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
(Twenty-first session, 1-10 July 2002,
agenda item **3(b))**

EXPLOSIVES, SELF-REACTIVE SUBSTANCES AND ORGANIC PEROXIDES

Classification of ammonium nitrate emulsions, suspensions and gels

Test results of ammonium nitrate (ANE) emulsions

Transmitted by the Expert from South Africa

Sasol Explosives in South Africa has been applying the draft UN Test Series 8 for ANE's in an attempt to find a rational basis for the classification of these materials. Their past experience with the "drum test" has been that the results can be difficult to interpret in the gray area between obvious detonations and definite non-events. This is especially undesirable since there is no agreed, formal procedure for this test. In addition, the test requires a very large area because of the noise and fragments, and is unlikely to be accepted as a world standard.

The results from the first attempts to apply Series 8 were disappointing. Two samples of emulsion formulations were submitted to the TNO laboratory in Holland for the Koenen test. At least one of them (with the higher water content) was expected to pass the test, and both failed. Sasol Explosives conducted the other Series 8 tests on the two emulsions themselves, and both passed all the tests. The results are given in annex A.

Taking Sasol's experience into account, the current set of tests is questionable as the sole route to classification of an ANE as UN 3375. When the results are compared with others conducted on similar emulsions we find the results achieved in the Koenen Test to be surprising. Further, we are concerned at the apparent irreproducibility of the Large Scale Vented Pipe Test based on results presented to the Working Group.

For the attention of the UN Working Group, the Research Scientist, who was responsible for this testing project, made the following comments:

The ANE Gap Test:

- Tests to be at transport temperature - does this include the ANE gap test? - it is not mentioned in the method
- The stand-off distance that should be allowed below the punch-plate should be prescribed in the method

Koenen test.

- A steel tube "drawn from sheet steel of suitable quality" is asked for. The type of steel could affect the result, especially as the fragments are counted, and the result depends on their number (2x passes, 3x fails). Surely all "suitable quality" steels will not have the same stress fracturing properties?

- The tube is filled to a height 15mm below the venting orifice. Expansion, bubbling or boiling, or decomposition of the test substance can get up it up to the orifice and block or restrict it at 1 and 2mm size, effectively changing the test conditions. This would be especially true if there are particles in the substance (prills, aluminium, etc.).

RECOMMENDATIONS

South Africa wishes to recommend a new way in which the status quo around the world can be embraced by the nascent ANE regulations. Our suggestion is based on the following consideration:

Bulk emulsions (both sensitized and unsensitized) have been used all over the world for over 20 years with a good safety record. The volumes of ANE material transported globally is of the order of 1,000,000 tons per year. Most of this bulk material uses AN solution strength of 78 - 83%. Most fuel phase contents are in the range of 7 - 9%. The most energetic bulk formulation used in significant quantities therefore has 83% AN solution and 7% fuel phase.

This gives an emulsion with a minimum of 15.8% water, which is a critical parameter of safety, especially with respect to possible deflagration-to-detonation (DDT) events.

It is believed that there is sufficient historical safety record to consider a special classification of emulsions as follows:

A candidate material shall be classified as UN 3375 provided that:

a) the definition of an ANE is satisfied and that all Series 8 tests are passed

   <u>or provided that</u>

b) it is a water-in-oil emulsion containing more than 15.8% water, more than 7% hydrocarbon fuel phase, and ammonium nitrate as the only oxidizer, and provided that such emulsion passes the 8(a) Thermal Stability Test and the 8(b) Gap Test.

We also support efforts by the Working Group to use engineering means (for example sufficient venting, rupture devices, etc) to control DDT events.

ANNEX A

division of Sasol Chemical Industries Limited
(Reg. No. 1968/13914/06)

Private Bag X10028
Randburg
2125
South Africa

Sasol SMX House
156 Hendrik Verwoerd Drive, Ferndale
Randburg 2194
South Africa

Telephone: +27 (0) 11 329 6700
Telefax: +27 (0) 11 329 6752
Internet: www.sasol.com

Management functions for:
Ensign-Bickford (SA) (Pty) Ltd. Reg. No. 1992/00103/07
Sasol Mining Initiators (Pty) Ltd. Reg. No. 1997/1425/07
SMI Technology (Pty) Ltd. Reg. No. 1995/13754/07
SMI Africa (Pty) Ltd. Reg. No. 2000/008144/07

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Testing of Ammonium Nitrate Emulsion intermediates for blasting explosives

Reason for testing — Screening of test emulsions considered for submission in UN Transport of Dangerous Goods Classification.

