

UN/SCETDG/52/INF.3/Add.2 UN/SCEGHS/34/INF.3/Add.2

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

31 October 2017

Sub-Committee of Experts on the Transport of Dangerous Goods

Fifty-second session

Geneva, 26 November - 6 December 2017

Item 10 (d) of the provisional agenda

**Issues relating to the Globally Harmonized System
of Classification and Labelling of Chemicals: Use
of the Manual of Tests and Criteria in the context
of the GHS**

Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals

Thirty-fourth session

Geneva, 6 - 8 December 2016

Item 2 (a) of the provisional agenda

**Work of the TDG Sub-Committee on matters of
interest to the GHS Sub-Committee**

Revision of the Manual of Tests and Criteria: Part II (sections 20 to 28)

Transmitted by the Chairman of the Working Group on Explosives on behalf of the Working Group

This document takes account of the amendments to the 6th revised edition of the Manual of Tests and Criteria agreed by the Working Group so far (see ST/SG/AC.10/C.3/102 paragraphs 95 to 97 and ST/SG/AC.10/C.4/66 paragraph 8).

PART II

**CLASSIFICATION PROCEDURES,
TEST METHODS AND CRITERIA
RELATING TO
SELF-REACTIVE SUBSTANCES ~~OF~~
~~DIVISION 4.1~~
AND ORGANIC PEROXIDES ~~OF~~
~~DIVISION 5.2~~**

CONTENTS OF PART II

NOTE 1: The country or organisation of origin of each test method is indicated in brackets after each test name.

NOTE 2: The test method recommended for use with each test type is indicated in **bold** and by an asterisk (see subsection 1.6 of the general Introduction).

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SECTION 20

INTRODUCTION TO PART II

20.1 Purpose

20.1.1 Part II of the Manual presents the United Nations schemes for the classification of self-reactive substances ~~of Division 4.1~~ and organic peroxides ~~of Division 5.2 (see respectively sub-section 2.4.2.3 and section 2.5.3 of the Model Regulations)~~. It includes a description of the procedures, test methods and criteria considered to be the most suitable for providing competent authorities with the necessary information to arrive at a proper classification of these substances ~~for transport~~. It should be used in conjunction with the classification principles given in Section 20, paragraphs 20.4.2 ~~(Division 4.1)~~ and 20.4.3 ~~(Division 5.2) and~~, the flow chart given in Figure 20.1 ~~of this Manual, sub-sections 2.4.2.3 and 2.5.3 of the Model Regulations, and Chapters 2.8 and 2.15 of the GHS (see also 2.4.2.3.3 and 2.5.3.3 in the Model Regulations)~~.

20.1.2 Self-reactive substances and organic peroxides are classified into seven types according to ~~the hazard~~ **their hazards**. The scheme for classifying these substances is illustrated in Figure 20.1. The tests are performed in two stages. ***In the first stage, for the safety of laboratory workers, preliminary small scale tests should be performed to ascertain the stability and sensitivity of the substance.*** ~~In the second stage,~~ **The** classification tests should be performed in the second stage.

20.2 Scope

20.2.1 New substances, capable of exothermic decomposition, ~~offered for transport~~ should be subjected to the classification procedures for self-reactive substances as set out in this section unless:

- (a) They are explosives ~~(see Part I) according to the criteria of Class 1;~~
- (b) They are oxidizing substances ~~according to the classification procedure for Division 5.1 (see section 34) except that mixtures of oxidizing substances which contain 5.0% or more of combustible organic substances shall be subjected to the classification procedure defined described~~ in the NOTE below;

NOTE: Mixtures of oxidizing substances ~~meeting the criteria of Division 5.1~~ which contain 5.0% or more of combustible organic substances, which do not meet the criteria mentioned in (a), (c), (d) or (e) ~~above~~, shall be subjected to the self-reactive substance classification procedure.

A mixture showing the properties of a self-reactive substance, type B to F, shall be classified as a self-reactive substance of Division 4.1.

A mixture showing the properties of a self-reactive substance, type G, according to the principle of 20.4.2 (g) shall be considered for classification as an oxidizing substance of Division 5.1 (see section 34).

