ANE Working Group Geneva July 2002.

Report of meeting.

Participants.

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Documents: 2002/22, INF 10, 13, 16, 18, 20, 22, 23, 59, 60, 61, WP1 (Canada) WP2 (Japan), WP3 (Australia), WP4 (USA)

Agenda Item 1

Vented Pipe Test (VPT). Reliable test (larger scale that Koenen and TST).

INF 16 (Swe)

Conclusions from Scandinavian tests:

- The time lapse from ignition to explosion was between 30-50 minutes. (Only 18 min. for the oil fire)
- With a nozzle opening of 3” all ANEs seem to explode/detonate, while with larger openings none of the emulsions seem to explode/detonate.
- Kimit AB, Forcit OY and Dyno Nobel ASA cannot recommend the proposed classification method “Test 8(d): USA vented pipe test” as a way of classing ANE matrixes.

Scandinavian group also concluded that aluminium tanks are liable to break open and relieve pressure

INF 18, RSA. Took 15.8% water ANE and did UN tests. Found formulations that passed VPT and failed Koenen tests. Feel that tests are not reliable or predictable.

DNE: experience over several years that Koenen test is very susceptible to minor variations and it is imperative to ensure that the precise UN specifications must be followed. The heat source will significantly affect the results. Early tests were failing some materials and when they rigorously standardised conditions to UN, all materials passed.

BAM: the Koenen test is very old (40 years). BAM standardises the steel in the shells for tests. Germany could make the specification available for inclusion in the MTC.

SASOL concludes that many years of experience show that ANE is acceptably safe in transport and the tests are not reliable. Their preference was to use the wealth of experience accumulated over many years of safe carriage to classify the materials.

Canada: feels that the materials are used with very little modification to make Class 1 and a test is needed to differentiate them from explosives.

DNE: there is a discriminatory test: The gap test clearly distinguishes between ANE and sensitised explosives.

INF 60, Australia
This paper presented test results using a gas burner as the heat source, calibrated to standardise the effects. The resultant observations were analysed scientifically.

Chairman: The paper and presentation from Australia was an injection of fundamental science to the test regime and great contribution to understanding the process.

The WG drew a number of conclusions from the tests:

- Tank pressure control is fundamental to the safe transport of ANE.
- VPT vessel is not indicative of any credible ANE transport tank and therefore seems to serve little purpose.
- Better emulsion results in more risk of explosion because fuel stays in mix for longer.
- The inclusion of glass microballoons in the test mixture facilitated the removal of fuel and made the material less explosive in the test.
- Porgera explosion in Papua New Guinea is not a directly valid basis for assessing the risk of transport fire explosions. The likely cause of the ANE detonation was impact from another explosion.
- VPT is arguably more dangerous than the risk of an explosion in transport because of the clouds of fumes and throw of shrapnel.

When asked, D Kennedy responded that the gap test seems to be the most reliable assessor of ANE behaviour.

Chairman: Australian tests have answered several basic questions of ANE behaviour and there appears to be a valid argument that test 8(d) should be deleted from the MTC. If this action is taken, the WG should then determine the transport conditions that apply, based on what it now knew from the Australian tests.

The WG considered consequences and options if it deleted Test 8(d).

It recalled that the 8(d) test was introduced to try to give more confidence in deciding if material was safe for transport in large quantities (tanker loads) rather than relying on the current tests on gram or smaller size.

Divergent opinions were expressed:

1 Tests are expensive, unreliable, 8(d) be deleted because the information in INF60 (Australia) gave a lot of clarity to the mechanism of the test and it was of dubious validity.

2 Tests are necessary to continue to develop knowledge of the behaviour of the materials, some larger scale test is still needed as a qualifying criterion for carriage in bulk, it can remain as an information (non-discriminatory) test.

Conclusion:
Majority opinion was that Test 8(d) remain in some form and that the modified form be developed over the next biennium. This was discussed further in Agenda item 5. See recommendation 1.

