UN/SCETDG/17/INF.3

Sub-Committee of Experts on the
Transport of Dangerous Goods
(Seventeenth session,
Geneva, 6-15 December 1999,
agenda item 5 (b))

MISCELLANEOUS DRAFT AMENDMENTS TO THE MODEL REGULATIONS ON THE TRANSPORT OF DANGEROUS GOODS

LISTING AND CLASSIFICATION (DIVISION 5.2)
TRANSPORT OF PEROXYACETIC ACID, 41% WITH WATER, IN TANKS

Transmitted by the observer of Finland
and
European Chemical Industry Council (CEFIC)

1. INTRODUCTION

Up till now, the transport in tanks of Peroxyacetic acid (PAA) 41% with water is granted by competent authority approvals. To extend the current practise of tank transport, Finland submitted proposals to the Sub-Committee of Experts on the Transport of Dangerous Goods. At the sixteenth session these proposals ST/SG/AC.10/1998/56 and ST/SG/AC.10/C.3/1998/56 were discussed. Based on the discussions it was clear that some transport conditions needed for a world-wide tank shipment of PAA 41% with water need further investigation and consideration. Finland and also CEFIC mentioned that ongoing test programmes on the thermal stability to determine the appropriate transport conditions were running. It was noted that Finland and CEFIC would submit a new joint proposal on the transport of PAA, 41% with water, in tanks.

An individual listing of the product in the organic peroxide table is proposed, because distilled PAA with concentrations up to 41% has essentially one composition and one classification whereas the already listed equilibrium PAA (i.e. mixtures of PAA, H_2O_2 and Acetic Acid) consists of various compositions with individual classification (e.g. organic peroxide type D, E and F).

In this proposal, the relevant test results, the proposed classification and transport conditions necessary for safe tank transport, in accordance with the UN classification principles for transport of organic peroxides, are given.

2. TEST RESULTS

2.1 Classification

According to section 2.5.3.3.2 (f), organic peroxide type F may be considered for transport in tanks. In Annex 1, the test report of PAA 41% with water is given. It is concluded that the product can be classified as organic peroxide type F.

The determination of control- and emergency temperature, as derived from the SADT of PAA 41%, in the tank is described in paragraph 2.2 of this proposal.

For tank transport the specific provisions of section 4.2.1.13 of the UN recommendations shall be met. This implies:

(a) to prove the compatibility of all materials normally in contact with the substance during transport; this is described in paragraph 2.3 of this proposal.

(b) to provide data for the design of the pressure and emergency relief devices taking into account the design characteristics of the portable tank. Emergencies to be taken into account are self-accelerating decomposition and fire engulfment; this is described in paragraph 2.4 of this proposal.

2.2 SADT and Control and Emergency temperature setting

The self-accelerating decomposition temperature (SADT) of PAA 41.5% was determined by using the Adiabatic Storage Test (AST), according to the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, test H.2.

In Annex 2, the details of the SADT determination of the product in 20 m^3 insulated tank is described. It is concluded that the SADT is 40 °C. According to section 7.1.4.3.1.2 of the UN recommendations, the control temperature should be 30 °C and emergency temperature 35 °C.

2.3 Additional compatibility tests

The compatibility of stainless steel 316L was already be taken into account in the Adiabatic Storage Tests (see Annex 2). Some additional Heat Accumulation Storage Tests (UN test H.4, 400 ml Dewar vessel) have been executed in the presence of passivated stainless steel 316L with and without a weld in the metal piece (area of metal piece representative for the vessel contact area during transport). Test temperature has been chosen at 55 °C, because at that temperature the product should be stable (taking into account the SADT of 40 °C in the 20 m^3 tank, which more or less equals an SADT of 60 °C in test H.2). Results are given in the following Table.

Material tested	Temperature	Test H.4 result
PAA, 40%	55 °C	No runaway reaction, 7 days
PAA, 40% with passivated steel	55 °C	No runaway reaction, 7 days
PAA, 40% with passivated steel and weld	55 °C	No runaway reaction, 7 days

It is concluded that the presence of passivated steel (even with a weld) does not lead to a lower stability of the product at 55 °C. This was in line with the test results described in Annex 2.