- (c) They are organic peroxides ~~according to the criteria of Division 5.2 (see 20.2.2);~~
- (d) Their heat of decomposition (see 20.3.3.3) is less than 300 J/g; or
- (e) Their self-accelerating decomposition temperature is greater than 75 °C for a 50 kg package.

20.2.2 New organic peroxides offered for transport classification should be subjected to the ~~classification~~ procedures as set out in this section unless the organic peroxide formulation contains:

- (a) Not more than 1.0% available oxygen from the organic peroxides when containing not more than 1.0% hydrogen peroxide; or

- (b) Not more than 0.5% available oxygen from the organic peroxides when containing more than 1.0% but not more than 7.0% hydrogen peroxide.

20.2.3 In this context a new substance is one which, in the opinion of the competent authority, involves any of the following:

- (a) A new self-reactive substance which meets the definition given in [20.2.1 paragraph 2.4.2.3.1.1 of the Model Regulations](#), or a mixture of already classified self-reactive substances which is considered to be significantly different from those already classified;
- (b) An activator is added to an already classified self-reactive substance (see paragraphs 2.4.2.3.2.1 and 2.4.2.3.2.2 of the Model Regulations) which decreases the thermal stability or alters the explosive properties; or
- (c) A new organic peroxide which meets the definition given in [20.2.2 paragraph 2.5.1 of the Model Regulations](#), or a mixture of already classified organic peroxides which is considered to be significantly different from those already classified.

20.2.4 Mixtures of organic peroxide formulations currently assigned to a generic entry [in the dangerous goods list of Chapter 3.2 of the Model Regulations](#) may be classified as the same type of organic peroxide as that of the most dangerous component and be transported under the conditions of transport given for this type. However, as two components can form a thermally less stable mixture, the self-accelerating decomposition temperature (SADT) of the mixture should be determined and, if necessary, the control and emergency temperature derived from the SADT in accordance with paragraph 2.5.3.4 of the Model Regulations.

20.2.5 The classification procedure should be undertaken before a new product is offered for [transport classification](#).

20.2.6 Any substance which shows the properties of a self-reactive substance (except type G) should be classified as such, even if this substance gives a positive test result according to the test method for self-heating substances [of Division 4.2](#) (see section 32.5.2 ~~of this Manual and Chapter 2.4 of the Model Regulations~~).

20.3 Preliminary procedure

20.3.1 General description

It is essential for the safety of laboratory workers that small-scale preliminary tests are performed before attempting to handle larger quantities. This involves tests for determining the sensitiveness of the substance to mechanical stimuli (impact and friction), and to heat and flame.

20.3.2 Test types

Generally four types of small scale test may be used to make a preliminary safety assessment:

- (a) A falling weight test to determine sensitiveness to impact;
- (b) A friction or impacted friction test to determine the sensitiveness to friction;
- (c) A test to assess thermal stability and the exothermic decomposition energy; and
- (d) A test to assess the effect of ignition.

20.3.3 Application of the test methods

20.3.3.1 *For safety, it is usual to perform the tests requiring the smallest quantity of material first.*

20.3.3.2 Impact and friction sensitiveness may be assessed using one of the tests in series 3 of the [Class 1 acceptance procedure for the class of explosives](#) (see Part I).

20.3.3.3 Thermal stability may be estimated using a suitable calorimetric technique such as differential scanning calorimetry or adiabatic calorimetry. Exothermic decomposition energy may be estimated using a suitable

calorimetric technique ~~such as differential scanning calorimetry~~. In using such techniques, special care should be taken in interpreting the results when:

- Sampling and testing mixtures;
- The material of the sample vessel may influence the result;
- Endotherms immediately precede exotherms;
- Evaporation of constituents will lower the exothermicity (sealed sample vessels should normally be used);
- The presence of air may critically affect the measured decomposition energy;
- There is a large difference between the specific heats of the reactants and products; and
- Using rapid heating rates (when differential scanning calorimetry is used, the heating rates should normally be in the range of 2 to 5 K/min).

