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COMMITTEE OF EXPERTS ON THE TRANSPORT OF DANGEROUS GOODS

**(Twenty-first session,
4-13 December 2000,
agenda item 2 (b))**

WORK OF THE SUB-COMMITTEE OF EXPERTS

Draft amendments to the Recommendations on the Transport of Dangerous Goods

Proposal resulting from the Working Group on classification of ammonium nitrate emulsions, Intermediate for blasting explosives

Transmitted by the Chairman of the Working Group

1. Introduction

A working group on classification of ammonium nitrate emulsions, intermediate for blasting explosives met during the July 2000 meeting of the Sub-Committee of Experts on the Transport of Dangerous Goods. Experts from Australia, Canada, France, Germany, Italy, Netherlands, Norway, Sweden, Switzerland, United Kingdom and the United States of America, as well as representatives from the Federation of European Explosives Manufacturers (FEEM), Hazardous Materials Advisory Council (HMAC), Institute of Makers of Explosives (IME) and International Society of Explosives Engineers (ISEE) participated in the meeting.

The discussion was based on the following documents:

- ST/SG/AC.10/C.3/2000/21 which contained the proposals from an informal working group hosted by the Federation of European Explosives Manufacturers (FEEM) in Engene, Norway from 4 to 8 October 1999;

- INF.47 from United Kingdom commenting on the proposal from the Engene working group;

- conference room papers from France (results of DDT tests and current regulations in France) and Canada (both on test methods and results).

During the discussions in the sub-Committee working group, several changes were made to the proposal in ST/SG/AC.10/C.3/2000/21, mainly to the flow charts and test methods. The working group decided that a new revised proposal should be presented to the Committee of Experts, and since the introduction of new test methods raises questions on whether the new methods are appropriate, it was also decided to produce test results showing the validity of the proposed new tests. These results will, due to the time restraint, appear in separate INF.-papers to the 21th session of the Committee.

The results from the discussions in the working group were presented in document UN/SCETDG/18/INF.70. In presenting the report, the working group expressed the opinion that there is urgent need for internationally agreed conditions for the transportation of these substance, since they are being transported in large amounts around the world, with various classifications and conditions for transport. The revised proposals, as set down by the working group, are listed below.

2. Proposal

(a) In the Dangerous Goods List of Chapter 3.2, create a new entry:

UN No.	Name and description	Class or division	Subsidiary risk	UN Packing Group	Special provisions	Limited Quantities	Packagings and IBCs		Portable tanks	
							PI	SPP	PTI	TP
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
3XXX	AMMONIUM NITRATE EMULSION, intermediate for blasting explosives	5.1		III	yyy	None	P503 IBC02		T2	TP17 TPxy

(b) In Chapter 3.3 create a new Special Provision yyy:

"This entry applies to non sensitised emulsions consisting primarily of a solution of ammonium nitrate dispersed in an oil phase, intended to produce a Type E blasting explosive only after further processing prior to use. The emulsion typically has the following composition: 60 – 85 % ammonium nitrate; 5 – 30 % water; 2 – 8 % oil; 0.5 – 4 % emulsifier, 0 – 10 % soluble flame suppressants and trace additives. Other inorganic nitrate salts may replace part of the ammonium nitrate. Formulations shall satisfactorily pass Test Series 8 in the Manual of Tests and Criteria, Part I, Section 18."

(c) In subsection 4.2.4.3 add a new portable tank special provision TP xy:

"Metal tanks shall have frangible disks and/or fusible elements with a total relief area of at least [0.005 m^2/m^3]. To avoid unnecessary confinement only tank types with a maximum allowable working pressure (MAWP) of not more than 2.65 bar shall be used."

(d) In subsection 4.1.4.2 Packing Instruction IBC02, add Special Packing Provision B yz:

" For UN 3XXX, metal IBCs shall have frangible disks and/or fusible elements with a total relief area of at least [0.005 m^2/m^3]."

Proposals for changes to be made to the Manual of Tests and Criteria [proposal (e) – (j)]: See the following pages.

Consequential changes to be made to the Manual of Tests and Criteria as a result from adopting the proposed changes:

- In 1.2.2, Table 1.1; in the column for "Test Series": Change "1 – 7" into "1 – 8".

- In 1.6, Table 1.2; add Test Series 8.

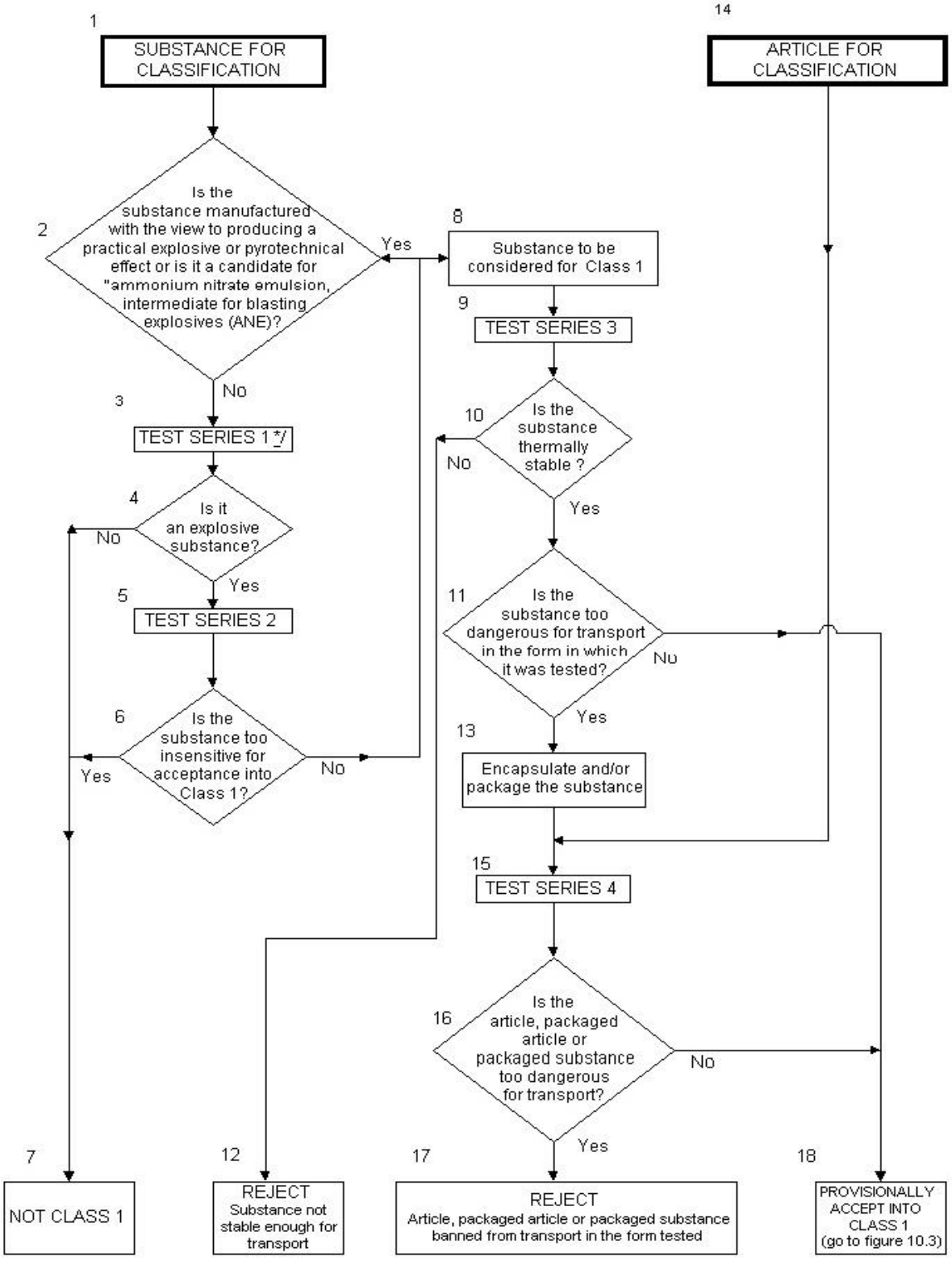
- In 10.1.1, last sentence; add "figure 1.4" and change "11 to 17" into "11 to 18".

