers, which have been made of steels AISI 304 or AISI 316.

2. Tank shall be fitted with an emergency relief device of at least 131 cm^2 (equivalent to diameter of 12.9 cm) when the volume of the tank is not more than 24 m^3.

3. SADT for this preparation is 55 ^oC, so the preparation can be transported without additional requirements towards temperature control.

Tests

The preparation has been tested by TNO Prins Maurits Laboratory, Netherlands according to the following regulations:

- United Nations Recommendations on the Transport of Dangerous Goods,(ST/SG/AC:10/1/Rev.9) 1995
- United Nations Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, (ST/SG/AC.10/11/Rev.2) 1995

Results of the testing are documented in test report nr PML 1996-C54.

Regulations applied

Marginal 2550 (8) of Annex A in ADR-agreement;
Marginal 550 (8) of Part II in RID-regulations;
Ministry of Transport and Communications decision relating to the carriage of dangerous goods by road (147/1992, 1772/1995) Annex A, marginal 2550(8);
Ministry of Transport and Communications decision relating to the carriage of dangerous goods by rail (394/1992, 1709/1995) Part II, marginal 550(8);

Director, Process Safety — Heikki Salonen

TUKES

Senior Safety Engineer — Harri Roudasmaa

Appendix The application with appendices

Finnish Maritime Administration

CARRIAGE OF DANGEROUS GOODS - SPECIAL LICENCE

The Finnish Maritime Administration has in accordance with the Decree on the Carriage of Dangerous Goods in Ships (357/80) and the International Maritime Dangerous Goods Code decided that the carriage at sea of peroxyacetic acid, maximum 38%, stabilized in IMO type 1 tanks, is permitted on the following conditions:

1 The substance is classified as

ORGANIC PEROXIDE TYPE F, LIQUID,
UN No 3109 of Class 5.2

This classification is based on the TNO Prins Maurits Laboratory report "PML 1996-C54 for the transport classification testing of a peroxyacetic acid 38.1% compound".

2 The maximum capacity of the tank is 24 m^3.

3 The minimum test pressure of the tank is 4.0 bar.

4 The tank shall be fitted with an emergency relief device of at least 131 cm^2 (equivalent to a diameter of 129 mm).

5 The tank shall comply with the requirements set out in Section 13.1.55 of the General Introduction to the IMDG-Code.

6 Every shipment shall be accompanied by:
- a copy of this Special Licence
- a certificate for the tank intended for the transport of the substance
- details of the emergency procedures and the medical advise to be followed in case of incidents.

The Self-Accelerating Decomposition Temperature (SADT) for this substance is 55 °C when it is loaded in a tank of not more than 24m^3, i.e. an additional temperature control is not required.

This Special Licence is valid until 31 December 1998.

Issued in Helsinki on 24 March 1997.

Gunnar Edelmann
Head of Division

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M.Sc.(Chem. Eng.)

No. 2/362/97
HR 664/97
Fee FIM 1000:-

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