It was agreed to modify 18.1 to make the 8(d) test not for discriminating between 1.5 and 5.1 but only to assess if the material tested may be transported in metal packagings and tanks. Consequential amendment to 18.7, assessment of results.

It was resolved to adopt the amendments proposed by USA in WP4.

INF 13 (Swe) presented an option for dealing with the tests: if use aluminium tanks then pressure does not present a problem and so the 8(d) test is unnecessary.

Agenda Item 2 Inclusion of Test Results

Japan (C3/2002/22 and INF 23) would like their results to be added to the Manual of Tests and Criteria results for TS 8.

This proposal was supported by the WG with the following amendments:
2002/22 amended to replace the annex with results in INF 23.
In INF 23, replace word “performed” with “perforated” in table 2 for ANE-J5 and J6 and delete test results for J3.

Annex of amended results for inclusion in the MTC is attached. See recommendation 2.

Spain indicated it has done tests on gels and intends to present the results to the Committee for inclusion in MTC. SASOL also has some test results.

Agenda Item 3 Possible new test.

INF22 (Canada) and WP 1 (Canada) re Minimum Burning Pressure Test (MBP) as an option.

MBP test was a response to the move from NG based explosives to emulsions and slurries where the old tests were not valid to assess the hazards. The test will distinguish between various types of emulsions and explosives and the conditions that will lead to DDT. The conditions of the test are described in the papers.

France: VPT useful for some research but very difficult to do in most places. INERIS agrees that MBP may be a valid test to helping classify but need to see more results.

SASOL concerned that test may not be relevant to transport. Canada: there definitely is no direct relation to transport pressures. However it does help to discriminate the sensitivities and reactivities of materials.

It was agreed that Canada would carry out further MBP tests with a view to ultimately presenting a formal proposal to the UN CETDG that may help distinguish between an ANE class 5 and Class 1 explosive.

Agenda Item 4 Tank Criteria

Chairman opened with statement about the importance of tank criteria because UN3375, as the most appropriate UN No must be used. The absence of tank criteria means ANE may not be transported internationally. There were two proposals before the WG: INF 13 (Swe) and INF 10 (USA).

The proposal for allowing aluminium tanks with minimal testing was contained in (INF 13). After discussion and agreement to the USA modifications to the TS8, this proposal was withdrawn.

Document INF 10 (USA) relates to the transport of 1.5 explosives but it essentially repeats the earlier USA paper relating to 5.1. The WG discussed INF10 to determine the requirements for UN3375 ANE.

In introducing the paper, USA stated that there is a need for tanks to be robust enough for safe transport but it is necessary that there be adequate vent capacity to avoid pressure build up with possible detonation consequences.

In general discussion, concern was expressed that without a general statement prohibiting their use the option remains that the tanks could be higher metal thickness than T1. This could result in over pressurisation in a fire.

The WG recalled that the Australian tests showed that the pressure in the VPT at failure of the bottom plate was some 86 bar. Similarly, the MBP of these materials is typically 40-50 bar. In this context, a tank with possible wall thickness designed to fail at 10bar with venting capacity down at 2.65 bar was unlikely to present a problem.

The WG considered WP4 and agreed with all the recommendations in it (see recommendation 3). These are presented in annexes 3 and 4.

Agenda Item 5 Modifications to the VPT

Australia spoke to WP 3 and led the WG through some suggestions for amending the VPT. The paper included modifications to the apparatus and materials, scientific calibration of the burner, a test procedure and criteria for assessing the results.

It was agreed that the proposals in WP 3 would be used by delegates to develop modifications to the VPT over the next biennium. WP3 is attached as Annex 1.

Agenda Item 6 Thermal Stability Test.

The current requirement in 18.4.1.1.2 is for the test to be carried out at 20deg above the transport temperature. It was agreed that the square brackets in that clause should be removed. (Recommendation 5).

