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COMMITTEE OF EXPERTS ON THE TRANSPORT OF DANGEROUS GOODS AND ON THE GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION AND LABELLING OF CHEMICALS

Sub-Committee of Experts on the Transport of Dangerous Goods
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EXPLOSIVES, SELF-REACTIVE SUBSTANCES AND ORGANIC PEROXIDES

Ammonium nitrate emulsions, suspensions and gels

Ammonium nitrate emulsions and suspensions – Effect of temperature cycling

Transmitted by the expert from the United Kingdom

1. In UN/SCETDG/22/INF.4 the expert from Spain made available to the Sub-Committee some sample test results for tests 8 (a), 8 (b) and 8 (c) of Test Series 8, and proposed that they be included in the tables of test results in Section 18 of the Manual of Tests and Criteria. The data relate to ammonium nitrate based formulations that contained inorganic perchlorate and organic amine nitrate sensitisers, and therefore do not fall within the limits of the composition for substances of UN3375 as laid down in Special Provision 309. The proposal was not adopted by the Sub-committee (ST/SG/AC.10/C.3/44, paragraphs 23 to 25).

2. Subsequently, at the 23rd session of the Sub-Committee, in ST/SG/AC.10/C.3/2003/13, the expert from Spain proposed extending the range of compositions given in SP309 to allow for the inclusion of levels of these sensitizing agents, but the Sub-Committee noted that further work on the issues raised was needed (ST/SG/AC.10/C.3/46, paragraph 24). During the debate on the composition of ammonium nitrate emulsions, suspensions and gels in Special Provision 309 several points were raised, one of which was the effect of temperature cycling on the stability and sensitivity of formulations containing alkali metal perchlorate and amine nitrate salt sensitizers.

3. The United Kingdom is performing work on the effect of temperature cycling on four ammonium nitrate based explosive precursor systems- two emulsions and two suspensions. The purpose of the work is to determine if dangerous phase separation can occur when the explosive precursors contain sensitizing agents and they experience the extremes of temperature that can normally be encountered during transport.

4. The work is still in progress, but some preliminary findings are presented in Appendix A which show that suspensions that meet the composition limits in SP309 as proposed in ST/SG/AC.10/C.3/2003/31 are not as stable as typical ammonium nitrate emulsions.

5. The Sub-Committee is invited to take note of these findings.

APPENDIX: TEMPERATURE CYCLING OF AMMONIUM NITRATE EMULSIONS AND SUSPENSIONS

A.1 Samples

Four different samples were examined, two emulsions and two suspensions; some information on their compositions, notably the water content and any sensitising components, is given in Table A.1.

Table A.1: Sample details

Sample	*Notes*
'Standard' ANE Matrix	Water 16.8%
'Sensitive' ANE Matrix	Water 12.8%; sodium nitrate replacing some of the ammonium nitrate
AN Suspension Type SP1	Ammonium nitrate 62.3%; sodium perchlorate 11.0%; water 13.0%; thickener 0.7%; glycol 13.0%
AN Suspension Type SP5	Ammonium nitrate 66.4%; sodium perchlorate 8.0%; hexamine 5.0%; nitric acid 2%; water 12.0%; thickener 0.6%; glycol 6.0%

A.2 Procedure

A.2.1 A nominal 30 g and a nominal 400 g sample of each substance, in closed containers fitted with a pinhole vent, were cycled between 6 ±1 °C and 50 ±1 °C five times. The samples were maintained at the holding temperatures for no less than 18 and no more than 24 hours; all of the samples experienced five excursions up to the higher temperature and five excursions down to the lower temperature. Aliquots of each sample, maintained at 20 ± 5 °C, were used as controls for comparative purposes.

A.2.2 Impact sensitivity was assessed by the procedure in UN Test Series 3 Test 3(a) (ii): BAM Fallhammer

A.3 Results

The results are given in Table A.3 and summarised below.

Exposure to extremes of temperature that can reasonably be expected to be experienced during transport has:

(i) no measurable effect on the impact sensitivity of either the emulsions or suspensions when tested in accordance UN Test 3(a) (ii): BAM Fallhammer, at least within the limits of discrimination afforded by the test; but

(ii) causes physical changes and phase separation (crystal growth) in the suspensions tested, which may make such materials more sensitive to initiation by stronger stimuli..

Sample	***Appearance***		***Mass Loss after cycling (%)[(a)]***	***Limiting Impact Energy (J)***	
	Control	***After Cycling***			
Standard ANE Matrix	Very viscous non-mobile wax; clear translucent; homogeneous	Unchanged	0.3 and 2.0	Control After cycling	>50 >50
Sensitive ANE Matrix	Very viscous non-mobile wax; white translucent; homogeneous	Unchanged	2.0 and 1.6	Control After cycling	>50 >50
AN Suspension Type SP1	Viscous, opaque fluid with two phases: Upper phase viscous liquid Lower phase, white solid dispersed in viscous liquid	Uniform fine-grained non-mobile suspension, opaque white. Some crystal growth on surface with a 'skin'. Rust coloured spot in both 'large' and 'small' samples	0.3 and 1.1	Control (liquid phase) (liquid & granule) After cycling (surface layer crystals) (liquid & granule) (rust spot)	>50 >50 >50 >50 >50 [(c)]
AN Suspension Type SP5	Viscous but fluid and opaque; two phases, upper 'syrup-like' Lower phase, as upper phase with dispersed white grainy solid	Layered, non-mobile suspension, opaque white. Some crystal growth on surface with a 'skin' of clear crystals. Thin layer of a viscous liquid on top of a similar phase containing white granules. The bottom layer is gritty white crystalline. Rust-coloured spot in both 'large' and 'small' samples	0.3 and 1.1	Control (liquid phase) (liquid & granule) After cycling (surface layer crystals) (liquid & granule) (granules & liquid) (rust spot)	>50 >50 >50 >50 >50 >50 [(c)]

Notes: (a) First value is the mass loss from 400 g samples; the second figure is the mass loss from 30 g samples
(b) UN Test Series 3 Test 3(a) (ii) BAM Fallhammer
(c) Based on no ignitions/report in a single trial.