If differential scanning calorimetry is used, the extrapolated onset temperature is defined as being the point of intersection of the tangent drawn at the point of greatest slope on the leading edge of the peak with the extrapolated baseline.

20.3.3.4 Any suitable method may be used to assess the effect of ignition provided it adequately identifies those materials which react violently under little or no confinement.

Figure 20.1(a): FLOW CHART SCHEME FOR SELF-REACTIVE SUBSTANCES AND ORGANIC PEROXIDES

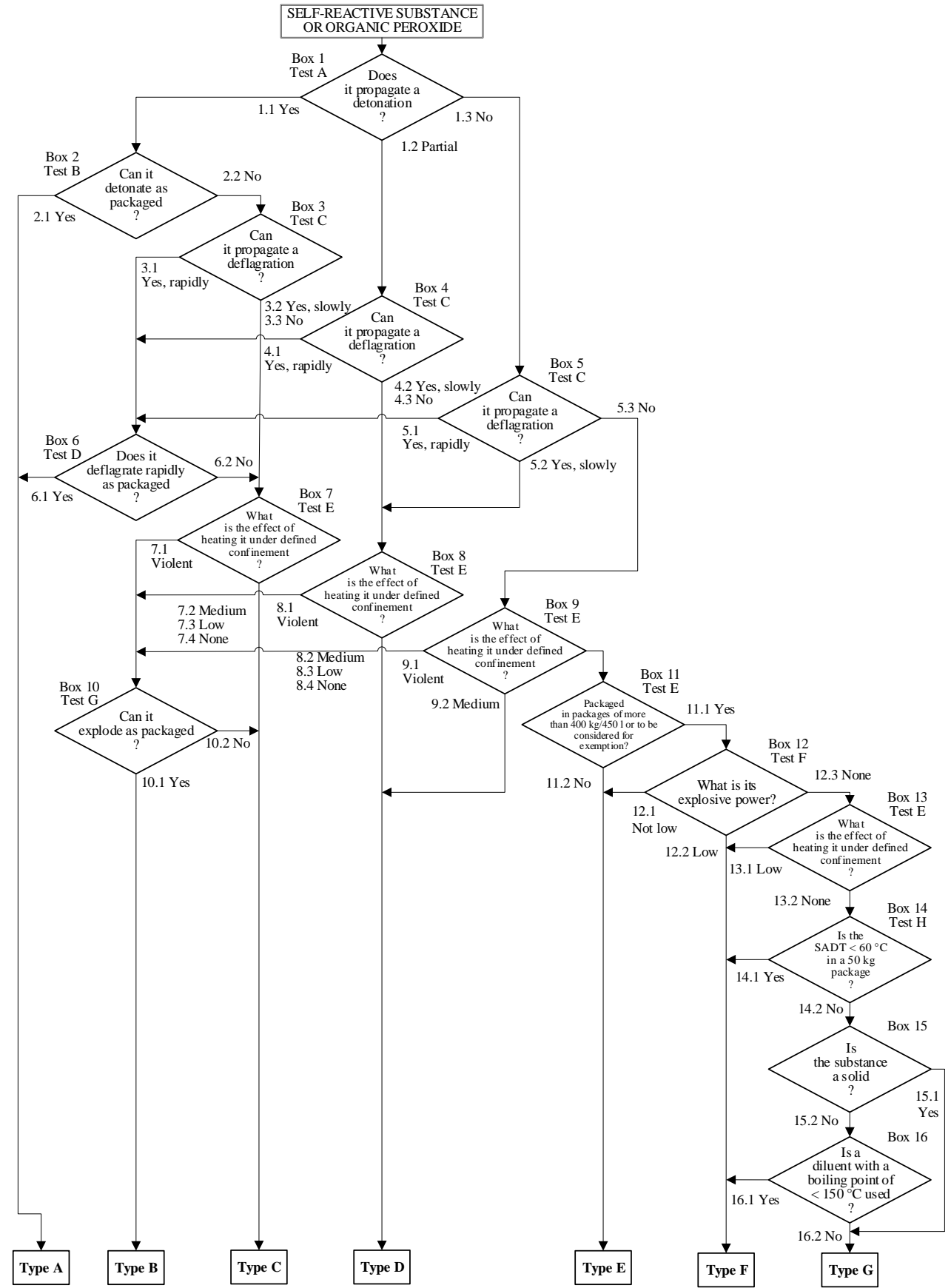


Figure 20.1 (b): FLOW CHART SCHEME FOR SELF-REACTIVE SUBSTANCES AND ORGANIC PEROXIDES (cont'd)