- In 10.4.3, renumber existing 10.4.3.7 to 10.4.3.8.

- In 10.5.1; change "figures 10.4 to 10.7" into "figures 10.5 to 10.8".

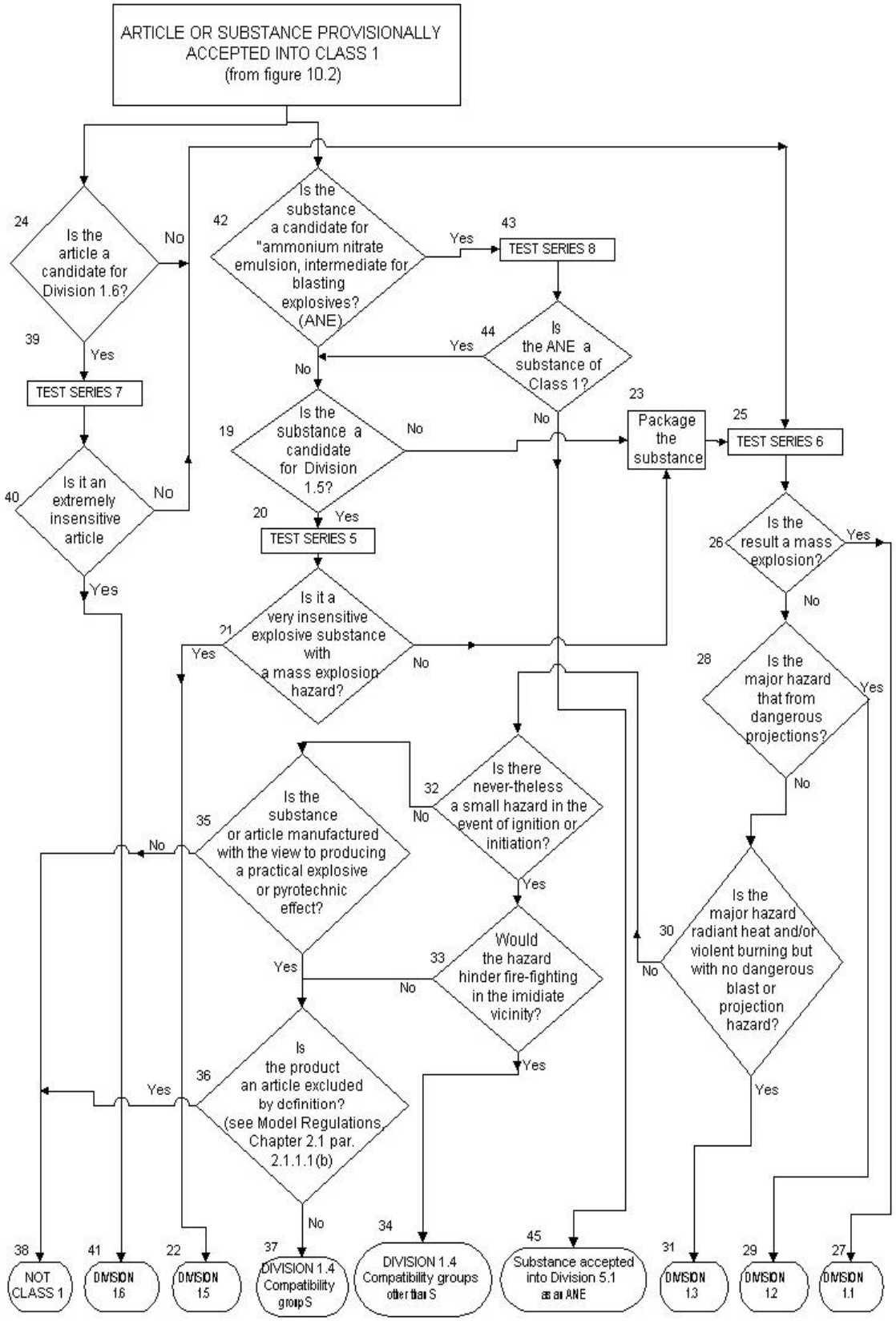
- In 10.5.2; change "figure 10.8" to "figure 10.9" and renumber existing Fig.10.4 to Fig. 10.8 to Fig. 10.5 - Fig. 10.9.

(e) Change Figure 10.2 to read:

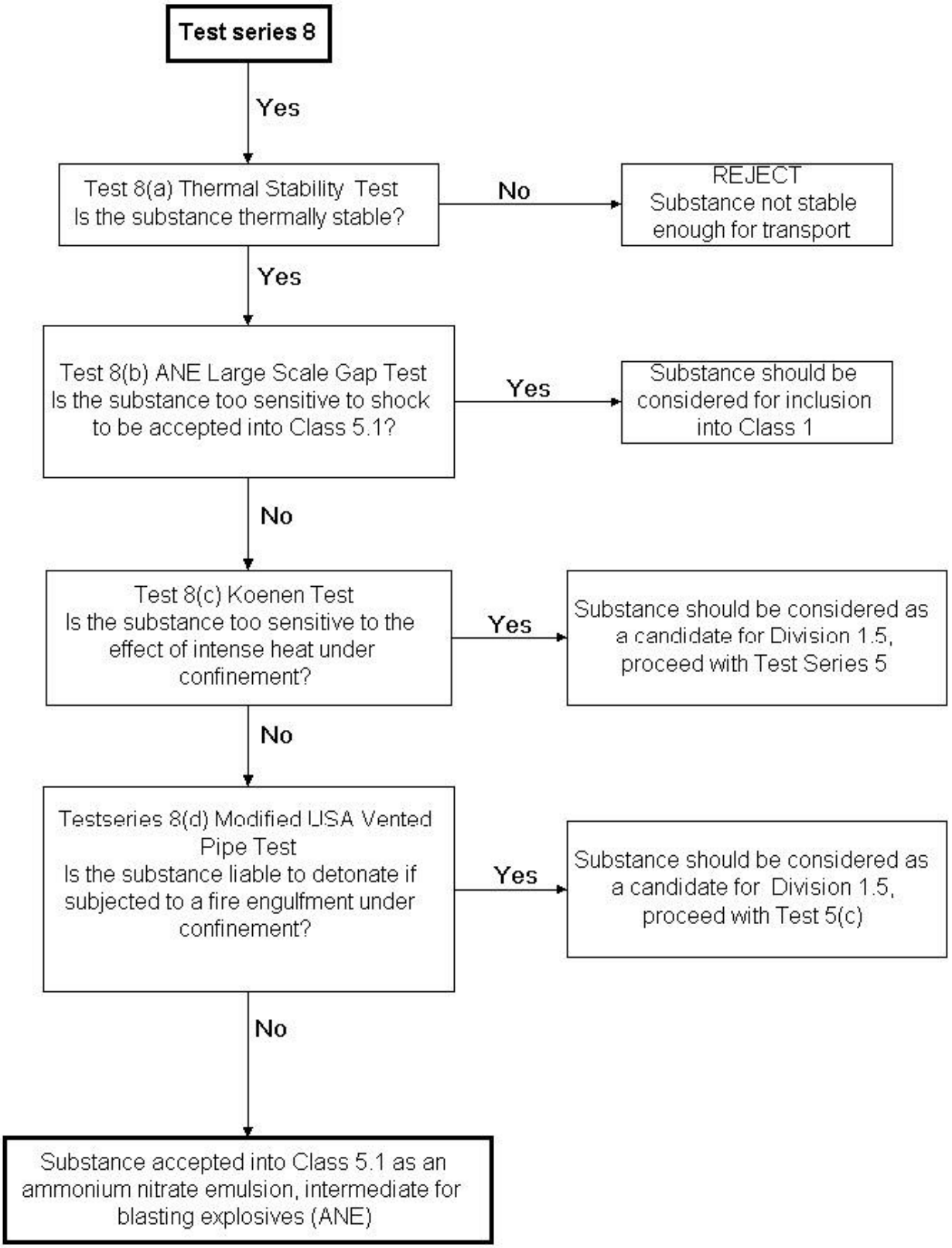


*/ For classification purposes, start with test series 2

(f) Change Figure 10.3 to read:



(g) Add new Table 10.4:



(h) Add new subsection 10.4.2.5:

10.4.2.5The question “Is the substance a candidate for “ammonium nitrate emulsion, intermediate for blasting explosives (ANE)?” (box 42, figure 10.3) is answered by series 8 tests and any candidate should pass each of the four tests comprising the series. The four test types are:

type 8 (a) - a test to determine the thermal stability;

type 8 (b) - a shock test to determine sensitivity to intense shock;

type 8 (c) - a test to determine the effect of heating under confinement;

type 8 (d) - a test to determine the effect of exposure to a large fire under confined, vented conditions.

(i) Add new subsection 10.4.3.7.

10.4.3.7Test types 8 (a) to 8 (d) should be used to establish whether an ammonium nitrate emulsion, intermediate for blasting explosives (ANE) may be assigned to Class 5.1.
Substances failing any of the tests may be considered as a candidate for Class 1 in accordance with Table 10.4.

(j) Insert a new Section 18, Test Series 8:

SECTION18

TEST SERIES 8

18.1 Introduction

The assessment whether a candidate for "ammonium nitrate emulsion, intermediate for blasting explosives (ANE)" is insensitive enough for inclusion in Division 5.1 is answered by series 8 tests and any such candidate for inclusion in Division 5.1 should pass each of the four types of tests comprising the series. The four test types are:

type 8(a) - a test to determine the thermal stability;

type 8 (b) - a shock test to determine sensitivity to intense shock;

type 8 (c) - a test to determine the effect of heating under confinement;

type 8 (d) - a test to determine the effect of exposure to a large fire under confined, vented conditions.

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 Large Scale Gap Test */	18.4.2
8 (c)	Koenen test */	18.4.3
8 (d)	USA vented pipe test */	18.4.4

*/ Recommended test

18.3 Test conditions

18.3.1 The substance should be tested as offered for transport, at the highest transport temperature (see 1.5.4 of this Manual).

18.4 Test Series 8 test description

18.4.1 ***Test 8(a) : Thermal stability test for ammonium nitrate emulsions***

18.4.1.1 *Introduction*

18.4.1.1.1 This test is used to measure the stability of a candidate for "ammonium nitrate emulsion, intermediate for blasting explosives" when subjected to elevated thermal conditions to determine if the emulsion is too dangerous to transport.

18.4.1.1.2 Ammonium nitrate emulsions are usually loaded into the transport tank at high temperatures, typically about [80 to 90 °C]. This test is used to determine whether the emulsion is stable at such temperatures. In the way this type of thest is normally carried out (see section 28.4.4), the 0.5 litre Dewar vessel is only representative for packagings, IBC's and small tanks. For the transport of ammonium nitrate emulsions, the test can be used to measure its stability during tank transport if the test is carried out at a temperature [20 °C] higher than the maximum temperature which may occur during transport, including the temperature at the time of loading.

18.4.1.2 *Apparatus and materials*

18.4.1.2.1 The experimental equipment consists of a suitable test chamber, appropriate Dewar vessels with closures, temperature probes and measuring equipment.

18.4.1.2.2 ***The test should be performed in a test cell capable of withstanding fire and overpressure and, preferably, should be fitted with a pressure relief system e.g. a blow out panel.*** The recording system should be housed in a separate observation area.

18.4.1.2.3 A thermostatically controlled drying oven (which may be fan-assisted) large enough to allow air circulation on all sides of the Dewar vessel may be used. The air temperature in the oven should be controlled so that the desired temperature for a liquid inert sample in the Dewar vessel can be maintained with a deviation of not more than " 1 °C for up to 10 days. The air temperature in the oven should be measured and recorded. It is recommended that the door of the oven be fitted with a magnetic catch or replaced by a loosely fitting insulated cover. The oven may be protected by an appropriate steel liner and the Dewar vessel housed in a wire mesh cage.

18.4.1.2.4 Dewar vessels with a volume of 500 ml with a closure system are used. The closure of the Dewar vessel should be inert. A closure system is illustrated in figure 18.4.1.1.

18.4.1.2.5 The heat loss characteristics of the system used, i.e. Dewar vessel and closure, should be established prior to performance of the test. Since the closure system has a significant effect on the heat loss characteristics, these can be adjusted to some extent by varying the closure system. The heat loss chracteristics can be determined by measuring the half time of cooling of the vessel filled with an inert substance having similar physical properties. The heat loss per unit of mass, L (W/kg.K) can be calculated from the half time of cooling, $t_{1/2}$ (s), and the specific heat, Cp (J/K), of the substance using the formula: $L = \ln 2 \, . \, Cp / t_{1/2}$.

18.4.1.2.6 Dewar vessels filled with 400 ml of substance, with a heat loss of 80 to 100 mW/kg.K are suitable.

18.4.1.2.7 The Dewar vessel shall be filled to about 80% of its capacity. In case of a sample with very high viscosity it may be required to have the sample provided with a shape which just fits into the Dewar vessel. The diameter of such a preshaed sample shall be just under the inner diameter of the Dewar vessel. The hollow lower end of the Dewar vessel may be filled with an inert solid substance prior to loading the sample into the vessel to facilitate the use of cilindrically shaped sample substances.

18.4.1.3 *Procedure*

18.4.1.3.1 Set the test chamber at a temperature which is [20 °C] higher than the maximum temperature which may occur during transport or, if higher, the temperature at the time of loading. Fill the Dewar vessel with the substance under test and note the mass of the sample. Make sure the sample is filled to about 80% of its height. Insert the temperature probe into the centre of the sample. Seal the lid of the Dewar in place and insert the Dewar vessel in the test chamber, connect the temperature recording system and close the test chamber.

