Changes in Test Series 8 for AN Emulsion or Suspension or Gel (ANE)

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Summary:

ANEs by volume are the largest type of explosive intermediates used today. The UN Manual of Tests and Criteria (MTC) has Test Series 8 (TS8), which these substances must be subjected to in order to be classified as an oxidizer, Division 5.1. One of the tests in TS8, the Koenen Test 8(c), was developed in the 1950s when ANEs were not in existence. Research carried out on ANEs in this test show that the test is unsuitable for certain types of ANEs. This paper outlines the development of the Koenen test, the reasons why this test with its criteria is unsuitable for some ANEs, and the alternate test that is now in the MTC for certain ANEs.

Introduction:

Ammonium Nitrate Emulsions and Test Series 8

The earliest patent publication on ammonium nitrate emulsions was the US patent in 1969 by Harold Bluhm[1] of the Atlas Powder Company, USA. However, it was not until the 1980s that ANEs became common as an intermediate in commercial blasting explosives. Water gels had been developed earlier, in the 1940s to overcome the detrimental effects of water on ammonium nitrate-fuel oil blasting agents.

The challenge facing both regulators and industry in the 1990s was the wide variability in the product classification for emulsions and slurries which, depending on the country, could be unclassified, Class 5 (oxidizer), Class 9 (miscellaneous dangerous good) or Class 1 (explosives). Furthermore, there was no testing regime for this new class of blasting agent.

In 1999 a UN working group was convened to address this issue. The output from the UN working group was a new UN number[2] and definition for ANEs as well as a new Test Series for these substances.

ANEs, assigned as UN3375, were added into the classification flowchart for Class 1 substances (Figure 1.). The decision box identifying ANEs would need to be considered if one were to move the substance into Test Series 8.

The testing regime for ANEs is Test Series 8 in the UN Manual of Tests and Criteria. The required tests are depicted in the flowchart in Figure 2.

These three classification tests 8 (a, b, and c) were prescribed based on tests that existed for other classes of substances, and, on limited testing on ANEs. The tests aim to answer the question: Is the substance Class 5, Division 5.1 or not? Test Series 8(d) is used to determine the suitability for the transport of ANEs in tanks and is not a classification test.

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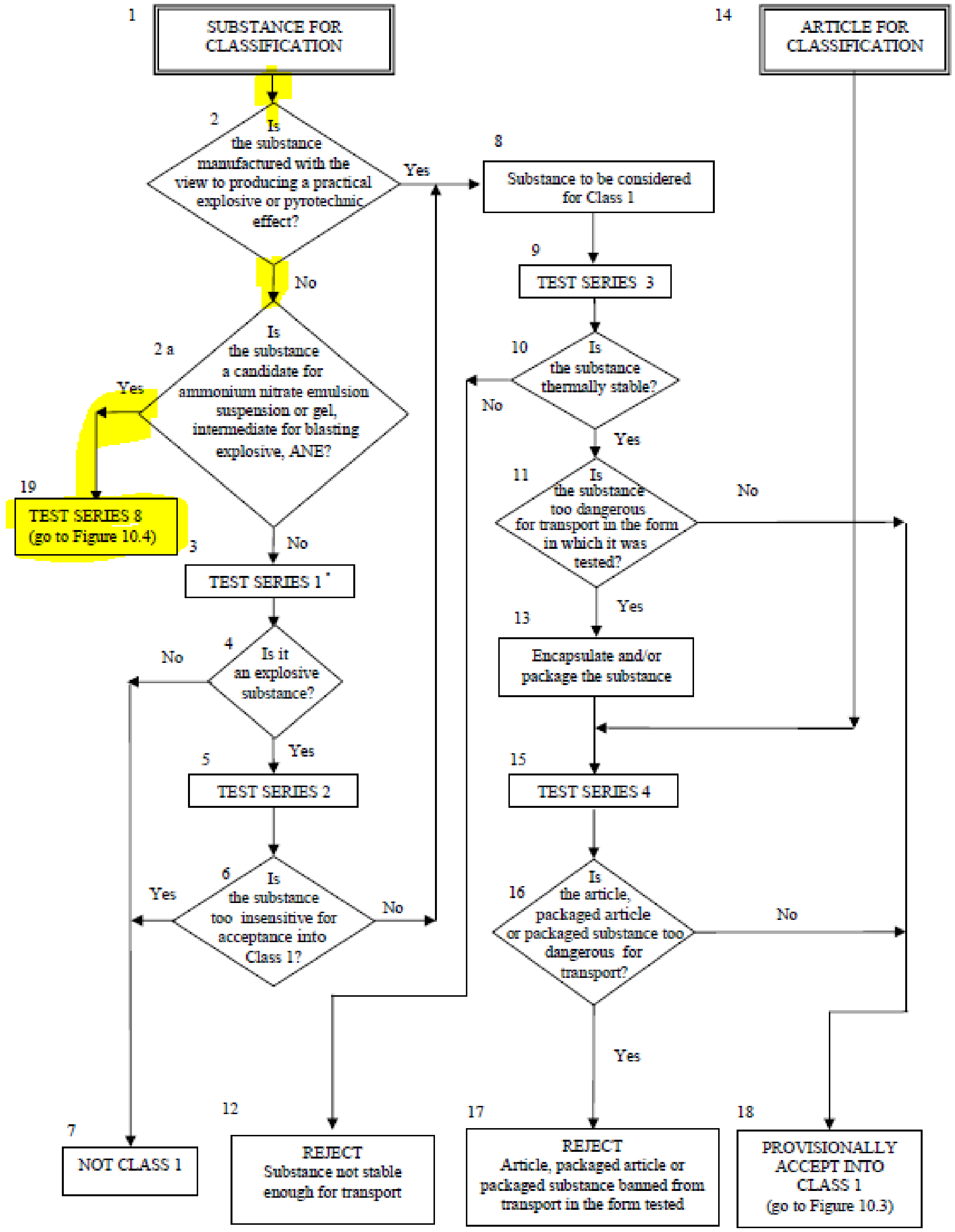
[1] US Patent 3,447,978 (1969)

[2] A four digit number that identify dangerous goods, hazardous substances and articles in the framework of international transport.