Test Products — Two emulsions, identified henceforth as SMX ANE1 and SMX ANE2

Test Product Compositions

	SMX ANE1	**SMX ANE2**
Fuel-oil component	7,0 %	7,0 %
Water	15,0 %	15,8%
Ammonium nitrate	78,0 %	77.2%

The tests were conducted according to the draft on the **Proposal resulting from the Working Group on classification of ammonium nitrate emulsions, suspensions and gels, intermediate for blasting explosives,** as confirmed on the Committee of Experts agenda of 2-6 July 2001.

The emulsions tested are considered for use as intermediates in the preparation of blasting explosives, and were tested in the intermediate form considered for transportation and handling prior to the preparation of the final blasting product.

Summary: - Conclusion of test results

The materials do not comply with all the (draft) requirements for classification as UN 3375, Ammonium Nitrate Emulsion, in Hazard Class 5.1. The materials show a positive response to intense heating under confinement.

Description of tests

The UN Series 8 tests as recommended by the Working Group are:

8(a) Thermal stability Test: Determines if the test substance is thermally stable.
8(b) ANE Gap Test: Determines if the test substance is too sensitive to shock to be accepted into class 5.1.

8(c) Koenen Test: Determines if the substance is too sensitive to the effect of intense heat under confinement for inclusion into class 5.1

8(d) Vented Pipe Test: Determines if the substance is liable to detonate if subjected to a fire engulfment under confinement.

Criterion

All tests listed above should produce negative results according to each ones' evaluation criteria for the test substance to qualify for acceptance into UN Class 5.1. If any test yields a positive result the material should be considered for inclusion in Hazard Class 1 (explosives).

Tests and Results

Thermal Stability Test – UN 8(a)

Test Description

This test is used to determine whether the emulsion is stable at temperatures encountered during transport. The emulsion is tested at temperatures 20°C higher than that, which may be encountered during transport. The maximum temperature, of the emulsion is 60°C. The Thermal Stability Test was therefor conducted at 80°C

Test Detail

A 500ml Dewar vessel with closure system according to the test description was used in a thermostatically controlled laboratory oven. The half time heat loss of the vessel and closure system was determined to be 55mW/kg.K. As this is less than the maximum allowable 100mW/kg.K, the test system was therefore found to be suitable in terms of the method requirement. The oven was conditioned at test temperature for 2 days before the test vessel containing the sample was placed in it. Two type K thermocouples were used to monitor temperatures, one in the sample vessel and one in the oven. The signals were relayed to a pen recorder. The commencement of the test period was taken from the co-incidence of the two recorded signals.

The testing system required 10h30min to heat the sample from ambient temperature (19°C) to 78°C (2 degrees below target temperature.)

Results: Thermal Stability test

Substance	Test Temperature (°C)	Sample Mass (g)	Dewar Heat loss (mW/kg.K)	Result
SMX ANE1	81	485	55	Thermally stable
SMX ANE2	81	493	55	Thermally Stable

Assessment

The test samples did not exceed the test chamber temperature by 6°C or more in either of the tests. The tested ammonium nitrate emulsions are considered thermally stable, and can be further tested as candidate for “ammonium nitrate emulsion intermediate for blasting explosives”.

8(b) ANE Gap Test

Test Description

This test is used to measure the sensitivity of a candidate ammonium nitrate emulsion (see test 8(a)) to a specified shock level. A test setup is prepared wherein a sample in a container (steel cylinder) is co-axially impacted by a shock wave from an explosive charge (donor) which is attenuated by a gap (spacer). In this way it is possible to control the level of impact imparted to the sample. The level of response by the test sample to the impact is measured from the effect on a steel witness plate placed directly below the sample cylinder. All materials used in the setup are measured in dimension or mass, and are made from specified materials.

The length of the cast PMMA (polymethylmethacrylate) gap can be varied to change the intensity of the shock pressure applied to the emulsion. A substance which detonates at a gap length of 70mm (which is considered to be between 3.5 and 4.5 GPa shock pressure), or more than 70mm, is not an "ammonium nitrate emulsion intermediate"

Test Detail

See figure 1 for a graphic showing the setup used.