18.4.1.3.2 The sample is heated and the temperature of the sample and test chamber continuously monitored. The time is noted at which the sample temperature reaches a temperature 2 °C below the test chamber temperature. The test is then continued for a further seven days or until the sample temperature rises to 6°C or more above the test chamber temperature if this occurs sooner. Note the time taken for the sample to rise from 2 °C below the test chamber temperature to its maximum temperature.

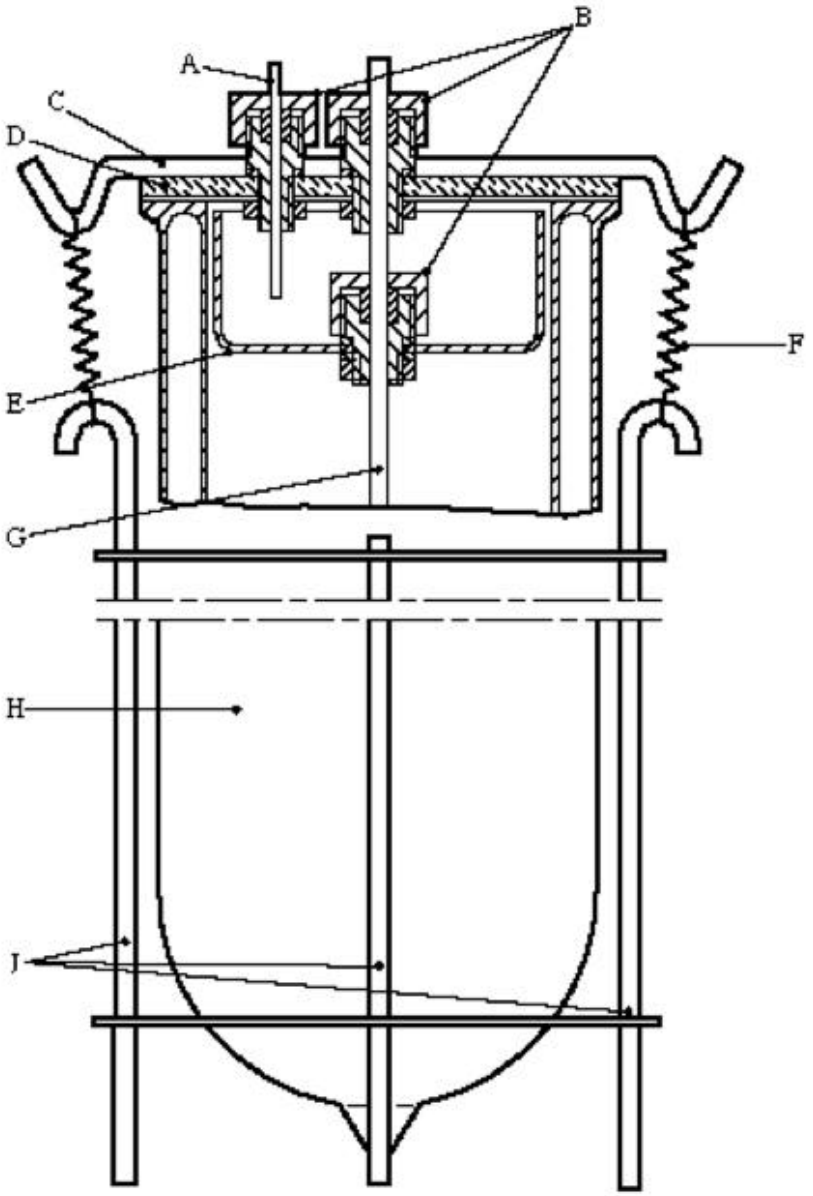
18.4.1.3.3 If the sample survives, cool and remove it from the test chamber and carefully dispose of it as soon as possible. The percentage mass loss and change in composition may be determined.

18.4.1.4 *Test criteria and method of assessing results*

18.4.1.4.1 If the sample temperature does not exceed the test chamber temperature by 6 °C or more in any test, the ammonium nitrate emulsion is considered to be thermally stable and can be further tested as a candidate for “ammonium nitrate emulsion, intermediate for blasting explosives”.

18.4.1.5 *Examples of results*

Substance	**Sample mass (kg)**	**Dewar heat loss (mW/kg.K)**	**Result**
to be added			



(A)	PTFE capillary tube	(B)	Special screw fittings (PTFE or Al) with O-ring seal
(C)	Metal strip	(D)	Glass lid
(E)	Glass beaker base	(F)	Spring
(G)	Glass protective tube	(H)	Dewar vessel
(J)	Steel retaining device		

Figure 18.4.1.1: DEWAR VESSEL WITH CLOSURE

18.4.2 Test 8 (b): Ammonium Nitrate Emulsion Gap Test

18.4.2.1 Introduction

This test is used to measure the sensitivity of a candidate for "ammonium nitrate emulsion, intermediate for blasting explosives" to a specified shock level, i.e. a specified donor charge and gap.

18.4.2.2. Apparatus and materials

The set-up for this test consists of an explosive charge (donor), a barrier (gap), a container holding the test charge (acceptor), and a steel witness plate (target).

The following materials are to be used:

(a) United Nations Standard detonator or equivalent.

(b) 95 mm diameter by 95 mm long pressed 50/50 pentolite or 95/5 RDX/WAX pellet with a density of 1,600 kg/m^3 ± 50 kg/m^3.

(c) Tubing, steel, cold drawn seamless, 95 mm outer diameter, 11.1 mm wall thickness ± 10% variations, by 280 mm long having the following mechanical properties:

- tensile strength = 420 MPa (± 20% variation)
- elongation (per cent) = 22 (± 20% variation)
- Brinell hardness = 125 (± 20% variation).

(d) Sample substances, with a diameter which is just under the inner diameter of the steel tubing. The air gap between the sample and tubing wall should be as small as possible.

(e) Cast polymethyl methacrylate (PMMA) rod, of 95 mm diameter by 70 mm long. [a gap length of 70 mm results in a shock pressure applied to the emulsion somewhere between 3.5 and 4 GPa, depending on the type of donor used, see attached tables derived from NATO STANAG 4488). ***Is this value the correct one to distinguish between sensitised and non sensitised emulsions or should the gap be adjusted?***]

(f) Mild steel plate, 200 mm by 200 mm x 20 mm, having the following mechanical properties:

- tensile strength = 580 MPa (± 20% variation)
- elongation (per cent) = 21 (± 20% variation)
- Brinell hardness = 160 (± 20% variation).

(g) Cardboard tubing, 97 mm inner diameter by 443 mm long.

(h) Wood block, 95 mm diameter and 25 mm thick, with a hole drilled through the centre to hold the detonator.

18.4.2.3 Procedure

As shown in figure 18.4.2.1, the detonator, donor, gap and acceptor charge are coaxially aligned above the centre of the witness plate. Care should be taken to ensure good contact between the detonator and donor, donor and gap and gap and acceptor charge. The test sample and booster should be at ambient temperature for the test.

To assist in collecting the remains of the witness plate, the whole assembly may be mounted over a container of water with at least a 10 cm air gap between the surface of the water and the bottom surface of the witness plate which should be supported along two edges only.