Figure 10.2: PROCEDURE FOR PROVISIONAL ACCEPTANCE OF A SUBSTANCE OR ARTICLE IN CLASS 1



* *For classification purposes, start with test series 2.*

Figure 1. Flowchart for Class 1 substances[3]

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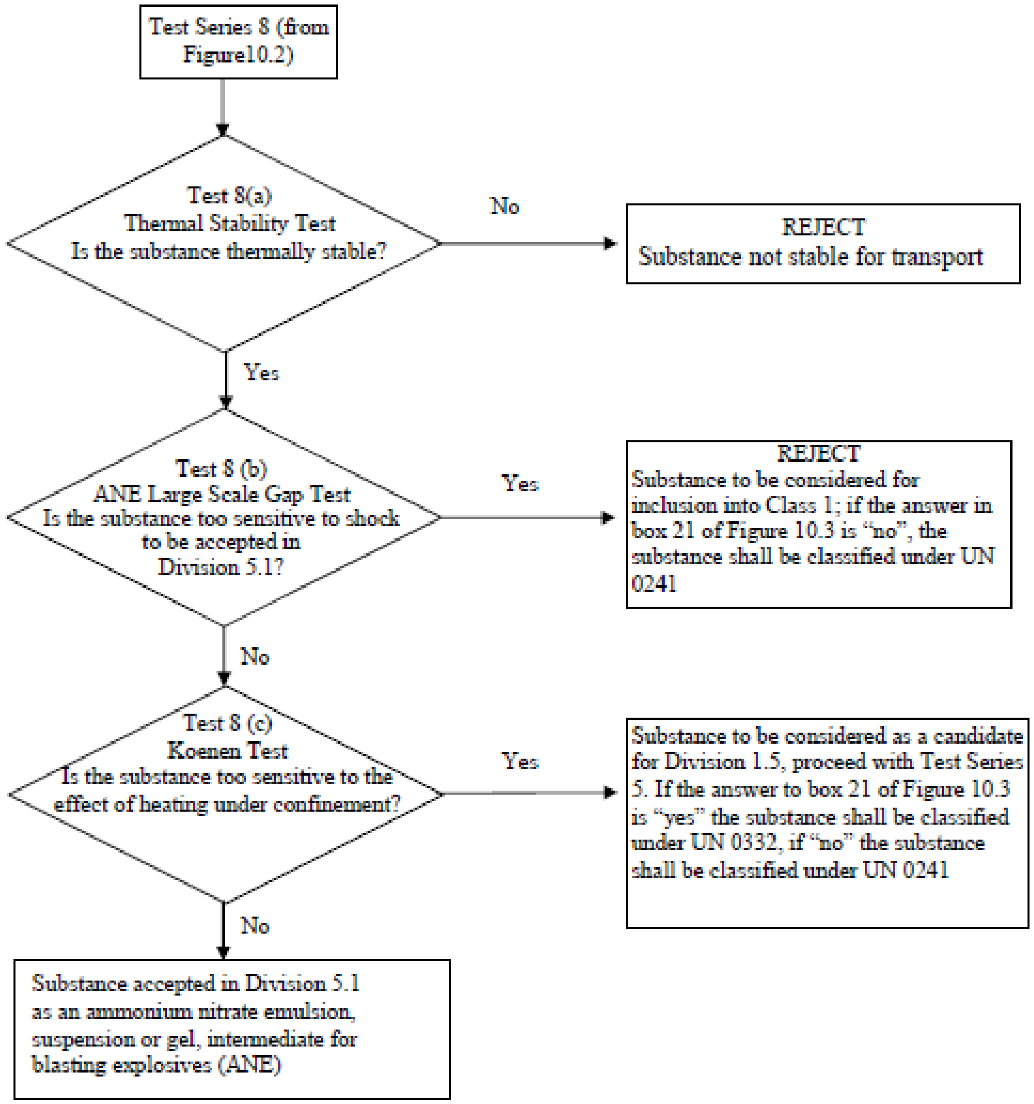
[3] UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fifth revised edition (2009)

Figure 10.4: PROCEDURE FOR AMMONIUM NITRATE EMULSION, SUSPENSION OR GEL, INTERMEDIATE FOR BLASTING EXPLOSIVES



Test Series 8 (from Figure10.2)

Test 8(a)
Thermal Stability Test
Is the substance thermally stable?

REJECT
Substance not stable for transport

Test 8 (b)
ANE Large Scale Gap Test
Is the substance too sensitive to shock to be accepted in Division 5.1?

REJECT
Substance to be considered for inclusion into Class 1; if the answer in box 21 of Figure 10.3 is “no”, the substance shall be classified under UN 0241

Test 8 (c)
Koenen Test
Is the substance too sensitive to the effect of heating under confinement?

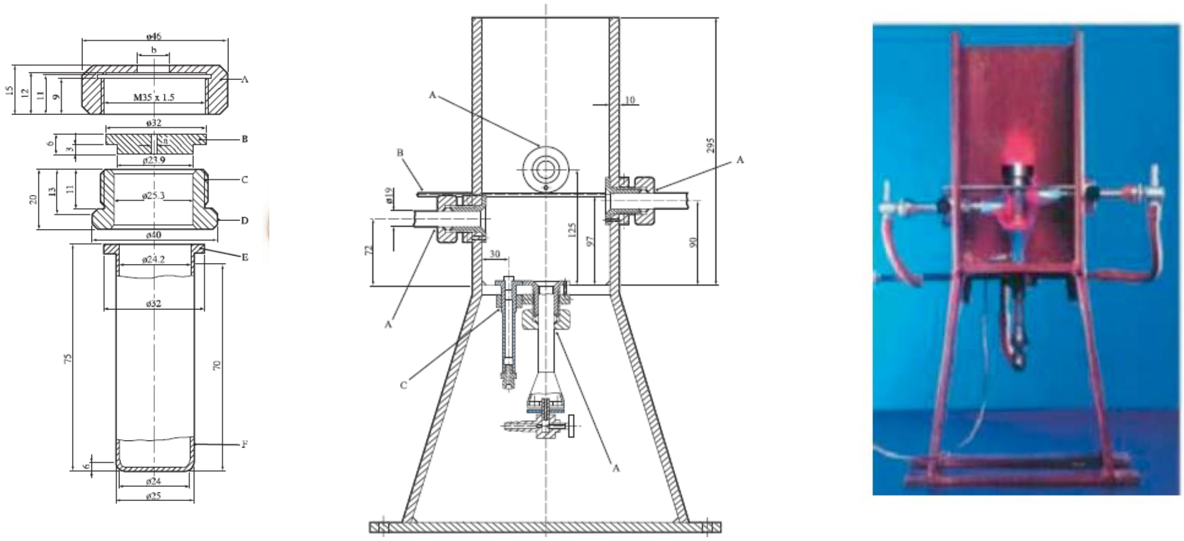
Substance to be considered as a candidate for Division 1.5, proceed with Test Series 5. If the answer to box 21 of Figure 10.3 is “yes” the substance shall be classified under UN 0332, if “no” the substance shall be classified under UN 0241