Note to Figure 20.1:

For transport:

- *Type A: not accepted for transport in that packaging;*
- *Type B: accepted for transport in packages of not more than 25 kg net mass with an “Explosive” subsidiary hazard label;*
- *Type C: accepted for transport in packages of not more than 50 kg net mass;*
- *Type D: accepted for transport in packages of not more than 50 kg net mass;*
- *Type E: accepted for transport in packages of not more than 400 kg/450 litres;*
- *Type F: may be considered for transport in IBCs or tanks;*
- *Type G: shall be considered for exemption.*

20.4 Classification procedures

20.4.1 General description

20.4.1.1 The principles of classification of self-reactive substances and organic peroxides are given in subsections 20.4.2 and 20.4.3 respectively ~~(see also paragraphs 2.4.2.3.3 and 2.5.3.3 of the Model Regulations)~~. The general scheme for classification (flow chart) is shown in Figure 20.1. Self-reactive substances and organic peroxides are classified into seven types according to ~~the hazard~~**their hazards**. In order to determine the substance type, it is necessary to determine the properties as requested in the boxes of the flow chart and the additional requirements in the classification principles. The types range from type A, which is not accepted for transport in the packaging in which it is tested, to type G which is exempted from the provisions for self-reactive substances ~~of Division 4.1~~ or organic peroxides ~~of Division 5.2~~. The classification of types B to F is directly related to the maximum quantity allowed in one packaging.

20.4.1.2 A self-reactive substance or organic peroxide formulation should be regarded as possessing explosive properties when in laboratory testing the formulation is liable to detonate, to deflagrate rapidly or to show a violent effect when heated under confinement.

20.4.1.3 The self-accelerating decomposition temperature (SADT) is defined as the lowest ambient temperature at which self-accelerating decomposition may occur in a substance in the packaging ~~as used in transport~~ ~~(see sub-section 2.5.3.4 of the Model Regulations)~~. An SADT should be determined in order to decide if:

- (a) A substance should be subjected to temperature control ~~during transport~~;
- (b) When appropriate, a substance conforms to the requirements of type G; or
- (c) When appropriate, a substance meets the SADT criterion for self-reactive substances.

20.4.1.4 When appropriate, the physical form of the substance should be determined as set out under definition of liquids ~~in paragraph 1.2.1 of the Model Regulations~~¹.

20.4.1.5 The substance type, physical form and whether or not temperature control is required are used to make the assignment of the substance to the appropriate generic entry **in the Dangerous Goods List of the Model Regulations**.

¹ *Liquid means a dangerous good which at 50 °C have a vapour pressure of not more than 300 kPa (3 bar), which is not completely gaseous at 20 °C and at a pressure of 101.3 kPa, and which has a melting point or initial melting point of 20 °C or less at a pressure of 101.3 kPa. A viscous substance for which a specific melting point cannot be determined shall be subjected to the ASTM D 4359-90 test; or to the test for determining fluidity (penetrometer test) prescribed in section 2.3.4 of Annex A of the European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR).*

20.4.2 Classification of self-reactive substances

~~The following principles should be applied to the classification of self-reactive substances not listed in paragraph 2.4.2.3.2.3 of the Model Regulations. Self-reactive substances are classified in one of the seven categories "Types A to G" according to the following principles²:~~

