Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

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Explosives and related matters: test series 8

UN Manual of Test and Criteria – Test series 8 review

Transmitted by the Australian Explosives Industry and Safety Group Inc. (AEISG)

Background

1. Ammonium Nitrate Emulsions, suspensions or gels, as an intermediate for blasting explosives (ANEs), had been manufactured, transported, stored and used for approximately 20 years prior to the introduction of a specific entry in the Recommendations on the Transport of Dangerous Goods Model Regulations (i.e. the UN Orange Book). These materials were treated in a number of different ways around the world, ranging from Class 1 materials through to unregulated products, and it was appropriate that some guidance be provided for safe, consistent transport and handling.

2. In Australia, where large quantities were used, they were previously handled under the NOS entries in Class 5.1, UN3139 and UN1479, depending on their physical characteristics. To ensure these ANEs were not Class 1 products, they were subjected to satisfactory testing using the UN Test Series 2 as detailed in the Recommendations on the Transport of Dangerous Goods Manual of Tests and Criteria (MTC).

3. These products have been transported in places around the world in very large quantities for well over 30 years now and continue to enjoy an excellent transport safety record.

4. During the twenty-first session of the Committee of Experts on the Transport of Dangerous Goods, December 2000, it was decided to create a new entry for Ammonium Nitrate Emulsions, suspensions or gels, intermediate for blasting explosives (ANEs), in 5.1 (UN No. 3375).

5. It was further decided to have a working group meeting during the spring of 2001 to discuss and give suggestions for suitable test methods to be used when assigning substances to this new entry. Such tests would become Test Series 8.

6. The working group established a number of tests addressing thermal stability, shock sensitivity and response to heating under confinement, such that it could be assured these materials were not Class 1 materials and that, given their handling in bulk, they were suitable for safe transport in tanks as UN3375.

7. The resultant series of tests proposed did not achieve agreement by consensus within the working group, but on a majority view it was considered the tests could be put forward to the Committee of Experts for further evaluation.

8. The specific entry for ANEs, UN3375, with defined formulation restrictions outlined in Special Provision (SP) 309, and its associated Test Series 8, have now been in use for 10 years and it is not unreasonable for the testing arrangements to be reviewed using the experience gained in that time.

9. Test Series 8 from the UN Manual of Tests and Criteria includes four (4) test types, three for classification purposes and one for portable tank transport suitability, and these are considered separately.

Test 8(a) Thermal Stability Test

9. This test method is intended for measuring the thermal stability of ANEs. These substances are restrictively defined in SP309 as:

> '*This entry applies to non sensitised emulsions, suspensions and gels consisting primarily of ammonium nitrate and fuel, intended to produce a Type E blasting explosive only after further processing prior to use.*
>
> *The mixture for emulsions typically has the following composition: 60 – 80% ammonium nitrate; 5 – 30% water; 2 – 8% fuel; 0.5 – 4% emulsifier agent; 0 – 10% soluble flame suppressants and trace additives. Other inorganic nitrate salts may replace part of the ammonium nitrate.*
>
> *The mixture for suspensions and gels typically has the following composition: 60 – 80% ammonium nitrate; 0 – 5% sodium or potassium perchlorate; 0 – 17% hexamine nitrate or monomethylamine*
>
> *nitrate; 5 – 30% water; 2 – 15% fuel; 0.5 – 4% thickening agent; 0 – 10% soluble flame suppressants and trace additives. Other inorganic nitrate salts may replace part of the ammonium nitrate.*

10. The substances specified within these formulations, and the emulsions, suspensions and gels resulting from the manufacturing processes, are thermally stable materials and do not possess the thermal instability of self reactive substances. Any such problems would have been identified over the past 30 years of manufacture, transport and storage in some high temperature environments. Further, the test data gathered over many years since the introduction of this test has confirmed this, with all tested products passing satisfactorily as expected.

11. It is considered that this test is inappropriate and unnecessary for this range of products included under UN3375 and that its continued inclusion be reviewed.

Test 8(b) ANE Gap Test

12. This test is to measure the sensitivity of a candidate for UN3375 to a specified shock level, i.e. a specified donor charge and gap.

13. A product which fails this test then moves to Class 1 as UN0241 (Hazard Division 1.1) or UN0332 (Hazard Division 1.5).

