

Recommendations on the

TRANSPORT OF DANGEROUS GOODS

Manual of Tests and Criteria

Fourth revised edition

Amendment 2



UNITED NATIONS

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FOREWORD

The Manual of Tests and Criteria contains criteria, test methods and procedures to be used for classification of dangerous goods according to the provisions of Parts 2 and 3 of the United Nations *Recommendations on the Transport of Dangerous Goods, Model Regulations*¹, as well as of chemicals presenting physical hazards according to the *Globally Harmonized System of Classification and Labelling of Chemicals (GHS)*².

As a consequence, it supplements also national or international regulations which are derived from the United Nations Recommendations on the Transport of Dangerous Goods or the GHS.

Originally developed by the Economic and Social Council's Committee of Experts on the Transport of Dangerous Goods which adopted a first version in 1984, it has been regularly updated and amended every two years. Presently, the updating is done under the auspices of the Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals, which replaces the original committee since 2001.

The fourth revised edition, published in 2003, reflected the recommendations of the new Committee of Experts at its first session (11-12 December 2002). A first set of amendments to the fourth revised edition was published in 2005, reflecting the recommendations of the Committee of Experts at its second session (10 December 2004).

The amendments listed in this publication were adopted by the Committee at its third session (14 December 2006)³.

They include:

- Amendments to the assignment procedure for ammonium nitrate emulsion, suspension or gel, intermediate for blasting explosives;
- Amendments to the specifications and quality control of steel tubes used in the Koenen test;
- The addition of a modified vented pipe test; and
- Amendments reflecting the inclusion of separate entries for lithium metal batteries and lithium ion batteries.

¹ ST/SG/AC.10/1/Rev.15. United Nations publication, sales No. 07.VIII.1.

² ST/SG/AC.10/30/Rev.2. United Nations publication, sales No. 07.II.E.5.

³ ST/SG/AC.10/34/Add.2.

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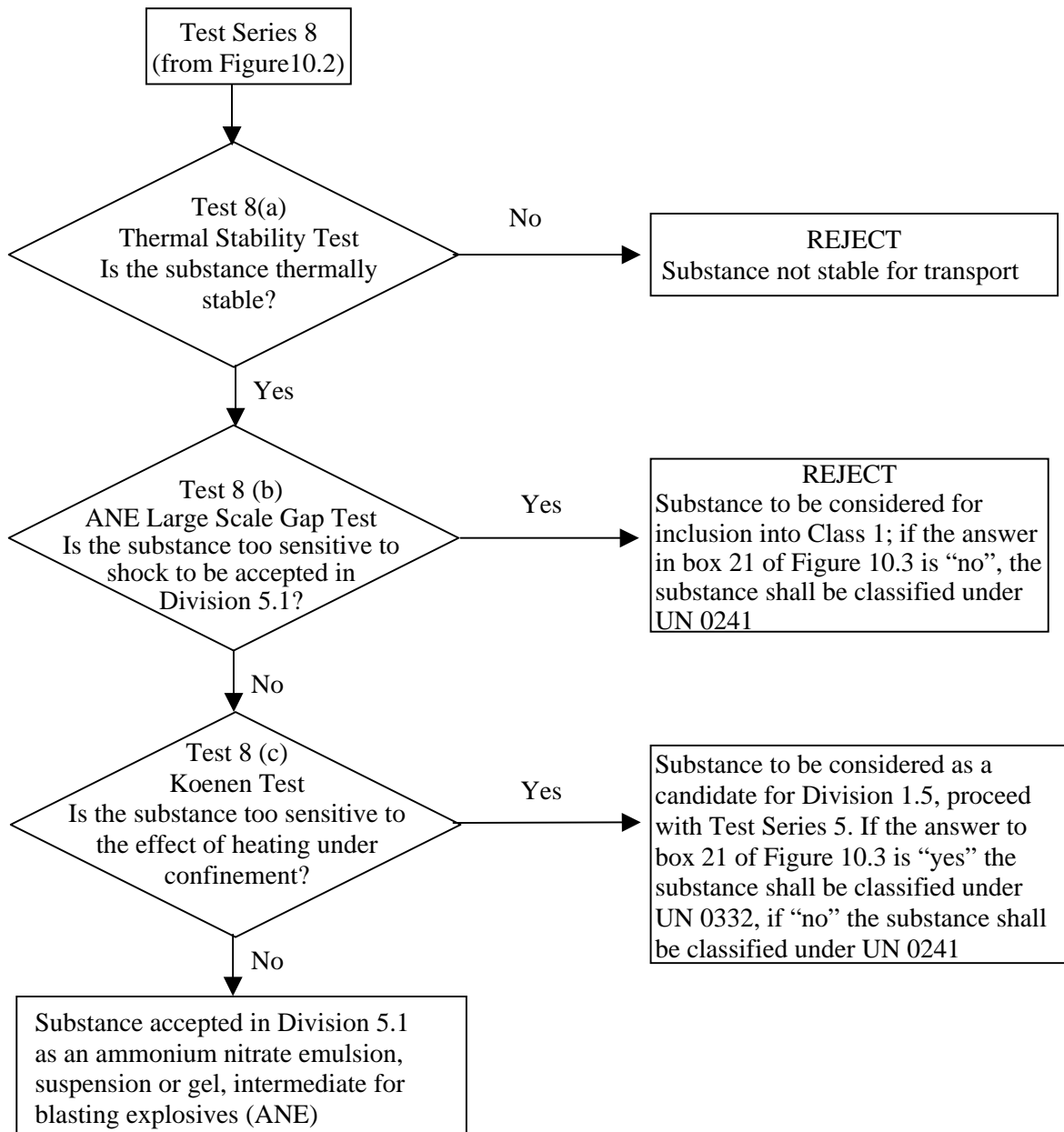
**AMENDMENTS TO THE FOURTH REVISED EDITION OF
THE MANUAL OF TESTS AND CRITERIA**