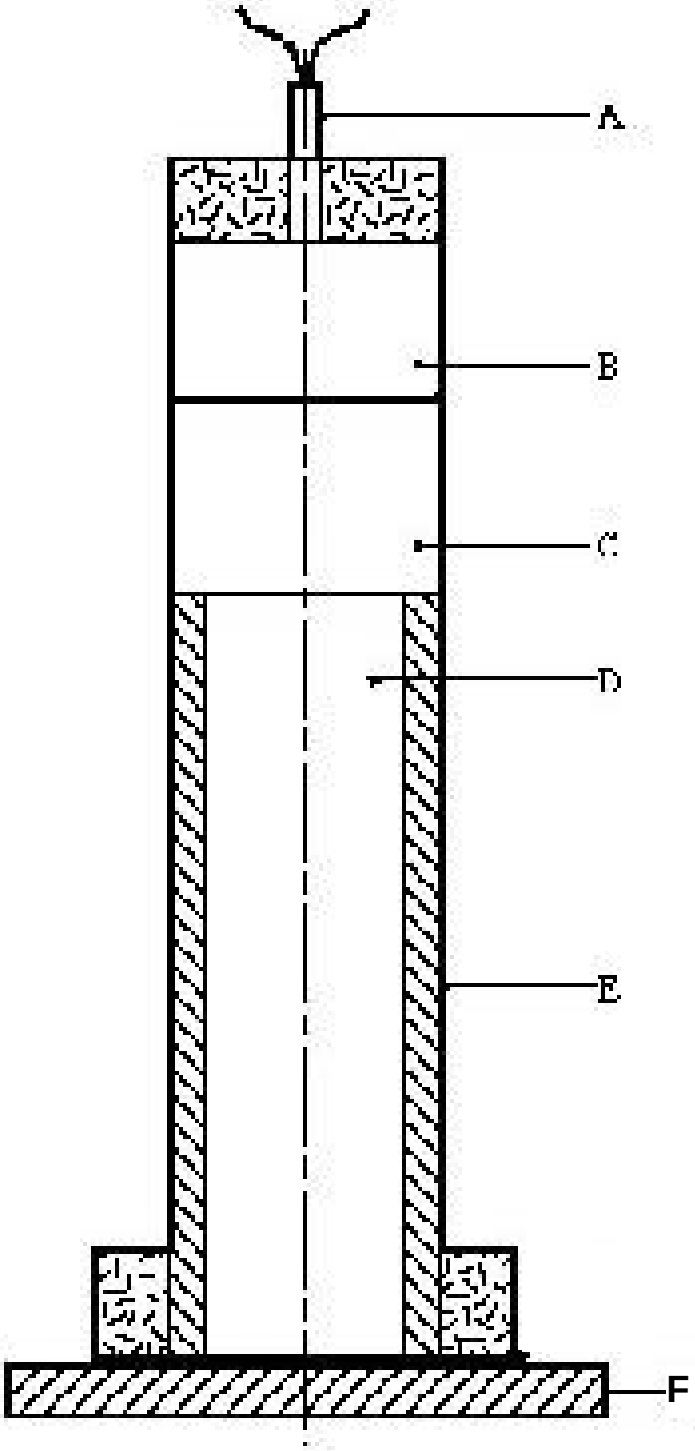
Alternative collection methods may be used but it is important to allow sufficient free space below the witness plate so as not to impede plate puncture. The test is performed three times unless a positive result is observed earlier.

18.4.2.4 Test criteria and method of assessing results

A clean hole punched through the plate indicates that a detonation was initiated in the sample. A substance which detonates in any trial **[at the gap length to be decided upon]** is not an “ammonium nitrate emulsion, intermediate for blasting explosives” and the result is noted as "+".

18.4.2.5 Examples of results

Substance	**Result**
to be added	



(A)	Detonator	(B)	Booster charge
(C)	PMMA gap	(D)	Substance under test
(E)	Steel tube	(F)	Witness plate

Figure 18.4.2.1: EXPANDED LARGE SCALE GAP TEST

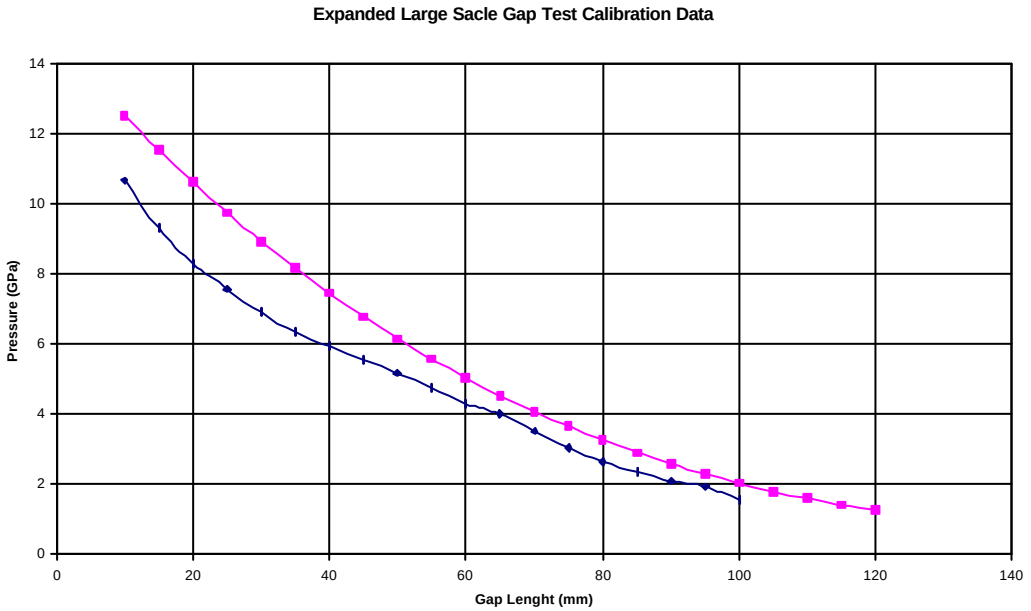
EXPANDED LARGE SCALE GAP TEST CALIBRATION DATA

PENTOLITE 50/50 DONOR

Gap length (mm)	Barrier pressure (GPa)
10	10.67
15	9.31
20	8.31
25	7.58
30	6.91
35	6.34
40	5.94
45	5.56
50	5.18
55	4.76
60	4.31
65	4.02
70	3.53
75	3.05
80	2.66
85	2.36
90	2.10
95	1.94
100	1.57

RDX/WAX/GRAPHITE DONOR

Gap length (mm)	Barrier pressure (GPa)
10	12.53
15	11.55
20	10.63
25	9.76
30	8.94
35	8.18
40	7.46
45	6.79
50	6.16
55	5.58
60	5.04
65	4.54
70	4.08
75	3.66
80	3.27
85	2.91
90	2.59
95	2.31
100	2.04
105	1.81
110	1.61
115	1.42
120	1.27



18.4.3 ***Test 8(c): Koenen test***

18.4.3.1 ***Introduction***

This test is used to determine the sensitiveness of a candidate ammonium nitrate emulsion, intermediate for blasting explosive, to the effect of intense heat under high confinement.