Substance accepted in Division 5.1 as an ammonium nitrate emulsion, suspension or gel, intermediate for blasting explosives (ANE)

Figure 2. Test Series 8 for ANEs

Development of the Koenen Test

A comprehensive history of the development and analysis of the Koenen Test can be found in a paper published in the UN Subcommittee of Experts on the Transport of Dangerous Goods[4]. The Koenen test as used today consists of a steel tube, which is filled with the substance and heated in four directions by a gas flame (Figure 3).



(a) (b) (c)

Figure 3: Koenen Test Apparatus[5] showing the tube and assembly (a); heating assembly (b); and the test underway (c).

The test was developed by Koenen and Ide in the 1950s. Figure 4 shows the original Koenen and Ide photographs (*Abb.8* and *Abb.9*), with the effect levels assessed according to increasing levels of deformation and fragmentation. For ANEs the limiting diameter is set to 2 mm. The substance is considered to pass or fail the test depending on the fragmentation pattern of the tube at this diameter. In Figure 4, the tube and fragments as shown in A to E will be considered a “pass”, while F and G are considered “Fails”. Figure 5 shows examples of tube deformation and fragmentation patterns in the UN Manual of Tests and Criteria Revision 6 (MTC6).

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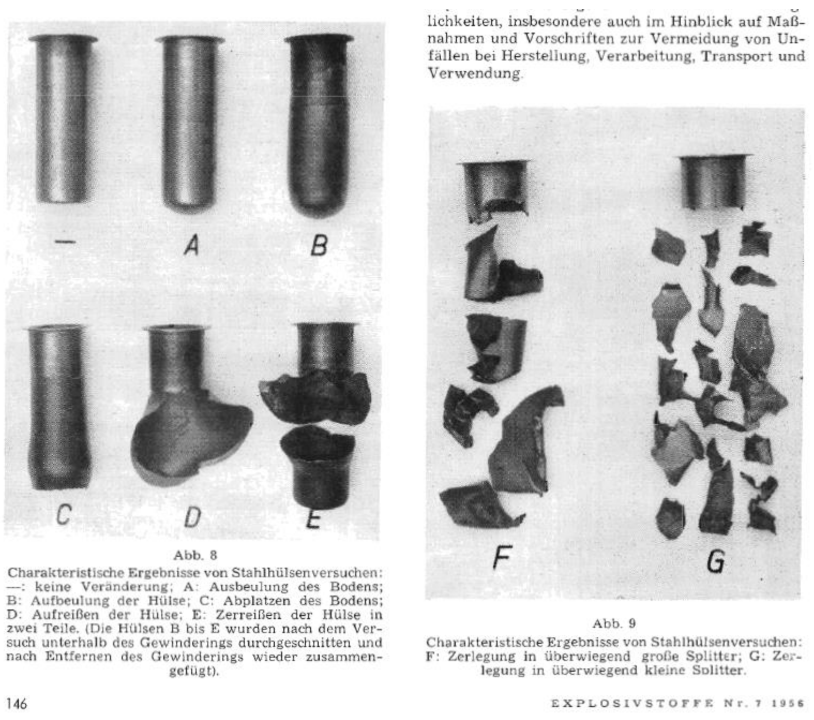
[4] http://www.unece.org/fileadmin/DAM/trans/doc/2011/dgac10c3/UN-SCETDG-39-INF.53e.pdf. The principal elements are presented in this SAFEX paper and the interested reader is encouraged to refer to the UN paper.

[5] Recommendations of the Transport of Dangerous Goods, Manual of Tests and Criteria, Sixth Revised edition, UN 2015



lichkeiten, insbesondere auch im Hinblick auf Maßnahmen und Vorschriften zur Vermeidung von Unfällen bei Herstellung, Verarbeitung, Transport und Verwendung.

Abb. 8

Charakteristische Ergebnisse von Stahlhülsenversuchen: —: keine Veränderung; A: Ausbeulung des Bodens; B: Aufbeulung der Hülse; C: Abplatzen des Bodens; D: Aufreißen der Hülse; E: Zerreißen der Hülse in zwei Teile. (Die Hülsen B bis E wurden nach dem Versuch unterhalb des Gewinderings durchgeschnitten und nach Entfernen des Gewinderings wieder zusammengefügt).

Abb. 9

Charakteristische Ergebnisse von Stahlhülsenversuchen: F: Zerlegung in überwiegend große Splitter; G: Zerlegung in überwiegend kleine Splitter.

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EXPLOSIVSTOFFE Nr. 7 1956

Figure 4. Tube deformation and fragmentation patterns reproduced from Koenen and Ide's 1956 papers

"E": Tube split into two fragments

"F": Tube fragmented into three or more mainly large pieces which in some cases may be connected with each other by a narrow strip;

Figure 5. Examples of tube deformation and fragments in MTC6.

Limitations of Koenen Test

Fragmentation of the tube is the sole criterion of this test and is a proxy for the reactivity of the substance being tested. However, a comparison test results can only be made when the bursting pressure of the tube is roughly constant, and the effect being evaluated is that of the behavior of the substance.