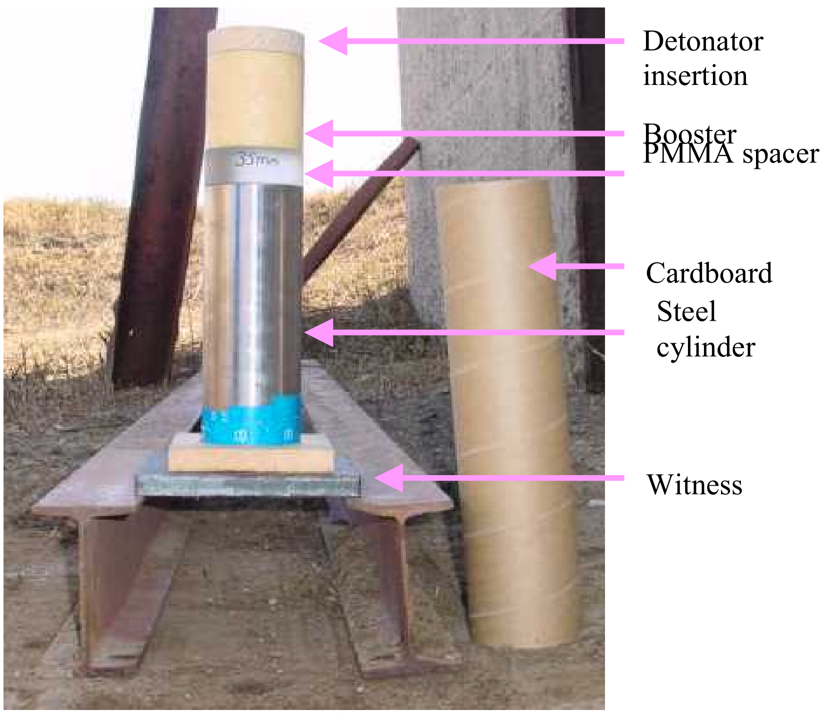

Figure 1. Setup of Test 8(b): ANE Gap Test

Results: ANE Gap Test

Substance	PMMA gap length (mm)	Result
SMX ANE1	70	-
SMX ANE2	70	-
SMX ANE1	35	-
SMX ANE2	35	-

Figure 2 Result of impact on witness plates for SMX ANE1.
The 35mm gaps' witness plate is on the left.

Assessment

The test calls for a result in triplicate with a 70mm gap without once punching a clean hole through the witness plate. The test was performed twice for each sample, once being with a 35mm PMMA gap, which represents an 79.6% higher shock impact level than with a 70mm gap. Not punching a hole through the plate with the smaller gap indicates a comfortable margin of compliance to the test criteria as an "ammonium nitrate emulsion intermediate"

8(c) Koenen Test

Test Description

This test is used to determine the effect of intense heat under high confinement.

The test consists of a drawn steel tube of predetermined specifications, fitted with a closure system, which allows the selection of variable size venting orifices. The sample is contained within the closed tube and energetically heated to decomposition with calibrated gas burners. The decomposition products escape through the venting orifice. The orifice diameter is varied to determine the largest diameter at which no “explosion” is obtained. If this diameter is less than 2.0mm (1.5 or 1.0mm) the substance is considered a candidate for Division 5.1

Test Detail

This test was not conducted by SMX R&T-Group, but was contracted to TNO Prins Mauritz Laboratory Research Group for Properties of Energetic Materials. The report is attached in Addendum 1

Results: Koenen Test

Substance	**Limiting diameter in mm**	**Result**	**Ref.**
SMX ANE1	2.0	+	
SMX ANE2	2.0	+	

Assessment

The limiting diameter for the Koenen test is 2mm. The test substances exhibit thermal explosive properties and should not be classified into Division 5.1

8(d) Vented Pipe Test

Test Description

The Vented Pipe Test is used to assess the effect of a *large* fire on a candidate for “ammonium nitrate emulsion intermediate” when it is under confined vented conditions.

A vented steel cylinder made according to material specifications is filled with the test substance. The container volume is 42litres. The container filled with the test substance is placed in an engulfing fire which should achieve a temperature of at least 800°C and burn for at least 30 minutes.

Test Detail

The observation distance was 350m, and temperatures were monitored by long lead thermocouple. One test had thermocouple failure, and the other registered 860°C. The emulsions fumed continuously. Some emulsion spluttered from the venting nipple, but remained unburned on the top of the test vessel. See fig.’s 3 and 4 for a graphics illustrating this test. The vessels were still quite full after testing. Each test emulsion was reduced to a hard crystalline mass in the vessel after the test. The % volume lost from each sample due to spluttering and any possible decomposition reactions was determined with water after the test.

Figure 3 Test vessel for Vented Pipe Test.

Figure 4 Vented Pipe Test in progress

Results: Vented Pipe Test

Substance	Sample % volume reduction	Result
SMX ANE1	26.2	-
SMX ANE2	12.8	-

Assessment

There was no explosion or any fragmentation of pipe observed in any of the tests. The test substances are not excluded from Division 5.1.

Mark Delagey
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