14. When originally proposed for the Series 8 tests, the shock test was a cap sensitivity test using a standard detonator, similar to that used in Test Series 5. The shock sensitivity was later (correctly) amended to employ a larger donor charge. However, in employing a donor charge of some 1Kg of pressed Pentolite or RDX/Wax, an inconsistency was established in shock sensitivity criteria for exclusion from Class 1.

15. The UN Manual of Tests and Criteria clearly states that Series 2 tests are used to answer the question ‘Is the substance too insensitive for inclusion in Class 1?’. Contained within Series 2 tests is the relevant shock sensitivity test Type 2(a) – UN Gap Test.

16. It would appear now that there are conflicting shock sensitivity tests for determining if substances are ‘too insensitive for inclusion in Class 1’

- For substances other than ANEs in UN3375, the Series 2, Type 2(a) – UN Gap Test,
- For substances considered for UN3375, the Series 8, Type 8(b) – ANE Gap Test

each with different donor charges and gaps.

17. The possibility arises, of course, that materials may fail the Type 8(b) gap test but satisfactorily pass the Type 2(a) gap test. The process would force such products into Class 1, despite satisfactorily passing the Series 2 tests.

18. The UN Series 2 tests had been the basis on which ANEs had been safely transported for more than 15 years prior to the introduction of UN3375, and which had continued for almost 10 years after its introduction, with these materials transported under the Class 5.1 NOS entries UN1479 and UN3139. Test Type 2(a) – UN Gap Test has also demonstrated that it can readily distinguish between sensitised and non sensitised ANEs.

19. It is considered, for logical consistency, that the Series 2 Type 2(a) – UN Gap Test could/should have been adopted for the required shock sensitivity test necessary for classifying materials for inclusion in UN3375, ie to distinguish between Class 1 and Class 5.1 materials. Indeed, to assess the effect of intense heat under high confinement, a direct grab of the Koenen Test from Test Series 2 was logically adopted.

20. Hence, the Series 8 Type 8(b) – ANE Gap Test is considered inappropriate, inconsistent and unnecessary. If Test Series 8 was non-existent, the Series 2 Type 2(a) – UN Gap Test would remain to determine if the relevant ANEs, considered for inclusion in UN3375, were indeed ‘too insensitive for inclusion in Class 1’.

21. A review of the appropriate Gap Test for these ANEs is considered warranted.

Test 8(c) Koenen Test

22. This test method is intended to determine the sensitiveness of a material to the effect of intense heat under high confinement.

23. It is, in fact, a direct copy of Series 2 Type 2(b) – Koenen Test, and it was selected, appropriately, because of the logic that the UN Series 2 tests are those that establish the criteria for determining whether materials are too insensitive for inclusion in Class 1.

24. If Test Series 8 was non-existent, the Series 2 Type 2(b) – Koenen Test would remain to determine if the relevant ANEs, considered for inclusion in UN3375, were indeed ‘too insensitive for inclusion in Class 1’.

Classification Summary

25. It is only these three tests , Types 8(a), (b) and (c), that are used for classification purposes, ie to determine if ANEs are sufficiently insensitive to allow inclusion in UN3375 as Class 5.1.

Type 8(a) Thermal Stability Test – considered inappropriate, unnecessary and of little use/benefit;

Type 8(b) ANE Gap Test – considered excessive, inconsistent, difficult to source specified test materials and illogical given the specific intent of Test Series 2;

Type 8(c) Koenen Test – a direct copy of Test Type 2(b) Koenen Test.

26. The relevant costs and safety of undertaking additional testing must always be considered, alongside the benefits obtained. Under these circumstances it is considered that Test Series 8 serves little additional benefit for classification of ANEs considered for inclusion in UN3375 (already restrictively defined in SP309 and otherwise subject to UN Test Series 2 tests) and warrants review of its ongoing application.

It is proposed that Test Series 8, for classification purposes, be reviewed and re-evaluated.

Test 8(d) Vented Pipe Tests

27. This test is not intended as part of the classification process but rather to determine the suitability of an ANE in UN3375, or an explosive in UN0332, for transport in bulk in tanks.

28. Firstly, the logic of considerations here need to be openly discussed. The intent, surely, is not to eliminate any possibility of explosion during the transport of ANEs, or indeed blasting explosives.