Australia registered a concern about the validity of the TST and stated that it saw very little value in it. They were advised that to remove the test they needed to submit a paper with a definite proposal.

Agenda Item 7 Tanks for Class 1.

INF 10 (USA, DGAC)
UK opposed the inclusion of UN0482 because it was an NOS entry. They accepted the rest of the paper.

DGAC supported the proposal on the basis that all materials carried that way passed the VPT.

Germany and Switzerland opposed the transport in tanks at all.

USA indicated that the proposal would have to be modified from its original form to effectively mirror the VPT requirements for ANE.

The majority view of the WG was to generally support the substance of the paper except for UN0482 and with the inclusion of the text for applying Test 8(d).

Recommendations:

Recommendation 1: Future work:
It was recommended that future work be done to develop Test 8(d) using the guidelines prepared by Australia in annex 1.

Parameters to be included in the new test regime were

1. a vessel that fails at 300kPa or a 3mm steel vessel rather than the original US VPT of 10mm.
2. base the test on a truck fire and perhaps terminate after 45 minutes. This time is reasonable based on Norwegian studies of many fires.
3. Standardise the burner, as the heat input (rate and source) is also important.

It was generally agreed that the size of the vessel was about right at 60L.

Recommendation 2
Recommended that the test results in the Annex 2 be included in the MTC.

Recommendation 3: that the amendments to the Model Regulations and the MTC as shown in annexes 3 and 4 be accepted. In brief, the proposal was to use TS8 to ascertain if material was suitable for transport in tanks and not for classification purposes.

Recommendation 4: that the same provisions in recommendation3 apply to class 1.5D explosives being UN0331 and UN0332.

Recommendation 5: to remove the square brackets in 18.4.1.1.2 of ST/SG/AC.10/C.3/38/Add.1

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Annex 1: Future Work.

Manual of Tests and Criteria. Test 8(d) - Vented Pipe Test

1 Introduction

The vented pipe test is used to assess the effect of exposure of a candidate for "ammonium nitrate emulsion or suspension or gel, intermediate for blasting explosives" to a large fire under confined, vented conditions. It will determine whether or not an ANE can be transported in tanks as a dangerous good of Class 5.1.

The ANE is subjected to this test **only** after it has passed Test 8(a), Test 8(b) and Test 8(c) and deemed to be a dangerous good of Class 5.1.

2 Apparatus and materials

The following items are needed:

(a) A vented vessel consisting of mild drawn steel pipe with an inner diameter of [265 ± 10 mm], a length of [580 ± 10 mm] and a wall thickness of [5.0 ± 0.5 mm]. Both the top and the base plates are made from 300 mm square, [6.0 ± 0.5 mm] thick mild steel plates. The top and base plates are fixed to the pipe with a single 5 mm fillet weld. The top plate has a vent diameter of [87 mm]. A further two small holes are drilled in the top plate to accommodate neatly thermocouple probes;

(b) A concrete block about 400 mm square and 50 to 75 mm thick;

(c) A metal stand for supporting the vessel at a height of 150 mm above the concrete block;

(d) A gas burner capable of accommodating an LPG flow rate of up to [35 ± 2 litres per minute]. Typically, this will deliver a heat flux of 118 ± 5 kW per square metre. This rests on the concrete block under the stand. A typical example of a suitable burner is a 32-jet Mongolian wok burner;

(e) A sheet metal shield to protect the LPG flame from side winds. This can be fabricated from approximately 0.5 mm thick galvanised sheet metal. The diameter of the wind shield is 600 mm and the height is 250 mm. Four adjustable vents 150 mm wide and 100 mm high are spaced equally around the shield to ensure adequate air reaches the gas flame;

(f) LPG bottle(s) connected via a manifold and fed into a pressure regulator. The pressure regulator should reduce the LPG bottle pressure from 650 kPa down to about 250 kPa. The gas then flows through a gas rotameter capable of measuring up to 40 litres per minute of LPG gas. An electrical solenoid valve is used to switch the LPG flow on and off remotely. Typically four 9kg LPG bottles will achieve the desired gas flow rate for the duration of up to five tests.