18.4.3.2 ***Apparatus and materials***

18.4.3.2.1 The apparatus consists of a non-reusable steel tube, with its re-usable closing device, installed in a heating and protective device. The tube is deep drawn from sheet steel of suitable quality. The mass of the tube is 25.5 ± 1.0 g. The dimensions are given in figure 18.4.3.1.1. The open end of the tube is flanged. The closing plate with an orifice, through which the gases from the decomposition of the test substance escape, is made from heat-resisting chrome steel and is available with the following diameter holes: 1.0 - 1.5 - 2.0 - 2.5 - 3.0 - 5.0 - 8.0 - 12.0 - 20.0 mm. The dimensions of the threaded collar and the nut (closing device) are given in figure 18.4.3.1.1.

18.4.3.2.2 Heating is provided by propane, from an industrial cylinder fitted with a pressure regulator, via a flow meter and distributed by a manifold to the four burners. Other fuel gases may be used providing the specified heating rate is obtained. The gas pressure is regulated to give a heating rate of 3.3 ± 0.3 K/s when measured by the calibration procedure. Calibration involves heating a tube (fitted with a 1.5 mm orifice plate) filled with 27 cm^3 of dibutyl phthalate. The time taken for the temperature of the liquid (measured with a 1 mm diameter thermocouple centrally placed 43 mm below the rim of the tube) to rise from 50 °C to 250 °C is recorded and the heating rate calculated.

18.4.3.2.3 Because the tube is likely to be destroyed in the test, heating is undertaken in a protective welded box, the construction and dimensions of which are given in figure 18.4.3.1.2. The tube is suspended between two rods placed through holes drilled in opposite walls of the box. The arrangement of the burners is given in figure 18.4.3.1.2. The burners are lit simultaneously by a pilot flame or an electrical ignition device. ***The test apparatus is placed in a protective area.*** Measures should be taken to ensure that any draughts does not affect the burner flames. Provision should be made for extracting any gases or smoke resulting from the test.

18.4.3.3 ***Procedure***

18.4.3.3.1 The substance is loaded into the tube to a height of 60 mm taking particular care to prevent the formation of voids. The threaded collar is slipped onto the tube from below, the appropriate orifice plate is inserted and the nut tightened by hand after applying some molybdenum disulphide based lubricant. It is essential to check that none of the substance is trapped between the flange and the plate, or in the threads.

18.4.3.3.2 With orifice plates from 1.0 mm to 8.0 mm diameter, nuts with an orifice of 10.0 mm diameter should be used; if the diameter of the orifice is above 8.0 mm, that of the nut should be 20.0 mm. Each tube is used for one trial only. The orifice plates, threaded collars and nuts may be used again provided they are undamaged.

18.4.3.3.3 The tube is placed in a rigidly mounted vice and the nut tightened with a spanner. The tube is then suspended between the two rods in the protective box. The test area is vacated, the gas supply turned on and the burners lit. The time to reaction and duration of reaction can provide additional information useful in interpreting the results. If rupture of the tube does not occur, heating is to be

continued for at least five minutes before the trial is finished. After each trial the fragments of the tube, if any, should be collected and weighed.

18.4.3.3.4 The following effects are differentiated:

"O": Tube unchanged;
"A": Bottom of tube bulged out;
"B": Bottom and wall of the tube bulged out;
"C": Bottom of tube split;
"D": Wall of tube split;
"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;
"G": Tube fragmented into many mainly small pieces, closing device undamaged; and
"H": Tube fragmented into many very small pieces, closing device bulged out or fragmented.

Examples for the effect types "D", "E" and "F" are shown in figure 18.4.3.1.3. If a trial results in any of the effects "O" to "E", the result is regarded as "no explosion". If a trial gives the effect "F", "G" or "H", the result is evaluated as "explosion".

18.4.3.3.5 The series of trials is started with a single trial using an orifice plate of 20.0 mm. If, in this trial, the result "explosion" is observed, the series is continued with trials using tubes without orifice plates and nuts but with threaded collars (orifice 24.0 mm). If at 20.0 mm "no explosion" occurs, the series is continued with single trials using plates with the following orifices 12.0 - 8.0 - 5.0 - 3.0 - 2.0 - 1.5 and finally 1.0 mm until, at one of these diameters, the result "explosion" is obtained. Subsequently, trials are carried out at increasing diameters, according to the sequence given in 18.4.3.2.1, until only negative results in three tests at the same level are obtained. The limiting diameter of a substance is the largest diameter of the orifice at which the result "explosion" is obtained. If no "explosion" is obtained with a diameter of 1.0 mm, the limiting diameter is recorded as being less than 1.0 mm.

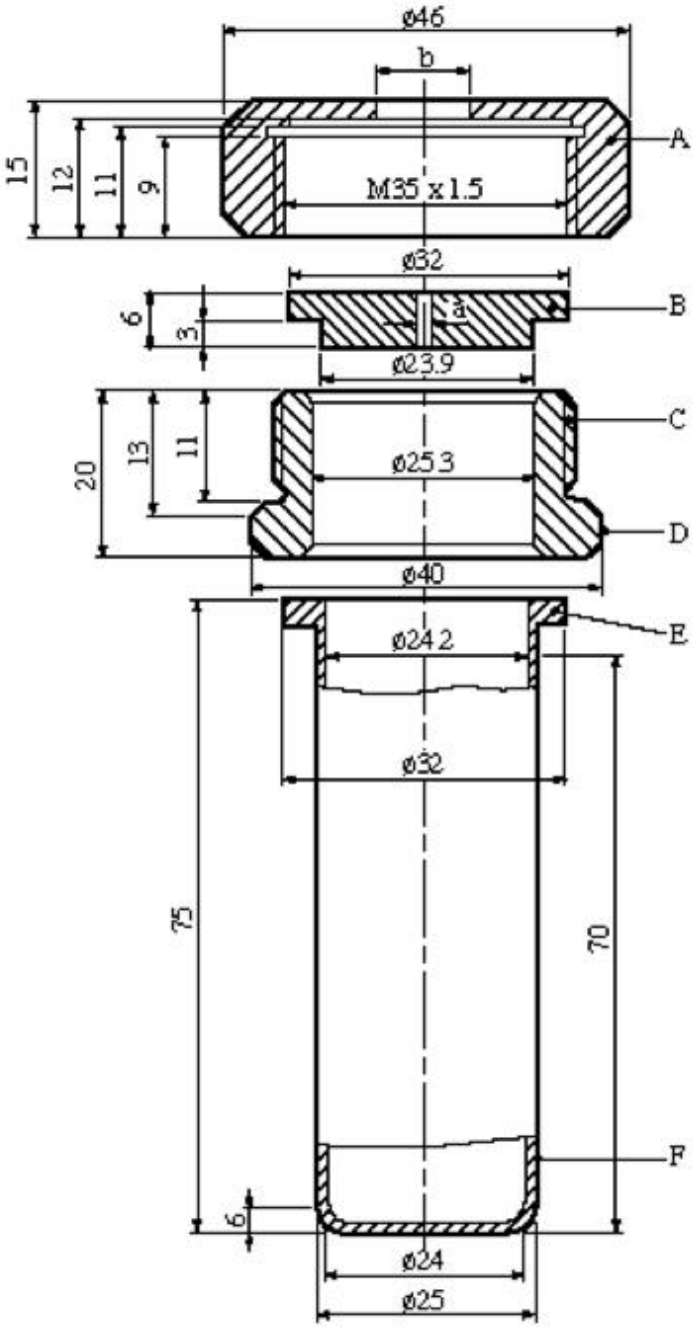
18.4.3.4 ***Test criteria and method of assessing results***

The result is considered "+" and the substance should not be classified in Division 5.1 if the limiting diameter is 2.0 mm or more. The result is considered "—" if the limiting diameter is less than 2.0 mm.