29. It is well accepted that modern water-based commercial explosives are intrinsically much less sensitive than traditional products such as dynamites or black powder (explosives of Classification Code 1.1D). However, it is considered perfectly acceptable to transport large tonnages (15 tonnes or more) of explosives of Classification Code 1.1D, inside a steel freight container, on public roads, albeit with proper identification as explosives and the relevant safety precautions that necessarily ensue.

30. Why then are there additional tests required for transporting a far less sensitive explosive (1.5D), or indeed a non-explosive (UN3375, Class 5.1), in bulk in steel tanks? Even if a tanker load of ANE of UN3375 was to be involved in a fire scenario, would not the appropriate emergency response still be to consider evacuation of the incident site? Satisfactory UN testing results do not come with 100% confidence levels.

31. The purpose of this test is to assess the effect of exposure of a product included in UN3375 to a large fire under confined, vented conditions.

32. With good intent, industry and testing organisations have carried out much costly testing of ANEs of varying types, with numerous problems/difficulties arising, including

- Safety for those conducting/monitoring the tests (more dangerous than the risk posed in
- Transport);
- Access to appropriate locations to conduct such large scale testing;
- Environmental considerations, with generation of significant NOx fumes;
- Learnings that sensitising ANEs may indeed assist test results;
- Conflicting/inconsistent results;
- Tests conducted under different fire conditions;
- Varying competent authority requirements, eg testing to be carried out on each and every product formulation, same product formulations from different plants, same product formulations with different source ingredients;

- Growing use of the UN Manual of Tests and Criteria as a standard, rather than a guide.

33. It has been documented by a number of parties that the test, as specified, is not indicative of any credible ANE transport tank scenario and therefore establishes excessive test criteria and/or serves little purpose (UN/SCETD/21/INF.69).

34. Accidental initiations of these materials are all thermal in origin, and two broad categories can be defined. When the temperature of a sizable mass of product is globally elevated above a critical value, a runaway decomposition reaction may result. This is usually termed 'thermal explosion (or cook-off)'. A different scenario results when mechanical or thermal energy is deposited locally into the product. In this case, a localized high temperature region, usually called 'hot spot', results. Depending on the size and the heat flux delivered by this hot spot, and on the initial physical conditions, initiation of a combustion reaction may result at the hot spot/material interface. The latter may propagate into a deflagration and even into a detonation, depending on the pressure and confinement conditions.

35. It has been found that, at atmospheric pressure, such local ignitions do not lead to self-sustained reactions in water-based explosives. This is because the initial stage of combustion is endothermic and, therefore, not self-propagating. Thus, for all water-based explosives, there is a minimum pressure required for combustion to take place. The latter is usually referred to as the 'Minimum Burning Pressure (MBP)' of the explosive. Below this pressure, the explosive cannot sustain combustion even if ignited by a strong hot spot. It is generally agreed that tank pressure control was fundamental in minimising risk.

36. Further, it has been pointed out that tanks with wall thicknesses designed to fail at 10 bar, with venting capacity down to 2.65 bar (as specified in TP32) was unlikely to present a problem with ANEs with MBPs typically in the range of 40 to 50 bar. Failure pressure in the Vented Pipe Test is estimated to be around 86 bar.

37. The Koenen Test, applied in both Test Series 2 Type 2(b) test and Test Series 8 Type 8(c) test, is carried out to determine the sensitiveness of a material (ANE) to intense heat under high confinement. It has demonstrated over the years that it can clearly distinguish between sensitised and non sensitised ANEs as outlined in testing results to date. Further, a comparison testing on a range of ANEs, both emulsions and suspensions, using both the Koenen Test and the Vented Pipe Test show a good correlation of results (ref. UN/SCETD/23/INF.32).

38. Hence, it can reasonably be argued that the existing Koenen Test in UN Test Series 2 provides sufficient information on which to assess a product's response to heating under pressure, without need to employ the larger, costly and more dangerous Vented Pipe Test outlined in Series 8 Type 8(d).

39. Other tests are currently being examined which may provide far more useful information on individual ANEs seeking inclusion in UN3375, and are limited to safer, small scale testing.

40. In the interim, however, and until the usefulness or otherwise of other possible test methods are selected and fully evaluated , it is considered the ongoing appropriateness of Series 8 Test Type 8(d) should be reviewed/reassessed, with more reliance placed on the results of the existing UN Series 2 Type 2(b) Koenen Test, if necessary, to answer the question 'Is the substance too insensitive for inclusion in Class 1?' <u>and</u> to indicate suitability for transport in portable tanks.