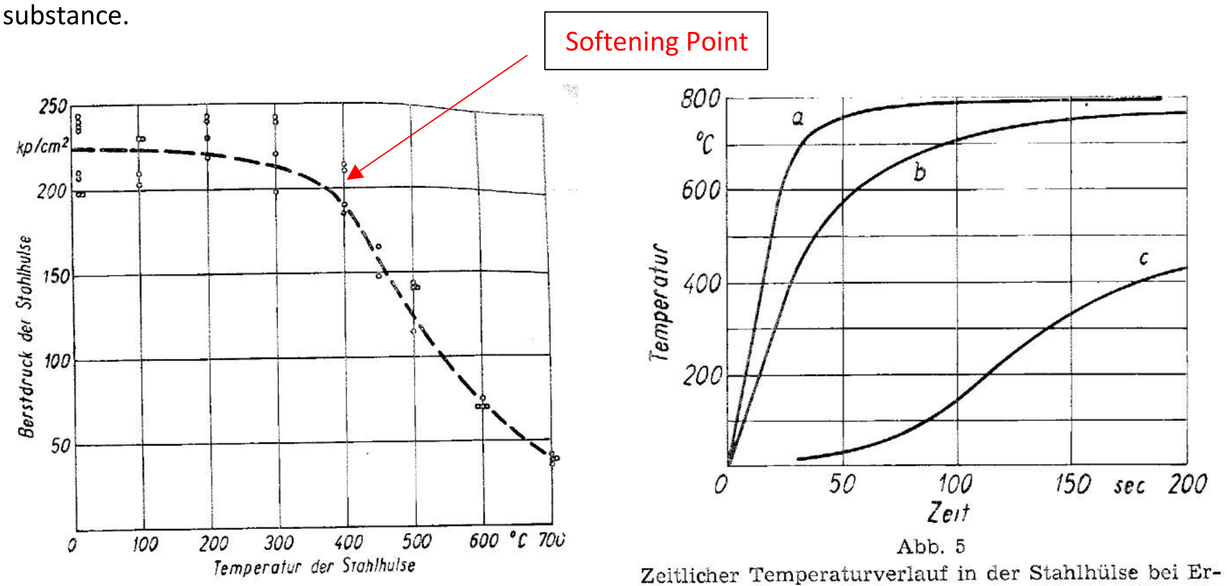

Abb. 7
Berstdruck der Stahlhülse 25 Ø × 0,5 × 75 mm in Abhängigkeit von ihrer Temperatur.

Abb. 5
Zeitlicher Temperaturverlauf in der Stahlhülse bei Erhitzung mit vier Gasbrennern im Schutzkasten, gemessen mit Thermoelement: a) und b) Temperatur am Boden der Hülse; a) ohne, b) mit Sandfüllung; c) Temperatur 25 mm über dem Boden in Sandfüllung.

Figure 6. Calibration data reproduced from Koenen and Ide's paper. (LHS) Bursting pressure versus temperature. (RHS) Temperature versus time.

The two calibration charts in Figure 6 shown that the burst pressure is relatively constant up to about 400°C (LHS chart). Using the RHS chart and reading off a temperature up to 400oC would give a usable time of approximately 25 seconds. Beyond that time, the tube is at its softening point and further temperature rise will drop its burst pressure precipitously. Thus, any test run where the time of reaction exceeds 25 seconds no longer becomes one in which the reactivity of the substance alone is being tested but is influenced by the strength of the containing tube.

ANEs did not exist when Koenen and Ide developed their test. Substances tested were molecular explosives that had reaction times in the tube in seconds – 1 to 15. In contrast, ANEs, which are relatively inert compared to the molecular explosives evaluated in the 1950s take significantly longer to react.

The chart in Figure 7 shows various substances tested over the years, including those by Koenen and Ide in the development of the test. Most of the ANEs take significantly longer than 25 seconds to react, with times from 100 to over 300 seconds observed. Since the criterion of pass/fail is based on the fracture pattern of the tube, samples where there were fractures and fragments beyond the 25 seconds were seen as false positives (fail) since the tube no longer had the burst pressure intended for testing.