(g) Three thermocouples with 500 mm long stainless steel probes and fiber-glass coated lead wires;

(h) A data-logger capable of recording the output from the thermocouples;

(i) Cine or video cameras, preferably high speed and normal speed, to record events in colour.

(j) Pure water for calibration.

(k) The ANE to be tested.

Blast gauges, radiometers and associated recording equipment may also be used.

3 Calibration

3.1 The vessel is filled to the [75%] level (ie to a depth of [440 mm]) with the pure water, and heated using the procedure specified in Section 4. The time taken to reach the boiling point of the water is recorded, and is used to define the "calibration time" for the given combination of vessel and heat source.

3.2 The "calibration time" is defined as the time taken to heat water from 25°C to boiling point within the test equipment and typically this time is about 25 minutes at STP.

3.3 If the initial temperature of the water was not 25°C, corrections to the "calibration time" must be made based on the measured mean heating rate over the temperature interval between 40°C and 80°C as recorded by the thermocouple in the water.

3.4 This calibration must be performed prior to the testing of any ANE substance, though the same calibration can be applied to any test conducted within a week of the calibration provided no change is made to the vessel construction, LPG burner type or gas supply.

4 Test Procedure

4.1 The concrete block is placed on a sandy base and levelled using a spirit level. The LPG burner is positioned in the centre of the concrete block and connected to the gas supply line. The metal stand is placed over the burner.

4.2 The vessel is placed vertically on the stand and secured from tipping over. The vessel is filled to [75 %] of its volume (to a height of [440 mm]) with the ANE under test without tamping during loading. The initial temperature of the ANE must be recorded. The substance is carefully packed to prevent adding voids. The wind shield is positioned around the base of the assembly to protect the LPG flame from heat dissipation due to side winds.

4.3 The thermocouple positions are:

- the first (T1) in the LPG flame;
- the second (T2) in the headspace 20 mm into the vessel;
- the third (T3) extending all the way into the vessel so that the tip is positioned 80 to 90 mm from the bottom of the vessel.

The thermocouples are connected to the data-logger and the thermocouple leads and data-logger are adequately protected from the test apparatus in case of explosion.

4.4 LPG pressure and flow is checked and adjusted to [250 kPa] and [35 litres per minute]. Video cameras and any other recording equipment are checked and started. Thermocouple functioning is checked and data logging is started. The test should not be performed under conditions where the wind speed exceeds 6 m/s.

4.5 The LPG burner may be started locally or remotely and all workers immediately retreat to a safe location. Progress of the test is followed by monitoring thermocouple readings and closed circuit television images.

4.6 The “run time” for the ANE is calculated as [twice] the “calibration time” for water, adjusted by a suitable correction based on the measured heating rate for water if the initial temperature of the ANE is not the normal shipping temperature.

4.7 The ANE is heated for this “run time”. At the end of this “run time”, or earlier if a rupture of the vessel has occurred, the LPG supply is switched off remotely using the solenoid valve.

4.8 Once the vessel and any remaining ANE have cooled to a safe handling temperature, the ANE should be disposed of in an environmentally responsible manner and according to local statutory requirements.

4.9 The test outcome is determined by the rupture of vessel.

4.10 Observations should be made and recorded on the following:

(a) Thermocouple traces

(b) evidence of violent venting or loud noise; and

(c) projection of fragments from the test area.

5 Test criteria and method of assessing results

The ANE is heated under the set test conditions for its “run time”.

If rupture of the vessel occurs during this period the ANE is <u>not</u> suitable for transportation in tanks as a dangerous good of Class 5.1.

If no rupture of the vessel occurs during this period the ANE is suitable for transportation in tanks as a dangerous good of Class 5.1.