PART I OF THE MANUAL

Section 10

10.4.3.3 (a) Replace “a qualified explosives expert” with “the competent authority”.

Figure 10.4 Amend to read as follows:



Section 11

11.5.1.2.1 Amend to read as follows:

“11.5.1.2.1 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 conforming to specification DC04 (EN 10027-1), or equivalent A620 (AISI/SAE/ASTM), or equivalent SPCEN (JIS G 3141). The dimensions are given in Figure 11.5.1.1. 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 11.5.1.1.

For quality control of the steel tubes, 1% of the tubes from each production lot shall be subjected to quality control and the following data shall be verified:

- (a) The mass of the tubes shall be 26.5 ± 1.5 g, tubes to be used in one test sequence shall not differ in mass by more than 1 g;
- (b) The length of the tubes shall be 75 ± 0.5 mm;
- (c) The wall thickness of the tubes measured 20 mm from the bottom of the tube shall be 0.5 ± 0.05 mm; and
- (d) The bursting pressure as determined by quasi-static load through an incompressible fluid shall be 30 ± 3 MPa.”.

Section 12

12.5.1.2.1 Amend to read as follows:

“12.5.1.2.1 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 conforming to specification DC04 (EN 10027-1), or equivalent A620 (AISI/SAE/ASTM), or equivalent SPCEN (JIS G 3141). The dimensions are given in Figure 12.5.1.1. 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 12.5.1.1.

For quality control of the steel tubes, 1% of the tubes from each production lot shall be subjected to quality control and the following data shall be verified:

- (a) The mass of the tubes shall be 26.5 ± 1.5 g, tubes to be used in one test sequence shall not differ in mass by more than 1 g;
- (b) The length of the tubes shall be 75 ± 0.5 mm;
- (c) The wall thickness of the tubes measured 20 mm from the bottom of the tube shall be 0.5 ± 0.05 mm; and
- (d) The bursting pressure as determined by quasi-static load through an incompressible fluid shall be 30 ± 3 MPa.”.

Section 17

17.6.1.4 Replace “277 kPa” with “27 kPa”. (*Correction*)

Section 18

Table 18.1 Against “8 (d)”, replace “test” with “tests”.

In note b after the table, replace “This test is” with “These tests are”.

18.6.1.2.1 Amend to read as follows:

“18.6.1.2.1 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 conforming to specification DC04 (EN 10027-1), or equivalent A620 (AISI/SAE/ASTM), or equivalent SPCEN (JIS G 3141). The dimensions are given in Figure 18.6.1.1. 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 18.6.1.1.

For quality control of the steel tubes, 1% of the tubes from each production lot shall be subjected to quality control and the following data shall be verified:

- (a) The mass of the tubes shall be 26.5 ± 1.5 g, tubes to be used in one test sequence shall not differ in mass by more than 1 g;
- (b) The length of the tubes shall be 75 ± 0.5 mm;
- (c) The wall thickness of the tubes measured 20 mm from the bottom of the tube shall be 0.5 ± 0.05 mm; and
- (d) The bursting pressure as determined by quasi-static load through an incompressible fluid shall be 30 ± 3 MPa.”.