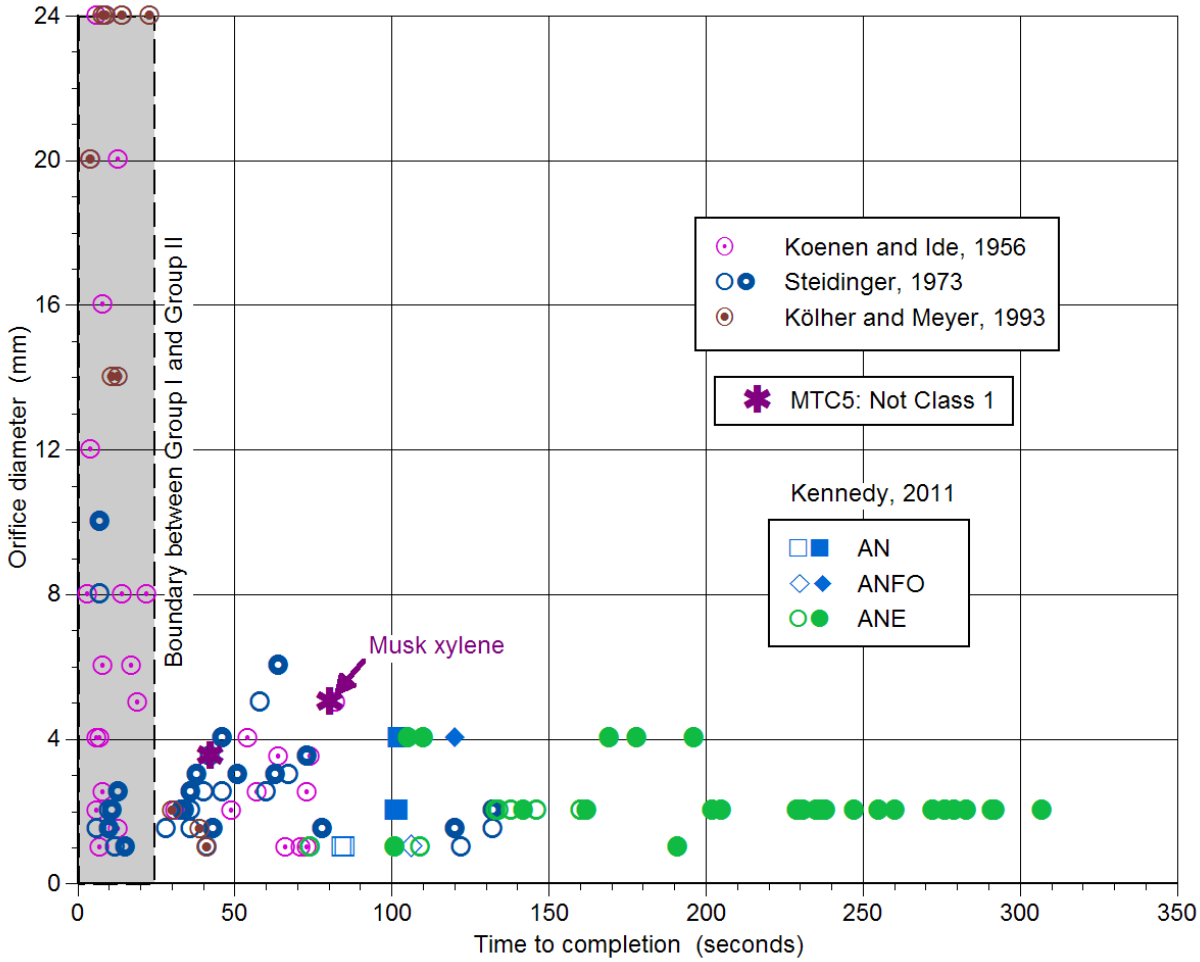

Figure 7. Orifice diameters versus times to completion in the Koenen test. (Open symbols refer to tests that terminated in tube rupture, while closed symbols refer to tests where the tube did not rupture.)

Proposals were made to limit the test time and to consider a larger limiting diameter to compensate for the tube ‘softening’ but these were not accepted by the UN Explosives Working Group. Note that in MTC6, under the procedure, it reads “the time to reaction and duration of reaction can provide additional information useful in interpreting the results”. However, this advice was ignored in setting the test criteria.

Parametric Analysis of Test Series 8 and ANE Bulk Transport Containers

The 8d test, or the Vented Pipe Test (VPT) is not a classification test but is used to determine if the substance is suitable for carriage in portable tanks. The VPT is in effect a larger scale Koenen Test, and therefore is subject to the same limitation, namely, that prolonged heating compromises the structural integrity and leads to false positives (fail). Orica, through the Australian Industry Explosives Safety Group

(AEISG) published a parametric analysis of TS8 and ANE bulk containers[6], a summary of which is given below.

The study was to determine the heat flux and burst pressures of the Koenen and Vented Pipe Tests and to compare these to typical tanks used in road transport.

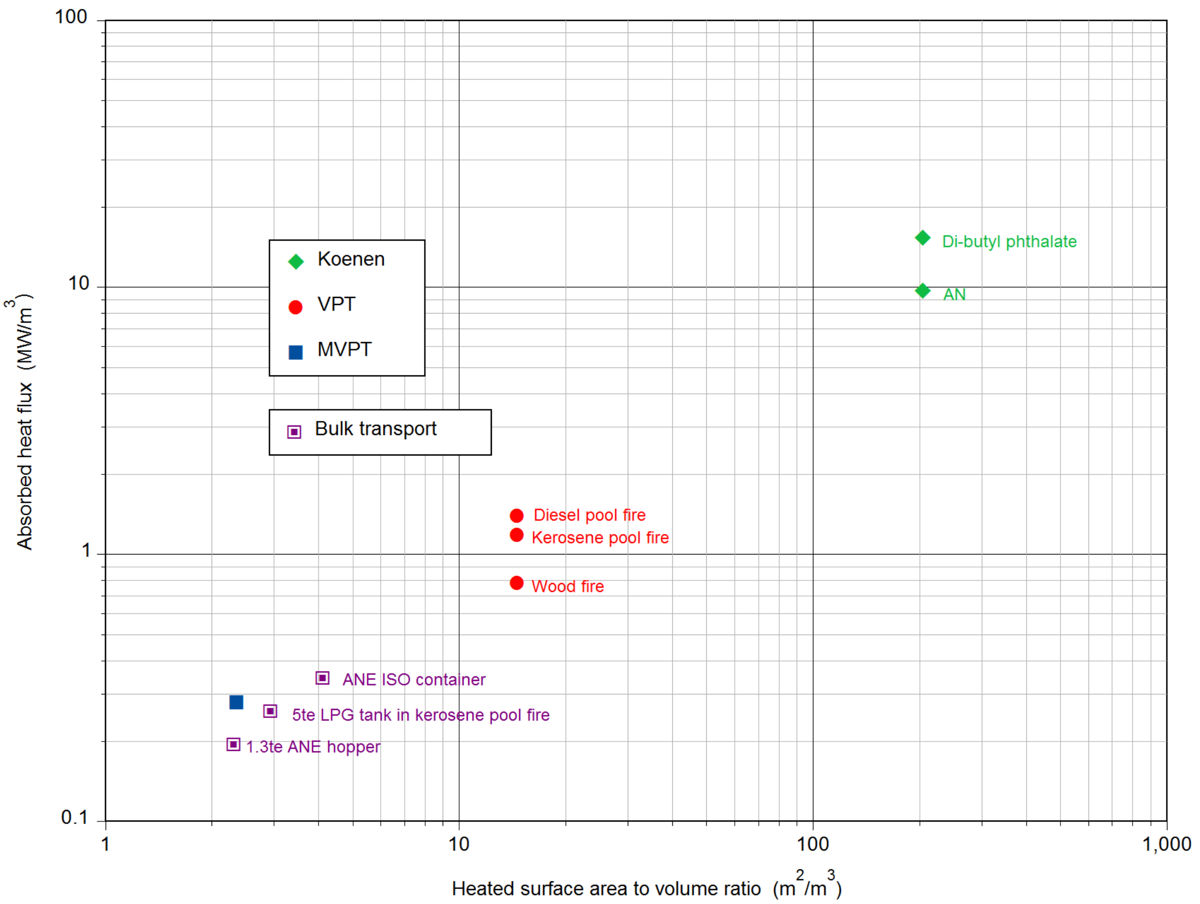

Figure 8. Heat Flux versus Heated Surface Area: Volume for TS8 and bulk transport.

A comparison of the estimated absorbed heat flux versus heated surface area to volume (S:V) ratio for the Test Series 8 vessels and for various forms of bulk transport is shown in Figure 8. The various data sets on this chart are as follows:

(i) The two data points for the Koenen test were calculated from the measured heating rates and the known heat capacities for di-butyl phthalate and for powdered ammonium nitrate (AN) – the lower estimated absorbed heat flux of the latter is likely due to the poorer thermal conductivity across the interface between the vessel wall and a powdered solid than with a liquid.

(ii) The MVPT point was calculated from the measured heating rate during calibration and the known heat capacity of water.