6 Examples of results

Example of calibration calculation:

Calibration for water:

Initial temperature of water = 32°C
Time to heat water to 100°C = 21 minutes 30 seconds
Mean heating rate between 40°C and 80°C = 3.50°C/minute
Calibration time = 21 minutes 30 seconds + (32°C -25°C)/3.5°C/minute = 23 minutes 30 seconds

Example of "run time" correction:

Example time correction for Test Substance 1:

Initial temperature of substance = 18°C
Normal shipping temperature = 60°C
Run time = [2]×(23 minutes 30 seconds) + (60-18)/3.50 minutes = 59 minutes 0 seconds

Example of typical results:

Substance		Result
1.	78.3 AN / 16.1 Water / 4.2 diesel oil / 1.6 emulsifier	-
2.	82.1 AN / 12.3 Water / 4.2 diesel oil / 1.6 emulsifier	-
3.	82.1 AN / 12.3 Water / 4.2 paraffin oil / 1.6 emulsifier	-
4.	68.4 AN / 17.6 SN / 6.5 Water / 5.7 diesel oil / 1.9 emulsifier	-
5.	74.8 AN / 9.7 SP / 9.0 Water / 3.7 paraffin oil / 2.7 emulsifier	+

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Annex 2: test results.

Table 1 Test 8(a) : Thermal Stability Test

Substances	Sample mass (g)	Test T (°C)	Result	Comments
ANE-J1 Ammonium nitrate 80%, Water 13%, Fuel/emulsifier 7%	613	80	-	Mass loss 0.1%
ANE-J2 Ammonium nitrate 76%, Water 17%, Fuel/emulsifier 7%	605	80	-	Mass loss 0.3%
ANE-J4 Ammonium nitrate 71%, Sodium nitrate 11%, Water 12%, Fuel/emulsifier 6%	602	80	-	Mass loss 0.1%

Table 2 Test 8(b) : ANE Gap Test

Substances	Density g/cm^3	Gap mm	Result	Comments
ANE-J1 Ammonium nitrate 80%, Water 13%, Fuel/emulsifier 7%	1.39	70	-	Tube fragmented. Plate indented.
ANE-J2 Ammonium nitrate 76%, Water 17%, Fuel/emulsifier 7%	1.42	70	-	Tube fragmented. Plate indented.
ANE-J4 Ammonium nitrate 71%, Sodium nitrate 11%, Water 12%, Fuel/emulsifier 6%	1.40	70	-	Tube fragmented. Plate indented.
ANE-J5 (sensitized by microballoons) Ammonium nitrate 71%, Sodium nitrate 5%, Water 18%, Fuel/emulsifier 6%	1.20	70	+	Tube fragmented. Plate perforated. VOD 5.7 km/s
ANE-J6 (sensitized by microballoons) Ammonium nitrate 80%, Water 13%, Fuel/emulsifier 7%	1.26	70	+	Tube fragmented. Plate perforated. VOD 6.3 km/s

Table 3 Test 8(c) : Koenen Test

Substances	Result	Comments
ANE-J1 Ammonium nitrate 80%, Water 13%, Fuel/emulsifier 7%	-	Effect type "O"
ANE-J2 Ammonium nitrate 76%, Water 17%, Fuel/emulsifier 7%	-	Effect type "O"
ANE-J4 Ammonium nitrate 71%, Sodium nitrate 11%, Water 12%, Fuel/emulsifier 6%	-	Effect type "A"

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Annex 3: Amendments to the Model Regulations

1. Amend entry **UN0331, UN0332 and UN3375** by adding “T1” in column (10) and TP17 and TPXXX in column (11).

Since assigning T1 authorizes shippers to use portable tanks with a minimum test pressure up to 10 bar there is a need to add a special tank provision to address concerns of over confinement if the portable tank is engulfed in a fire. To address this issue it is proposed to set the pressure relief device to function at a lower pressure than the test pressure for portable tanks with a test pressure greater than 4 bar by adding a new special tank provision (TPXXX). This new tank provision is proposed to address the set pressure, relief capacity and the types of pressure relief devices that can be used. Additionally, TP17 is proposed to indicate that only inorganic non-combustible material may be used for the thermal insulation.

