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

30 June 2023

Sub-Committee of Experts on the Transport of Dangerous Goods

Sixty-second session Geneva, 3-7 July 2023 Item 2 (b) of the provisional agenda Explosives and related matters: Improvement of test series 8

Response to informal document UN/SCETDG/62/INF.10

Transmitted by the Institute of Makers of Explosives (IME)

Introduction

1. At the sixty-second session, RPMASA submitted SCETDG/62/INF.10 with the proposal for the continued use of the 8(d) test. That document was in response to official document ST/SC/AC/10/C.3/2023/16, which proposed that those ammonium nitrate emulsions (ANE) subjected to the 8(e) CanmetCERL Minimum Burning Pressure test should not be subjected to the 8(d) test.

2. In document ST/SC/AC/10/C.3/2023/16, the IME proposal of exclusion of the 8(d) test was not for all ANEs, only for those that have been subjected to and satisfied the 8(e) test.

3. All figures referred to in this document may be found in the annex hereto.

Background

4. The numerical modelling studies in informal document UN/SCETDG/58/INF.8, cited in informal document SCETDG/62/INF.10, showed that the heating rate of 24 kW/m² results in water evaporation from the ANE forming a crust of ammonium nitrate (AN) at the inner heated surface. The heating rate used was from published studies where the heat flux from a tire fire was measured from an experimental setup with a tire. Inspections of the ANEs after transport fire events have validated this phenomenon. The numerical modelling studies¹ show that increasing the heat flux to 80 kW/m² results in the AN crust starting to react (presented at CIE/IGUS 2022). This phenomenon, the decomposition of AN on exposure to intense heat, is well known, and the modeled prediction is in agreement with empirical observations.

5. In the scenario of AN solids transport, where there is no water present in the product, the reaction times seen from transport fires involving AN that have led to a mass explosion are in the range of 20 to 30 minutes from the onset of the fire.

6. To date, there has been only one ANE mass explosion event during transport, that was preceded by a fire that persisted for two hours. All other events produced no mass explosion, with the fire abating within one hour. The ANEs from these latter events were transferred out of the tanker using a pump, and the product shows no sign of heat degradation. Following testing and verification where a full load was involved the transferred product was certified for use as there was no heat damage.

¹ Presented at IGUS-CIE Conference in Huntsville, Alabama; April 24-28, 2022

Discussion

7. The Koenen Test 8(c) results are not given for the ANEs used in informal document SCETDG/62/INF.10. Prior communication indicated that ANEs 1 to 4 had negative results in the Koenen Test². Eligibility for the 8(e) test requires that the ANE fails the Koenen Test (yields positive results), has a reaction time greater than 60 seconds, and contains at least 14% water. These ANEs must then exhibit a minimum burning pressure (MBP) greater than 5.6 MPa. Therefore, the products tested in INF.10 would be ineligible for the 8(e) test route that IME proposes.

8. The test configuration and imparted heat flux presented in informal document INF.10 is very different from a typical road transport scenario and does not create the conditions of a realistic threat.

9. The test configurations used in informal document INF.10 have a similar surface area to volume ratio of the vented pipe test 8(d), and this ratio is approximately four times that of a transport tanker. The similarity in the surface area to volume ratio between the vented pipe test and the fast-heating munitions test used in informal document SCETDG/62/INF.10 ties in with the observation that both tests gave similar results, as shown in Table 2 of the paper.

10. The higher surface area to volume will mean that the heat flux into the ANE will be higher in the test configurations of the fast-heating munitions test and the vented pipe test compared to that seen in a road tanker involved in a fire.

11. In informal document UN/SCETDG/61/INF.43, it was identified that the research presented in informal document UN/SCETDG/60/INF.42 was intended to study the behaviour of an ANE in blastholes under extreme heating. The configuration used in the fastheating munitions test in SCETDG/62/INF.10 is identical to that used in informal document UN/SCETDG/60/INF.42 and is thus similar to that of a blasthole rather than a road tanker. An illustration of the 10 m steel tube compared to a road tanker is given in Figure 1.

12. The fast cook-off test setup (Figure 1 in informal document SCETDG/60/INF.42) is a long cylindrical pipe in a vertical orientation. Consequentially, the driving force for buoyant convection is several orders of magnitude larger in this experimental setup than would be seen in a tanker. This is due to the modified Rayleigh number effects. The Rayleigh number is the ratio of the characteristic buoyancy-driven convective heat transfer to thermal diffusion and is directly proportional to the length scale in the direction of gravity to the fourth order. Since the long cylindrical pipe is one order of magnitude larger than the radius of the tank modelled in the simulations, the convective heat transfer is 1x104 larger than thermal diffusion.

13. Discussions with RPMASA/AECI confirmed that the research was intended to study the behaviour of the ANE in blastholes under extreme heating. As such, the document does provide insight into the behaviour of the ANE when it is loaded in a borehole.

14. Further numerical modelling studies also used a higher heat flux than would be seen during a tire fire scenario. The results from these studies, in which a heat flux of 80 kW/m² was applied, show that the AN crust that forms from the water evaporation begins to decompose. As is well known, such a decomposition can become violent, leading to a mass explosion. At 80 kW/m² the modelling studies show that the AN crust begins to decompose.

15. The numerical modelling studies using a heat flux of 80 kW/m² showed a reaction of the AN crust beginning around 7 minutes into heating (Figure 2.). The observations made in the tests in informal document SCETDG/62/INF.10 are consistent with a very high heat flux, where equilibration of the temperature in the pipe was seen in under 10 minutes. The increased buoyancy effect and the decomposition gases created by the decomposing AN provide both forced and natural convection leading to the rapid equilibration in temperature of the ANE within the pipe, as well as within the modified pup tanker.

16. The studies in informal document SCETDG/62/INF.10 do not quantify the heat flux to the 10 m steel pipe or the modified pup tanker trailer. The steel trough used for the 10 m

² Communication from AECI with IME on November 24, 2022

steel pipe was filled with 4200 litres of fuel (paraffin). This volume is over 7 times that contained in a road tanker, which typically has a fuel tank of 570 litres capacity. Furthermore, having the ANE in a tanker exposed to this entire volume is 4200 litres is an unrealistic scenario for a road transport event.

17. The observation in paragraph 10 of informal document SCETDG/62/INF.10 that recycled oil produced a detonation points to trace or remnant product in the recycled oil that reacts adversely with AN. Since ANE5 was not tested, the observation that "the water content of the ANE does not affect the outcome of the reaction" is not supported by the results: ANE7 with 24.19% water vented compared with ANE6 with 20.45% water that detonated.

Conclusion

18. IME is grateful for RPMASA's submittal of informal document INF.10.

19. The informal document INF.10 has experiments that were carried out with ANE samples that would not be subjected to the 8(e) test, the products being addressed in document ST/SC/AC/10/C.3/2023/16.

20. Furthermore, these ineligible ANEs were also subjected to extreme heat in a configuration not seen in road transport.

21. The paper does provide insight into the behavior of an ANE in a borehole that is in hot, or hot and reactive ground, as the configuration of the fast cook-off test is closer to that of a borehole and not to a road tanker.

22. Hence this paper does not provide evidence to support maintaining the 8(d) test for ANEs described in the IME document ST/SC/AC/10/C.3/2023/16, in which the proposed exclusion of the 8(d) test applies only to ANEs that show a positive with the Koenen Test, have a reaction time greater than 60 seconds, a water content > 14%, and a minimum burning pressure of \geq 5.6MPa.





UN/SCETDG/62/INF.37



Figure 2. Numerical Modelling Results showing the advancing crust formation (blue) and start of reaction of AN (red)