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[6] UN/SCETDG/49/INF.60

(iii) The data for the VPT under three different types of fuel were estimated from comparisons of the observed reaction times of whatever ANE samples were common to these variants of the VPT and to the calibrated MVPT and their respective S:V ratios.

(iv) The 5te LPG tank datum point was derived from the measured heat flux published by K. Moodie et al[7].

(v) The two data points for the 1.3te ANE hopper and the ANE ISO container have been estimated from the 5te LPG tank point based on the respective heat capacities of LPG and ANE and the respective S:V ratios of the containers.

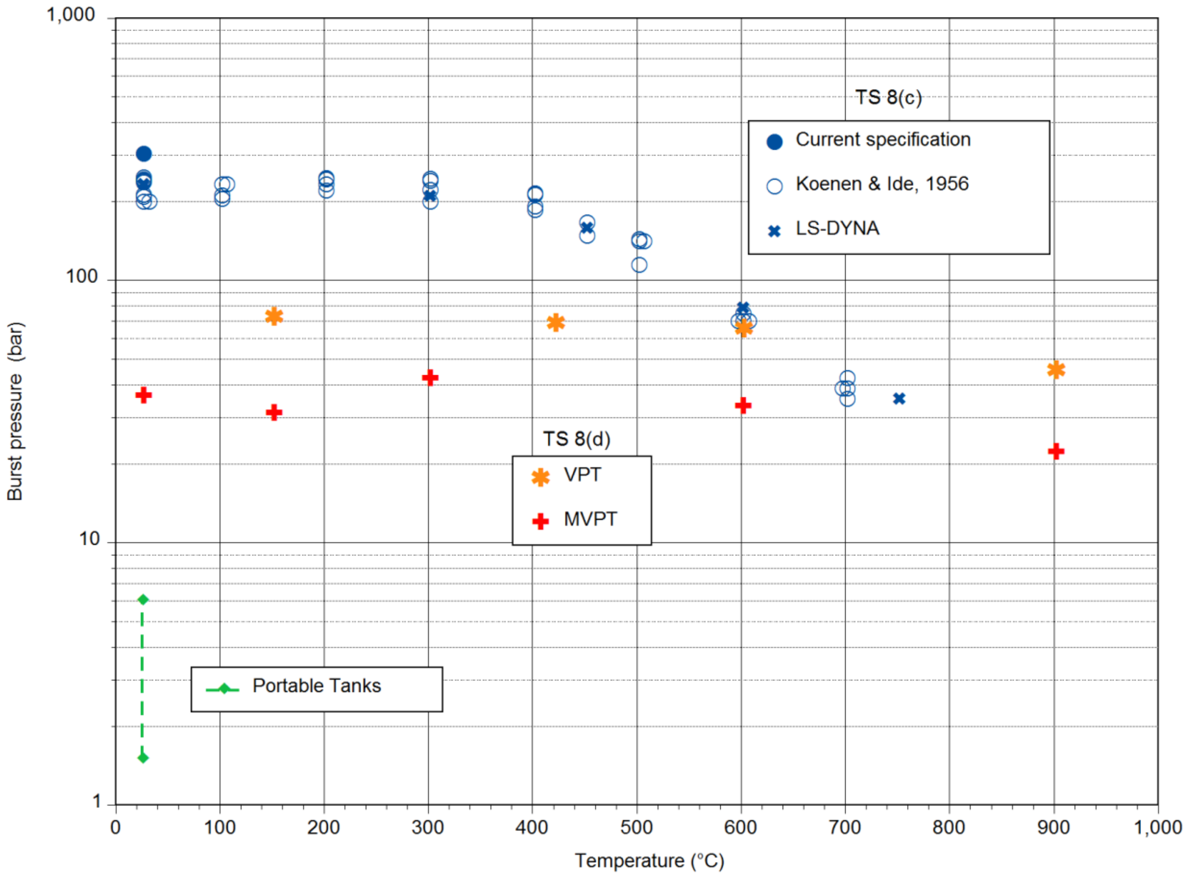

Figure 9. Burst Pressures for TS8 Vessels and Bulk Transport Containers

The current specification of the burst pressure of the Koenen tube is 30 ± 3 MPa (300 ± 30 bar) and it refers to its strength at ambient temperature. Figure 9 shows measurements by Koenen and Ide who examined the variation of burst pressure with temperature for the original vessels manufactured from corrosion-resistant steel. Also shown are burst pressures predicted by the finite element hydrocode LS-DYNA based on the variation of yield strength with temperature for this type of steel. The burst pressures for the VPT and MVPT vessels have been predicted by LS-DYNA again based on the variation of yield strength with temperature for their type of steel.

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[7] Fire engulfment tests on a 5 tonne LPG tank", J. Haz. Mat. 20 (1988) pp 55-71

For comparison of the Koenen Test tubes to burst pressures for transport tanks, an indication is given of the range of burst pressures expected for these tanks prior to fire exposure. These tank pressures vary from the minimum burst pressure specified for T1/T2 Portable Tanks to 50% higher than the minimum burst pressure specified for T9/T10 Portable Tanks.

One expects testing regime to be conservative with respect to possible scenarios encountered during transport. It is observed from the chart in Figure 9 however, that there is at least one order of magnitude difference from the Koenen Test steel to that used in transport.

Minimum Burning Pressure Test

The research carried out by Orica shows that the Koenen Test is unsuitable for certain types of ANEs – those that have a very long reaction time – and hence the question arose as to what would be a suitable alternative test for these types of ANEs. The industry uses the minimum burning pressure (MBP) test to determine suitability of ANEs for pumping, and it was decided to advocate the use of the MBP test for those ANEs that fail the Koenen Test.

The minimum burning pressure is an intrinsic property of an energetic material. At pressures below the MBP a substance cannot sustain burning regardless of the mass and amount of energy used to ignite it. The substance must therefore be at, or higher than, its MBP for an explosion to propagate. In 2015 the expert from Canada submitted a paper to the UN[8] on the MBP test, where the test procedure is described in detail, and the test is also proposed as an alternate to the Koenen and Vented Pipe Tests. Canada (Canadian Explosives Research Labs) was one of the developers of the MBP test and presently uses it for classification of ANEs.

The principle of the MBP test is that the substance, contained in a cell, has a nichrome wire that runs through the center of the cell (Figure 10). This apparatus is held in a pressure vessel where the initial pressure within this vessel can be varied. Power is turned on to heat the wire and the substance and the pressure at which there is full combustion of the sample is taken as its MBP.