2.4 Fire engulfment and Self Accelerating Decomposition

The required venting capacity was determined on a 10-litre scale, the results of which were extrapolated to the foreseen tank transport scale. The experiments were performed in a horizontal stainless steel vessel with a capacity of 10 litres as described in the UN Manual of Tests and Criteria, Appendix 5.

It is concluded that on a 10 litre scale, a relief opening of 28 mm^2 is sufficient to vent all decomposition products. If these results are further assessed in accordance with the criteria given in Appendix 5 of the UN Manual of Tests and Criteria, the required emergency relief area for a 20 m^3 tank is about 560 cm^2, corresponding with a circular area of 26 cm diameter.

In practice, tanks used for transporting Peroxyacetic acid are often equipped with a 10 inch (25.4 cm) diameter rupture disc. In view of the conservative calculations as in Annex 3, a 10 inch diameter rupture disc is sufficient.

2.5 Competent authority approval

Approval for PAA 41% with water has been granted by, amongst other authorities, the competent authority of The Netherlands. A copy of the approval is given in Annex 4.

3. PROPOSALS

It is proposed to add to 2.5.3.2.4 the following entry:

2.5.3.2.4 List of currently assigned organic peroxides

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 risks and remarks
PEROXYACETIC ACID WITH WATER, TYPE F, stabilized	#41					M	30	35	3119	13, 29

29) Peroxyacetic Acid originating from #41% with water, total active oxygen (Peroxyacetic Acid+H_2O_2) #9.5%, which fulfills the criteria of 2.5.3.3.2 (f)

It is proposed to add to 4.2.4.2.6, portable tank instruction T23, the following entry:

UN No.	Substance	Minimum test pressure (bar)	Minimum shell thickness (mm-reference steel)	Bottom opening requirements	Pressure relief requirements	Filling limits	Control temperature	Emergency temperature
3119	ORGANIC PEROXIDE, TYPE F, LIQUID, TEMPERATURE CONTROLLED PEROXYACETIC ACID WITH WATER, TYPE F, stabilized **/	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 4.2.1.13.13	*/ +30 °C	*/ + 35 °C

**/ Peroxyacetic Acid originating from #41% with water, total active oxygen (Peroxyacetic Acid+H_2O_2) #9.5%, which fulfills the criteria of 2.5.3.3.2 (f)

Annex 1: Classification test report

TEST REPORT ON THE CLASSIFICATION OF PEROXYACETIC ACID, 41 % WITH WATER

1.	Name of substance		
2.	General data		
2.1	Composition	:	41.5% Peroxyacetic Acid < 2% Acetic Acid < 2% H_2O_2 Balance Water
2.2	Molecular formula	:	$C_2H_4O_3$
2.3	Available oxygen content	:	9.4%
2.4	Physical form	:	Liquid
2.5	Colour	:	Colourless
2.6	Apparent density	:	1068 kg/m^3
3.	Detonation (test series A) Box 1 of the flow chart	:	Does the substance propagate a detonation?
3.1	Method 1	:	BAM 50/60 steel tube test (test A.1)*
	Method 2	:	UN detonation test (test A.6)
3.2	Sample conditions	:	Ambient temperature
3.3	Observations	:	Method 1: 17 and 20 cm of tube fragmented
		:	Method 2: 19 and 19 cm of tube fragmented
3.4	Result	:	No
3.5	Exit	:	1.3
	* BAM report available on request		
4.	Deflagration (test series C) Box 5 of the flow chart	:	Does the substance propagate a deflagration?
4.1	Method 1	:	Time/pressure test (test C.1)
4.2	Sample conditions	:	Ambient temperature
4.3	Observations	:	< 2070 kPa
4.4	Result	:	No
4.5	Method 2	:	Deflagration test (test C.2)
4.6	Sample conditions	:	Temperature 30EC
4.7	Observations	:	Deflagration rate 0.0 mm/s (no propagation)
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 it under defined confinement?
5.1	Method 1	:	Koenen test (test E.1)
5.2	Observation	:	Limiting diameter < 1.0 mm, F=0
5.3	Result	:	No
5.4	Method 2	:	Dutch pressure vessel test (test E.2)

5.5	Sample conditions	:	50.0 g
5.6	Observations	:	Limiting diameter <1.0 mm
5.7	Result	:	No
5.8	Overall result	:	No
5.9	Exit	:	9.4