18.4.3.5 ***Examples of results***

Substance	**Result**
to be added	

*/ The upper part of the tube remaining in the closing device is counted as one fragment.



(A)	Nut (b = 10.0 or 20.0 mm) with flats for size 41 spanner	(B)	Orifice plate (a = 1.0 → 20.0 mm diameter)
(C)	Threaded collar	(D)	Flats for size 36 spanner
(E)	Flange	(F)	Tube

Figure 18.4.3.1.1: TEST TUBE ASSEMBLY

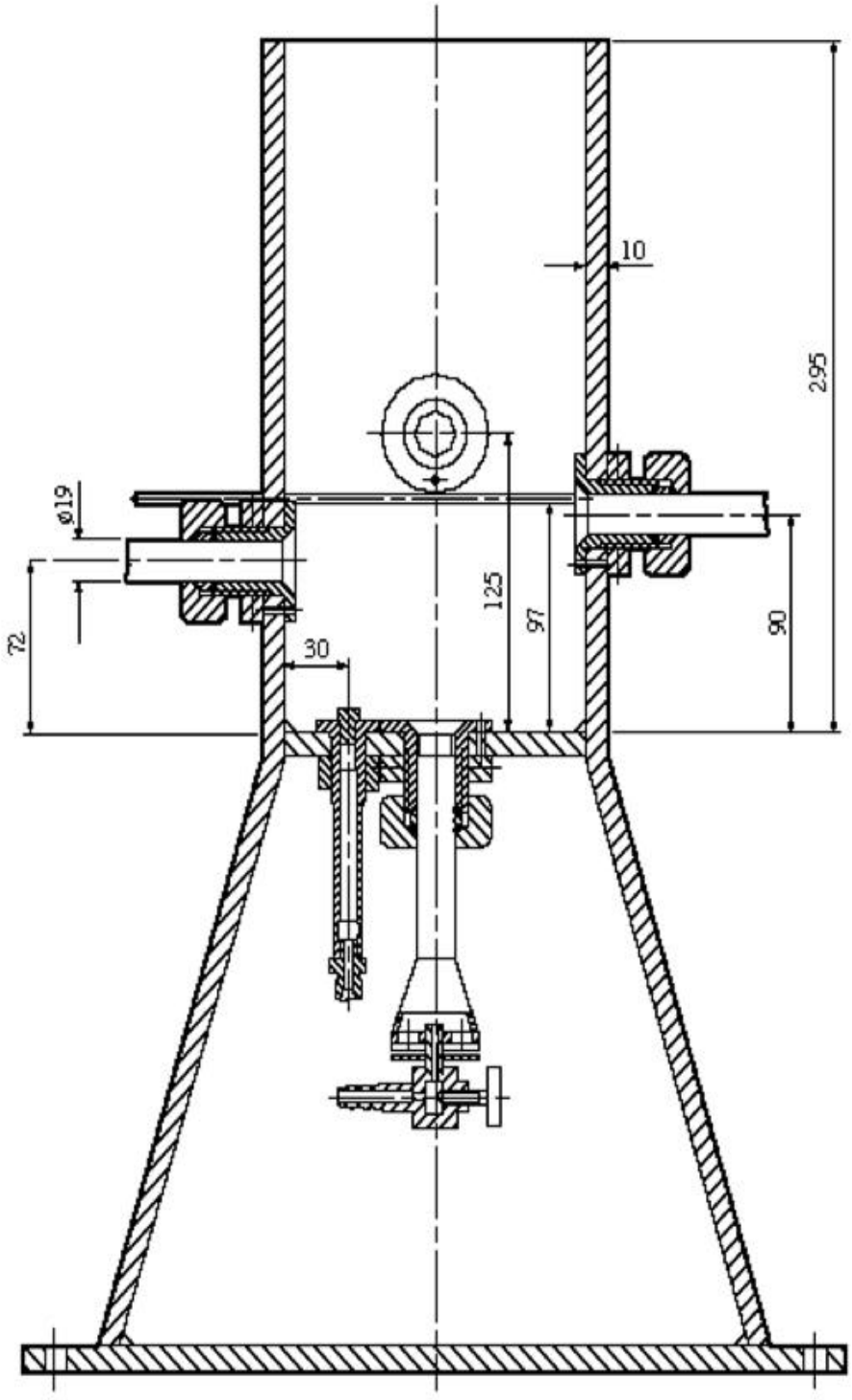


Figure 18.4.3.1.2: HEATING AND PROTECTIVE DEVICE

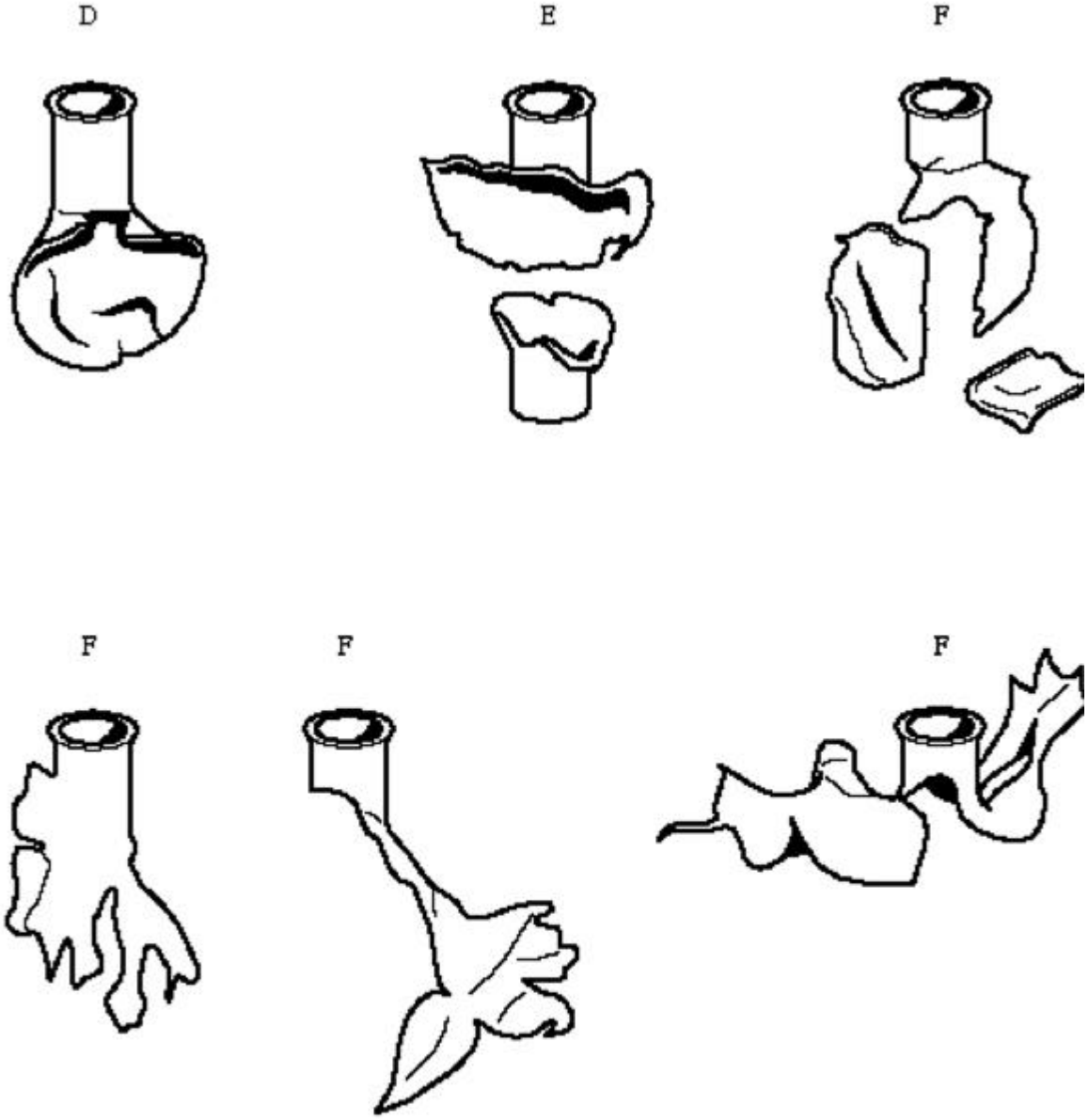


Figure 18.4.3.1.3 EXAMPLES OF EFFECT TYPES D, E AND F

18.4.4 ***Test 8 (d): USA vented pipe test***

18.4.4.1 ***Introduction***

The vented pipe test is used to assess the effect of exposure of a candidate ammonium nitrate emulsion, intermediate for blasting explosives to a large fire under confined, vented conditions.

18.4.4.2 ***Apparatus and materials***

The following items are needed:

(a) A steel pipe ***(specification to be provided by USA)*** 30 ± 1 cm diameter and 60 ± 1 cm long, welded close at the bottom with a 38 cm square, 10 ± 0.5 mm thick mild steel plate. The top of the pipe is welded to a 38 cm square, 10 ± 0.5 mm thick mild steel plate that contains a 76 mm diameter vent hole centrally located in the plate to which a 150 mm long steel pipe nipple of 76 mm internal diameter is welded. (See figure 18.4.4.1.1) ***(Further specifications on inner/outer diameter, wall thickness and tolerances to be provided)***

(b) A metal grid strong enough to support the filled pipe above the fuel and allow adequate heating.