18.7.1 Replace “8 (d)” with “8 (d) (i)”.

18.7.1.2 (a) Replace “ 31 ± 1 cm” with “ 310 ± 10 mm”, “ 61 ± 1 cm” with “ 610 ± 10 mm” and “38 cm” with “380 mm” (twice).

Figure 18.7.1.1 Replace “1.2” with “10” (twice) and change the measurements to millimetres. Insert the following new sentence below the figure: “All measurements are in millimetres.”.

Add a new 18.7.2 to read as follows:

“18.7.2 *Test 8 (d) (ii): Modified vented pipe test*

18.7.2.1 *Introduction*

This test is not intended for classification but is included in this Manual for evaluating the suitability of bulk substances to be transported in tanks.

The modified 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.

18.7.2.2 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 fillet weld with a thickness of at least 5 mm. The top plate has a vent diameter of $85 \text{ mm} \pm 1.0$ 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 a propane flow rate of up to 60 g/min. 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 propane 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) Propane bottle(s) connected via a manifold and fed into a pressure regulator. Other fuel gases may be used providing the specified heating rate is obtained. The pressure regulator should reduce the propane bottle pressure from 600 kPa down to about 150 kPa. The gas then flows through a gas rotameter capable of measuring up to 60 g/min of propane and a needle valve. An electrical solenoid valve is used to switch the propane flow on and off remotely. Typically three 9 kg propane bottles will achieve the desired gas flow rate for the duration of up to five tests. The gas pressure and flow are regulated to give a heating rate of 3.3 ± 0.3 K/min when measured by the calibration procedure;
- (g) Three thermocouples with 500 (2) and 100 (1) 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-cameras 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.

18.7.2.3 Calibration

18.7.2.3.1 The vessel is filled to the 75% level (i.e. to a depth of 435 mm) with the pure water, and heated using the procedure specified in 18.7.2.4. Water is heated from ambient temperature up to 90 °C, monitoring temperature by the thermocouple in the water. Temperature-time data must fit a straight line whose slope will be the “calibration heating rate” for the given combination of vessel and heat source.

18.7.2.3.2 The gas pressure and flow must be regulated to give a heating rate of 3.3 ± 0.3 K/min.

18.7.2.3.3 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 day of the calibration provided no change is made to the vessel construction or gas supply. New calibration has to be made every time that the burner is changed.

18.7.2.4 *Procedure*

18.7.2.4.1 The concrete block is placed on a sandy base and levelled using a spirit level. The propane 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.

18.7.2.4.2 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 435 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 propane flame from heat dissipation due to side winds.

18.7.2.4.3 The thermocouple positions are as follows:

- (a) The first 500 mm long probe (T1) in the gas flame;
- (b) The second 500 mm long probe (T2) extending all the way into the vessel so that the tip is positioned 80 to 90 mm from the bottom of the vessel;
- (c) The third 100 mm long probe (T3) in the headspace 20 mm into 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.

18.7.2.4.4 Propane pressure and flow is checked and adjusted to the values used during the water calibration described in 18.7.2.3. Video cameras and any other recording equipment are checked and started. Thermocouple functioning is checked and data logging is started, with a time set between thermocouple readings not exceeding 10 seconds, and preferably shorter. The test should not be performed under conditions where the wind speed exceeds 6 m/s. With higher wind speed, additional precautions against side winds are required to avoid dissipation of the heat.

18.7.2.4.5 The propane 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. The start time of the trial is defined by the time at which the flame thermocouple trace T1 first begins to rise.

18.7.2.4.6 The gas reservoir should be large enough to bring the substance to a possible reaction and provide a fire duration lasting beyond total consumption of the test sample. If the vessel does not rupture, the system should be allowed to cool down before carefully dismantling the test set-up.

18.7.2.4.7 The test outcome is determined by whether or not a rupture of the vessel is observed when the test reaches conclusion. Evidence of test conclusion is based on:

- (a) The visual and aural observation of vessel rupture accompanied by loss of thermocouple traces;
- (b) The visual and aural observation of vigorous venting accompanied by peaking of both vessel thermocouple traces and no substance remains in the vessel; or

- (c) The visual observation of decreased levels of fuming following the peaking of both vessel thermocouple traces at temperatures in excess of 300 °C and no substance remains in the vessel.