6. Explosive power (test series F)

	Box 12 of the flow chart	:	What is the explosive power ?
6.1	Method 1	:	Trauzl (test F.3)*
6.2	Observations	:	10 g, 4 ml
6.3	Method 2	:	Modified Trauzl (test F.4)
6.4	Observation	:	net expansion 4 ml, 6 ml
6.5	Result	:	Low
6.6	Exit	:	12.2

* BAM report available on request

7. Thermal stability (test series H)

7.1	Method	:	Adiabatic Storage Test (test H.2) and Heat Accumulation Storage Test (test H.4)
7.2	Sample conditions and execution of tests	:	See Annex 2 of this proposal
7.3	Observations	:	Critical temperature 36-38°C for an 20 m^3 insulated stainless steel tank with heat-loss factor of 0.0023 W/kg.K
7.4	Result	:	Self Accelerating Decomposition Temperature of product in tank is 40 °C, temperature control required
7.5	Control temperature	:	30 °C (in 20 m^3 insulated tank)
7.6	Emergency temperature	:	35 °C (in 20 m^3 insulated tank)

Annex 2: Determination of Self Accelerating Decomposition Temperature

The tests on the SADT determination have been executed by TNO Prins Maurits Laboratory, The Netherlands. The applied testmethod to determined self-accelerating decomposition temperature (SADT) of PAA 41.5% was the Adiabatic Storage Test (AST), according to the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, test H.2.

The SADT is derived from the critical temperature, which in term, is defined as the highest ambient temperature at which the substance as packaged, in this case the insulated tank, does not show self-accelerating decomposition. The SADT results as the critical temperature rounded off to the next higher multiple of five degrees.

The critical temperature depends on the balance between the heat generation within and the heat transfer from the vessel. As such, it depends on the heat production by chemical reaction patterns (measured by the AST) on the one hand and on the type, size of the vessel and insulation on the other hand. The characteristics of the vessel are incorporated in the critical temperature calculations as a heat loss factor (HLF). This heat loss factor is defined as UA/m, in which U is the heat transfer coefficient [$W/m^2.K$], A the heat transfer area [m^2] and m the sample mass [kg] in the vessel.

In principle, the heat loss factor of the type of container that will be used for the actual transport should be used for the SADT calculations. Based on the information supplied by the assignor, the heat loss factor can be accurately calculated. Within the supplied documents, a UA value of 40 kcal/hr is specified for the 20 m^3 insulated tank container. If combined with a specified payload of 20,000 kg the UA value yields a heat loss factor of 0.00233 W/kg.K.

A number of three AST experiments were performed with the PAA 41.5% formulation. The experiments differ with respect to the presence of a metal plate in the test (representative for the vessel contact area during transport) and increased stabiliser levels. The metal plate was made of stainless steel 316L and had dimensions of 2*4 cm and 1 mm thick. Before used in the tests, the metal plate was subsequently washed with a degreasing detergent, passivated with diluted nitric acid and rinsed with the PAA solution.

The test results showed that despite a difference in the presence of a metal plate or additional stabiliser, a critical temperature with a small variance between 36.2 and 37.7 °C was determined with an HLF of 0.0023 W/kg.K. The reason for the nearly constant critical temperature lies in the fact that the effect of the metal plate or additional stabiliser only manifest at elevated temperatures. At temperatures below approximately 45 °C, the differences in heat production and thus critical temperature become small. Based on the determined critical temperature, an SADT value of 40 °C follows, for an insulated tank container with a heat loss factor of 0.0023 W/kg.K.

According to the section 7.1.4.3.1.2 of the UN recommendations, the control temperature should be 30 °C and the emergency temperature should be 35 °C.

Annex 3: Emergency vent testing

The required venting capacity was determined on a 10-litre scale, the results of which were extrapolated to the foreseen tank transport scale. The experiments were performed in a horizontal stainless steel vessel with a capacity of 10 litres. Two separate test series facilities have been executed by TNO Prins Maurits Laboratory. Similar tests have been executed by Akzo Nobel with identical test results and conclusions.