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[8] https://www.unece.org/fileadmin/DAM/trans/doc/2015/dgac10c3/ST-SG-AC.10-C.3-2015-41e.pdf

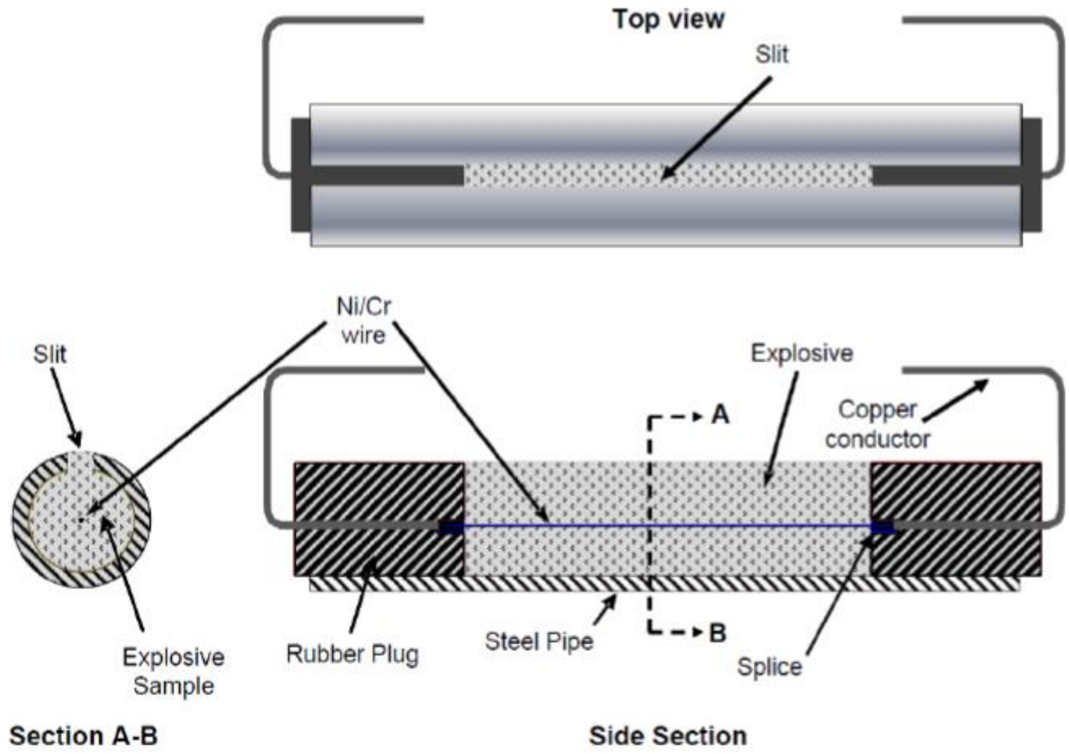

Figure 10. Test Cell for CERL MBP test

Once the power is turned on the pressure in the vessel is monitored. If the sample burns completely the result is deemed to be a ‘go’. The pressure is decreased if that is the result. If the sample does not burn the result is deemed to be a ‘no-go’ and the next test will be carried out at a slightly higher pressure.

Examples of go/no-go pressure traces and the resulting samples observed in the test cell are shown in Figures 11 and 12, respectively.

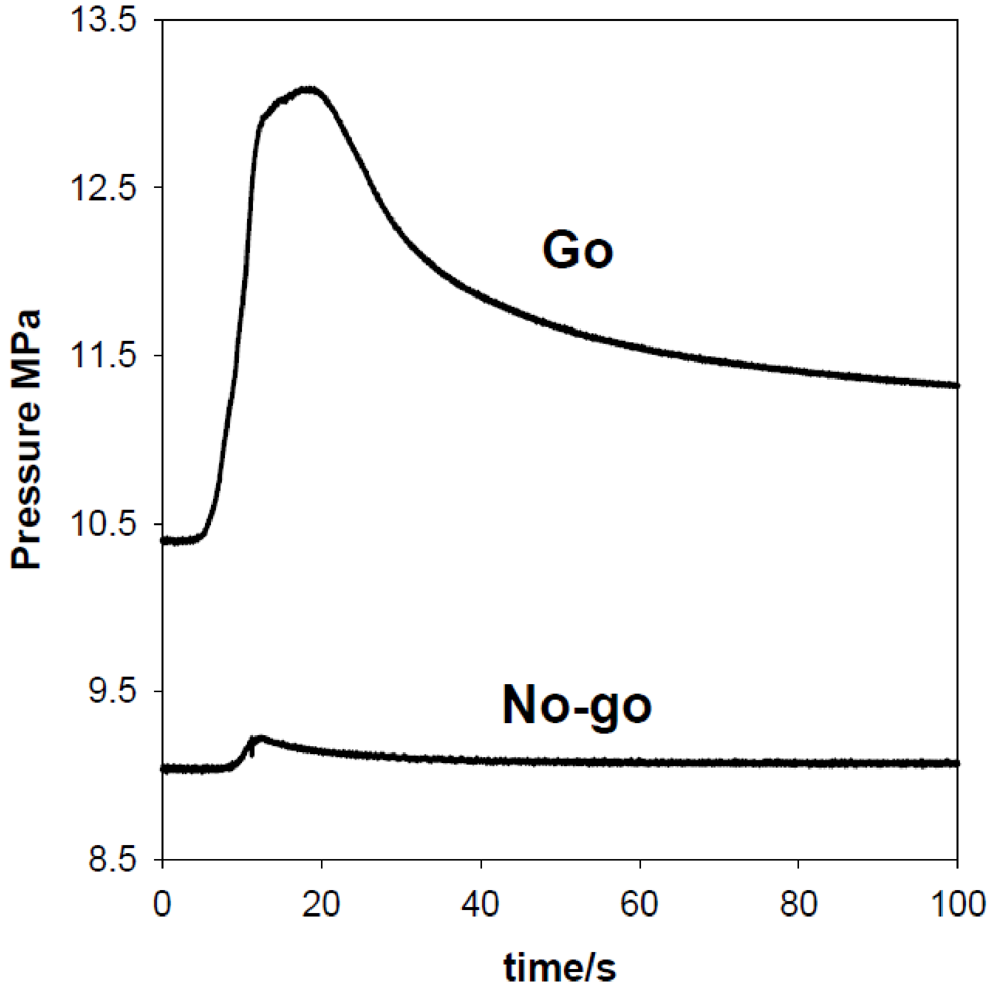

Figure 11. Pressure traces for Go and No-go results

Figure 12. Typical sample results after a Go and No-go result

UN Test Serie 8 – Revised

In December 2018 the UN Subcommittee of Experts on the Transport of Dangerous Goods voted to include the MBP test as an alternate to the 8(c) Koenen Test. This conclusion followed several discussions at the UN Explosives Working Group based on formal and informal papers submitted by the Australian Explosives Industry Safety Group, the Institute of Makers of Explosives and the Expert from Canada.