For the purposes of assessing results, the term “rupture” includes any failure of welds and any fracture of metal in the vessel.

18.7.2.4.8 The test is performed two times unless a positive result is observed.

18.7.2.5 *Test criteria and method of assessing results*

The test result is considered “+” and the substance should not be transported in tanks as a dangerous substance of Division 5.1 if an explosion is observed in any trial. Explosion is evidenced by rupture of the vessel. Once the substance is consumed in both trials and no rupture of the vessel is observed, then the result is considered “-”.

18.7.2.6 *Examples of results*

Substances	Result
76.0 ammonium nitrate / 17.0 water / 5.6 paraffin oil / 1.4 PIBSA emulsifier	-
84.0 ammonium nitrate / 9.0 water / 5.6 paraffin oil / 1.4 PIBSA emulsifier	+
67.7 ammonium nitrate / 12.2 sodium nitrate / 14.1 water / 4.8 paraffin oil / 1.2 PIBSA emulsifier	-
67.4 ammonium nitrate / 15.0 methylamine nitrate / 12.0 water / 5.0 glycol / 0.6 thickener	-
71.4 ammonium nitrate / 14.0 hexamine nitrate / 14.0 water / 0.6 thickener	-

”.

PART II OF THE MANUAL

Section 23

23.2.1 Insert “of one, or if necessary both,” after “of the results”.

Section 25

25.4.1.2.1 Amend to read as follows:

“25.4.1.2.1 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 conforming to specification DC04 (EN 10027-1), or equivalent A620 (AISI/SAE/ASTM), or equivalent SPEN (JIS G 3141). The dimensions are given in Figure 25.4.1.1. 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 25.4.1.1.

For quality control of the steel tubes, 1% of the tubes from each production lot shall be subjected to quality control and the following data shall be verified:

- (a) The mass of the tubes shall be 26.5 ± 1.5 g, tubes to be used in one test sequence shall not differ in mass by more than 1 g;
- (b) The length of the tubes shall be 75 ± 0.5 mm;
- (c) The wall thickness of the tubes measured 20 mm from the bottom of the tube shall be 0.5 ± 0.05 mm; and
- (d) The bursting pressure as determined by quasi-static load through an incompressible fluid shall be 30 ± 3 MPa.”.

PART III OF THE MANUAL

Section 32

32.3.1.6 (b) Insert “or environmentally hazardous” at the end.

32.3.1.7 (c) In the table, replace “-5 and below” with “no limit”.

Section 38

38.3 Amend the heading to read: “Lithium metal and lithium ion batteries”.

38.3.1 Replace “lithium cells” with “lithium metal and lithium ion cells” and, in the parenthesis, replace “and 3091” with “, 3091, 3480 and 3481”.

38.3.2.1 In the first sentence, replace “Lithium cells” with “Lithium metal and lithium ion cells”.

In the second sentence, replace “Lithium cells” with “Cells” at the beginning.

In the last sentence, replace “lithium cell” with “cell”.

38.3.2.2 In the definitions of *Large battery* and of *Small battery*, at the beginning, replace “battery” with “lithium metal battery”.

In the definitions of *Large cell* and of *Small cell*, at the beginning, replace “cell” with “lithium metal cell”.

In the definition of *Large cell*, delete “or lithium equivalent content”.

In the definition of *Aggregate lithium content* delete “or lithium equivalent content”.

Delete the definitions of *Equivalent lithium content* and *Lithium-equivalent content*.

In the definition of *Large battery*, insert the following phrase at the end “, or in the case of a lithium ion battery, means a battery with a Watt-hour rating of more than 6 200 Wh”.

In the definition of *Large cell*, insert the following phrase at the end “, or in the case of a lithium ion cell, means a cell with a Watt-hour rating of more than 150 Wh”.

In the definition of *Small battery*, insert the following phrase at the end “, or in the case of a lithium ion battery, means a battery with a Watt-hour rating of not more than 6 200 Wh”.

In the definition of *Small cell*, insert the following phrase at the end “, or in the case of a lithium ion cell, means a cell with a Watt-hour rating of not more than 150 Wh”.

Add a new definition to read as follows:

“*Watt-hour rating*, expressed in Watt-hours, is calculated by multiplying a cell’s or battery’s rated capacity, in ampere-hours, by its nominal voltage.”.

38.3.3 In the last sentence, replace “in which the aggregate lithium content of all anodes, when fully charged, is more than 500g” with “of a size comparable to a large battery”.