In one test series the vessel set-up differs slightly from the set-up as described in the UN Manual of Tests and Criteria, Appendix 5. However, these minor deviations do not influence the outcome of the tests. The vessel is equipped with two vent openings: (1) a permanent opening with a variable orifice diameter, and (2) a large opening which is closed with a rupture disc with a bursting pressure of 28 bar. The design pressure of the vessel is 70 bar. The vessel is heated by means of an external electrical heating coil that is wound around the vessel.
A series of two experiments with varying relief openings was performed using a 40.9% PAA formulation. The filling degree of the vessel was about 90%.

In the first experiment, the permanent opening was equipped with an orifice of 1 mm diameter (0.78 mm^2) and the vessel contents were heated with a rate of 3.5 °C/min. At a liquid temperature of 45 °C a quick pressure rise to about 4 bars was observed, within a few minutes thereafter the pressure exceeded the operating pressure of the rupture disc. The disc ruptured 27 minutes after the start of the experiment. A maximum liquid temperature of about 60 °C was observed.

In the second experiment, the permanent opening was equipped with an orifice of 6 mm diameter (28.3 mm^2) and the vessel contents were heated with a rate of 3.0 °C/min. All decomposition products could be vented, even after a prolonged period of heating (nearly one hour). A maximum liquid temperature of 110 °C was observed (i.e. the boiling temperature) and no pressure effect was observed.

It is concluded that on a 10 litre scale, a relief opening of 28 mm^2 is sufficient to vent all decomposition products. If these results are further assessed in accordance with the criteria given in Appendix 5 of the UN Manual of Tests and Criteria, the required emergency relief area for a 20 m^3 tank is about 560 cm^2, corresponding with a circular area of 26 cm diameter. The 10 litre scale experiments were performed at relief openings of 0.78 mm^2 and 28.3 mm^2 only, i.e. a factor of 36 difference in venting capacity. However, the calculations have been based on the larger opening. Therefore, a relief vent area of 560 cm^2 on a 20 m^3 tank can be considered as a very conservative vent requirement. In practice, tanks used for transporting Peroxyacetic acid and/or hydrogen peroxide are often equipped with a 10 inch (25.4 cm) diameter rupture disc. In view of the conservative calculations as outlined above, a 10 inch diameter rupture disc is sufficient.

Annex 4: Competent authority approval

APPROVAL

1	Approval number	99D2/2422
2	Issued by	The competent authority of The Netherlands for the classification of organic peroxides for road and rail transport, TNO Prins Maurits Laboratory P.O. Box 45 2280 AA Rijswijk telephone +31-15-2843358 telefax +31-15-2843997
3	Applicant	Akzo Nobel Eka Chemicals P.O. Box 10 7400 AA Deventer The Netherlands
4	Synopsis	The material specified in paragraph 8 is approved for transportation under the terms specified in paragraphs 9 and 10
5	Relevant regulations	• Recommendations on the Transport of Dangerous Goods, eleventh revised edition, 1999, United Nations, New York and Geneva (ST/SG/AC.10.1/Rev.11) • Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, second revised edition, 1995, United Nations, New York and Geneva (ST/SG/AC.10.11/Rev.2) • Regeling vervoer over land van gevaarlijke stoffen (VLG) • European Agreement concerning the international carriage of dangerous goods by road (ADR)
6	Relevant parts	Marginals 2550(8) and 212.511 of ADR
7	Basis	Application by Akzo Nobel Eka Chemicals, dated 23-11-1999, with report number RPS 9900920.

Approval 99D2/2422 (cont)

8	Technical name of the product	peroxyacetic acid, <41% in water
9	Class or division Subsidiary risk UN number Proper shipping name Packing type Control temperature Emergency temp.	5.2 8 3119 ORGANIC PEROXIDE TYPE F, liquid, temperature controlled M 30 °C 35 °C
10	Conditions	The total active oxygen content shall be lower than 9.5% The tank container shall meet the following requirements: • it is provided with a 85 mm relief vent, set at 2.9 barg • it is provided with a 30 cm diameter emergency relief vent, closed with a 4.0 barg bursting disk • the test pressure of the tank is at least 4.0 barg • the tank is provided with at least two temperature indicators All other relevant requirements of ADR have to be met
11	Remarks	A copy of this approval must accompany the cargo This approval is valid until 31 December 2000
12	Date	24 November 1999
13	Authorization	i.a. [signature] (classification expert) Research Group Properties Energetic Materials

Approval sent to:

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