2. In paragraph 4.2.5.3, add a new portable tank special provision TPXXX, to read as follows:

TPXXX – For UN0331, UN0332 and UN3375, portable tanks may be used subject to the following conditions:

1. *To avoid unnecessary confinement, each portable tank constructed of metal shall be fitted with a pressure-relief device that may be of the reclosing spring loaded type, a frangible disc or a fusible element. The set to discharge or burst pressure, as applicable, shall not be greater than 2.65 bar for portable tanks with minimum test pressures greater than 4 bar. The pressure-relief devices shall have sufficient relief capacity to prevent rupture of the shell due to over pressurization or vacuum resulting from filling, discharging or from heating of the contents including fire engulfment.*

2. *Explosives or ANE to be transported in portable tanks must be demonstrated for suitability for carriage in tanks. One method to evaluate this suitability is Test Series 8 (d).*

3. *Material shall not be allowed to remain in the portable tank for any period that could result in caking. The tank shall be inspected and cleaned frequently enough to minimize the accumulation and packing of material.*

18.2 Test methods

The test methods currently used are listed in table 18.1.

Table 18.1: TEST METHODS FOR TEST SERIES 8

Test code	Name of Test	Section
8 (a)	Thermal Stability Test for ANE */	18.4.1
8 (b)	ANE Gap Test */	18.4.2
8 (c)	Koenen test */	18.4.3
8 (d)	**Vented pipe test +/**	**18.4.4**

*/ This test is used for classification.
+/ This test is provided here for information for those who may want to use it to evaluate the suitability for bulk transport.