(c) Enough fuel to keep a fire burning for at least 30 minutes or, if necessary, until the substance has clearly had enough time to react to the fire.

(d) Suitable means of ignition, e.g. fuel oil and pyrotechnic igniter with wood wool.

Video or movie cameras may be used.

18.4.4.3 ***Procedure***

18.4.4.3.1 The pipe is filled with the substance under test without tamping during loading. The substance is carefully packed to prevent adding voids. The steel pie is placed vertically on the grid. Fuel is placed beneath the grid so that the fire will engulf the pipe. Precautions against side winds may be required to avoid dissipation of the heat. Suitable methods of heating include a wood fire using a lattice of wooden laths, liquid or a gas fuel fire, that produces a flame temperature of at least 800° C. ***The fire shall be started from a safe place. If the pipe does not rupture, the system should be allowed to cool down before carefully dismantling the test set-up and emptying the pipe.***

18.4.4.3.2 Observations are made on the following:

(a) evidence of explosion;

(b) loud noise; and

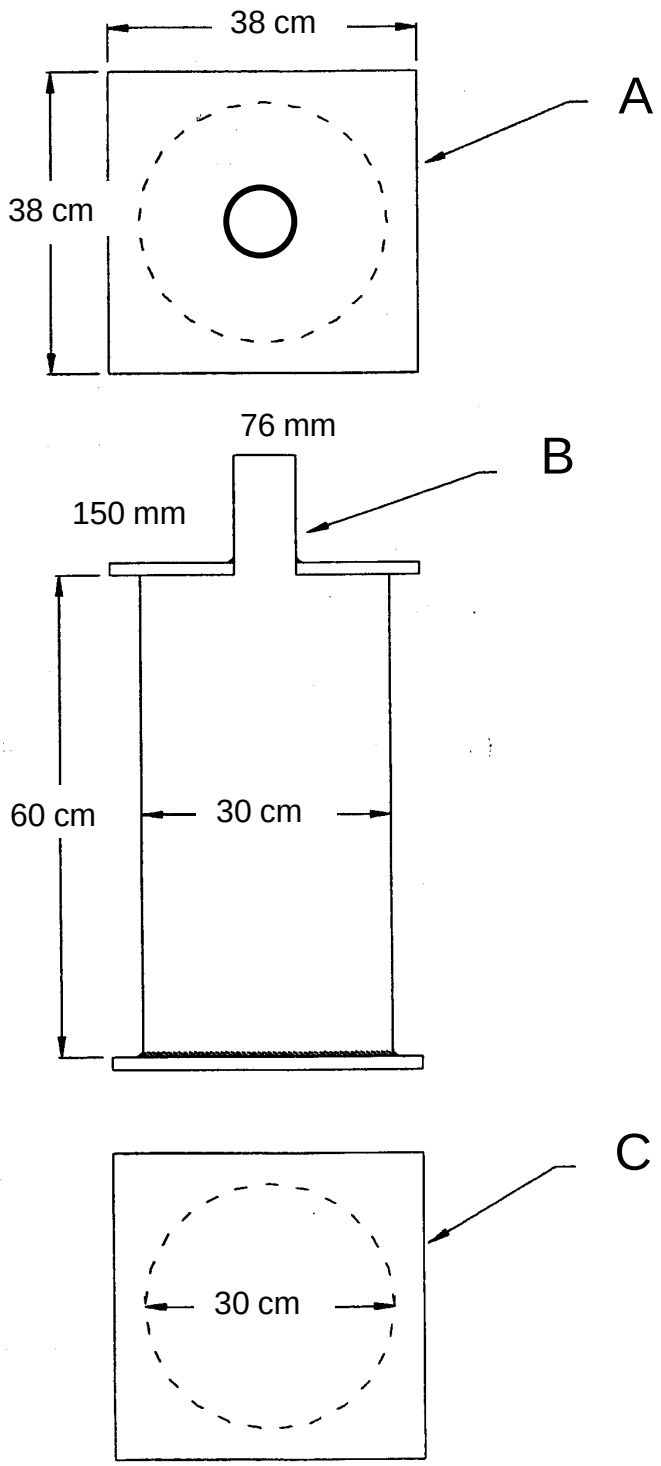
(c) projection of fragments from the fire area.

18.4.4.4 ***Test criteria and method of assessing results***

The test result is considered "+" and the substance should not be classified in Division 5.1 if an explosion or a rupture of the pipe is observed. If no explosion or rupture of the pipe is observed then the result is considered "—".

18.4.4.5 ***Examples of results***

Substance	**Result**
to be added	



(A) Top plate
(B) Steel pipe nipple
(C) Bottom plate

Figure 18.4.4.1: VENTED PIPE TEST