The new flowchart, which will be published in the 7th Revision of the UN Manual of Tests and Criteria will have the MBP test as 8(e), and will be a permitted test for an ANE candidate if it fails the Koenen test, has more than 15% water, and has a time of reaction greater than 60 seconds. The criterion for the 8(e) test is that the MBP of the ANEs must be equal to or greater than 5.6MPa to be considered as an oxidizing liquid. The revised flowchart is shown in Figure 13, where test 8(e) is added with the required parameters as new boxes and the modified flow.

Figure 10.4: PROCEDURE FOR AMMONIUM NITRATE EMULSION, SUSPENSION OR GEL, INTERMEDIATE FOR BLASTING EXPLOSIVES

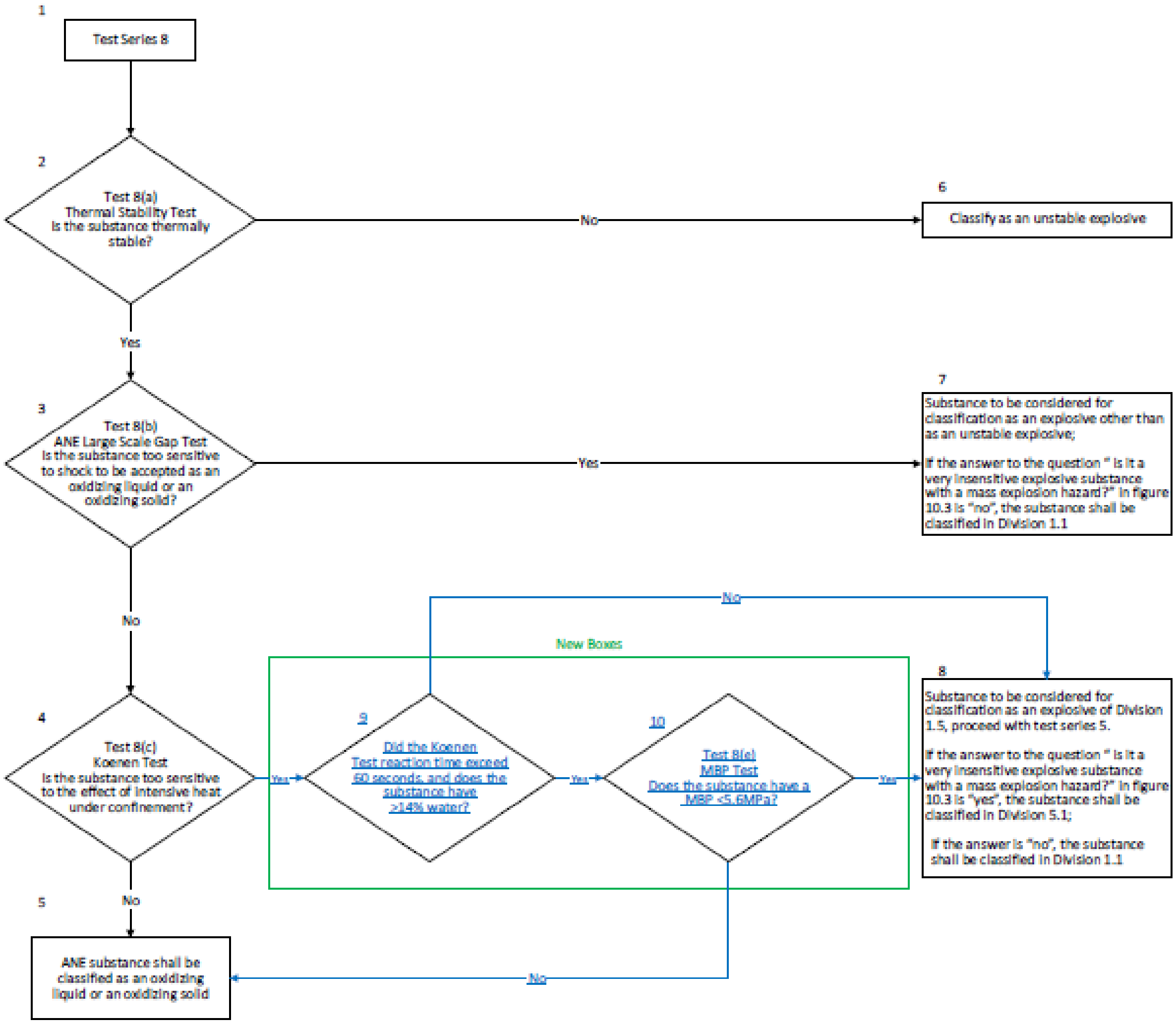

Figure 13. Revised Flowchart in UNMTC Figure 10.4 for ANEs

Concluding Remarks

Since its development in the 1950s the Koenen Test has been proven useful for establishing the behavior of substances under heating and confinement. This test has been shown to have limitations for certain ANEs, especially those with a high (>14%) water content. The revised Test Series 8 takes into consideration the properties of ANEs, a substance not in existence at the time the Koenen Test was developed.

ANEs have been manufactured and transported for over three decades. Although there are accidental explosions with ANEs, there is sufficient doubt as to whether these substances actually caused the explosions, or in one case as to whether it is a bona fide UN3375 substance. Their relatively inert behavior is largely attributed to their high water content.

Since the Vented Pipe Test is in practical terms a larger scale Koenen Test, high-water ANEs will also show false negatives. Discussions are underway at the UN Explosives Working Group to consider removal of the VPT for ANE samples that go through the MBP test, since unlike the Koenen Test, where there could be an effect of scale, MBP, an intrinsic property of the substance is scale invariant.

Acknowledgements

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