Paras. 18.3 – 18.6.1.5 and Figures 18.6.1.1 – 18.6.1.3 here

18.7 Series 8 Type (d) Test prescription

18.7.1 *Test 8 (d): Vented pipe test*

18.7.1.1 *Introduction*

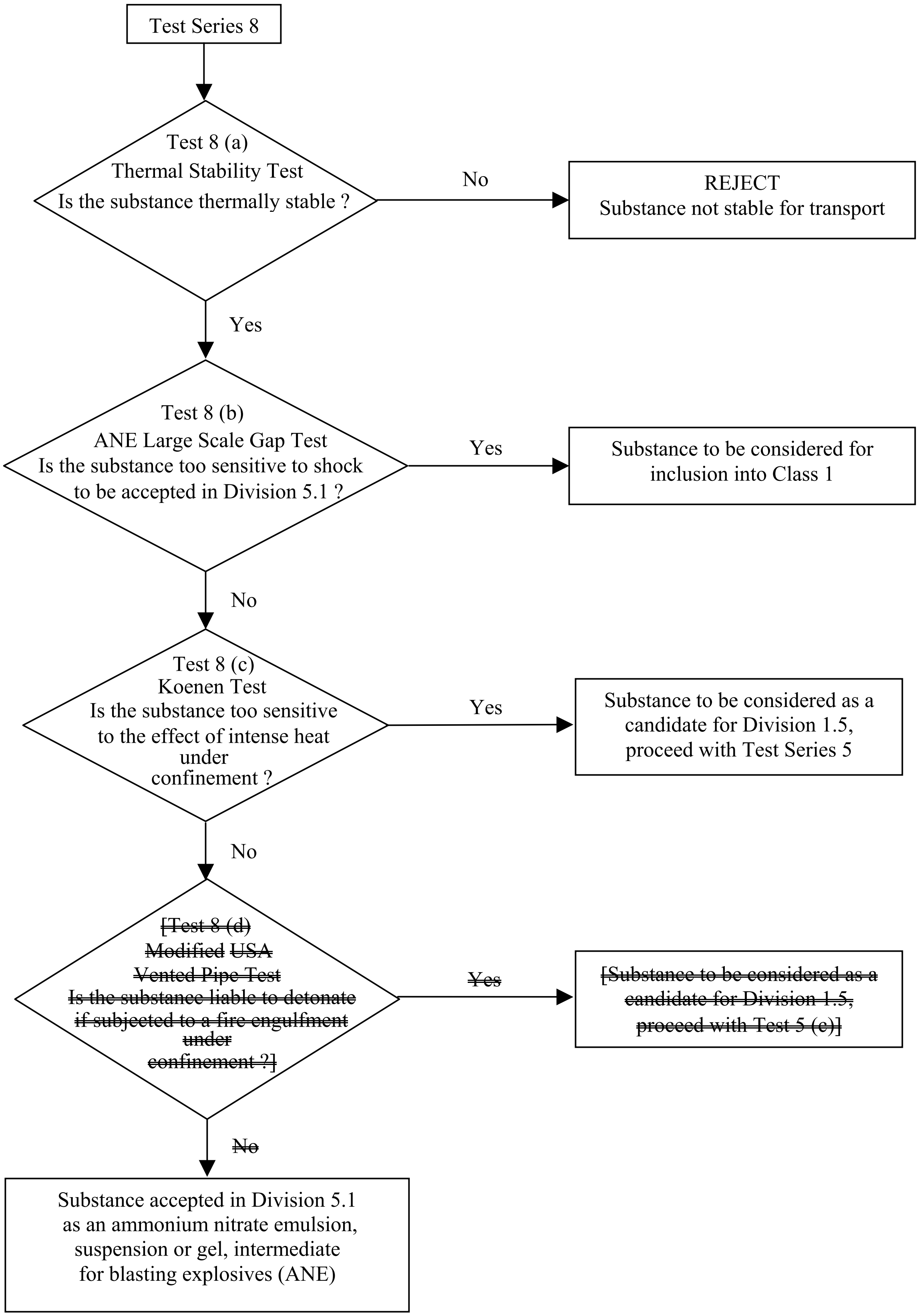
This test is not used for classification but is included here for those who may want to use it to evaluate suitability for bulk transport. The vented pipe test is used to assess the effect of exposure of a candidate for "ammonium nitrate emulsion or suspension or gel, intermediate for blasting explosives" to a large fire under confined, vented conditions.

18.7.1.2 *Apparatus and materials*

Insert current text here

18.7.1.4 *Test criteria and method of assessing results*

The test result is considered "+" and the substance should not be **transported in tanks** if an explosion and/or fragmentation of the pipe is observed. If no explosion and/or fragmentation of the pipe is observed then the result is considered "-".


Test Series 8
Test 8 (a)
Thermal Stability Test
Is the substance thermally stable ?
No
REJECT
Substance not stable for transport
Yes
Test 8 (b)
ANE Large Scale Gap Test
Is the substance too sensitive to shock
to be accepted in Division 5.1 ?
Yes
Substance to be considered for
inclusion into Class 1
No
Test 8 (c)
Koenen Test
Is the substance too sensitive
to the effect of intense heat
under
confinement ?
Yes
Substance to be considered as a
candidate for Division 1.5,
proceed with Test Series 5
No
~~[Test 8 (d)~~
~~Modified USA~~
~~Vented Pipe Test~~
~~Is the substance liable to detonate~~
~~if subjected to a fire engulfment~~
~~under~~
~~confinement ?]~~
~~Yes~~
~~[Substance to be considered as a~~
~~candidate for Division 1.5,~~
~~proceed with Test 5 (c)]~~
~~No~~
Substance accepted in Division 5.1
as an ammonium nitrate emulsion,
suspension or gel, intermediate
for blasting explosives (ANE)