- (a) Any self-reactive substance which can detonate or deflagrate rapidly, as packaged ~~for transport, should be prohibited from transport under the provisions for self-reactive substances of Division 4.1 in that packaging~~ (will be defined as self-reactive substance type Type A, exit box A of Figure 20.1);
- (b) Any self-reactive substance possessing explosive properties and which, as packaged ~~for transport, neither detonates nor deflagrates rapidly, but is liable to undergo a thermal explosion in that package, should also bear an "EXPLOSIVE" subsidiary risk label. Such a substance may be packaged in amounts of up to 25 kg unless the maximum quantity has to be limited to a lower amount to preclude detonation or rapid deflagration in the package~~ (will be defined as self-reactive substance type Type B), exit box B of Figure 20.1);
- (c) Any self-reactive substance possessing explosive properties ~~may be transported without an "EXPLOSIVE" subsidiary risk label when the substance as packaged (maximum 50 kg) for transport cannot detonate or deflagrate rapidly, or undergo a thermal explosion~~ (will be defined as self-reactive substance type Type C, exit box C of Figure 20.1);
- (d) Any self-reactive substance which in laboratory testing:
 - (i) detonates partially, does not deflagrate rapidly and shows no violent effect when heated under confinement; or
 - (ii) does not detonate at all, deflagrates slowly and shows no violent effect when heated under confinement; or
 - (iii) does not detonate or deflagrate at all and shows a medium effect when heated under confinement;
~~may be accepted for transport in packages of not more than 50 kg net mass~~ (will be defined as self-reactive substance type Type D, exit box D of Figure 20.1);
- (e) Any self-reactive substance which, in laboratory testing, neither detonates nor deflagrates at all and shows low or no effect when heated under confinement ~~may be accepted for transport in packages of not more than 400 kg/450 litres~~ (will be defined as self-reactive substance type Type E, exit box E of Figure 20.1);
- (f) Any self-reactive substance which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows only a low or no effect when heated under confinement as well as low or no explosive power ~~may be considered for transport in IBCs or tanks~~ (will be defined as self-reactive substance type TYPE F, exit box F of Figure 20.1); for additional provisions, see Model Regulations, sub-section 4.1.7.2 and packing instruction IBC520, sub-section 4.2.1.13 and portable tank instruction T23;
- (g) Any self-reactive substance which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows no effect when heated under confinement nor any explosive power, ~~should be exempted from classification as a self-reactive substance of Division 4.1~~ provided that the formulation is thermally stable (self-accelerating

² ~~For transport, the following~~ these principles should be applied to the classification of self-reactive substances not listed in the Table of paragraph 2.4.2.3.2.3 of the Model Regulations.

decomposition temperature 60 °C to 75 °C for a 50 kg package) and, for liquid mixtures, any a diluent meets the requirements of paragraph 2.4.2.3.5 of the Model Regulations (defined as self-reactive substance type G, exit box G of Figure 20.1) having a boiling point greater than or equal to 150 °C is used for desensitization will be defined as self-reactive substance TYPE G. If the formulation-mixture is not thermally stable or a compatible-diluent having a boiling point less than 150 °C is used for desensitization, the formulation-mixture should shall be defined as self-reactive liquid/solid substance TYPE F.

20.4.3 Classification of organic peroxides

The following principles should be applied to the classification of organic peroxide formulations not listed in Table of paragraph 2.5.3.2.4 of the Model Regulations Organic peroxides are classified in one of the seven categories "Types A to G" according to the following principles³:

- (a) Any organic peroxide formulation which, as packaged, can detonate or deflagrate rapidly, as packaged for transport, should be prohibited from transport in that packaging under Division 5.2 (will be defined as organic peroxide TYPE A, exit box A of Figure 20.1);
- (b) Any organic peroxide formulation possessing explosive properties and which, as packaged, for transport, neither detonates nor deflagrates rapidly, but is liable to undergo a thermal explosion in that package, should bear an "EXPLOSIVE" subsidiary risk label. Such an organic peroxide may be packaged in amounts of up to 25 kg unless the maximum quantity has to be limited to a lower amount to preclude detonation or rapid deflagration in the package (will be defined as organic peroxide type B, exit box B of Figure 20.1);
- (c) Any organic peroxide formulation possessing explosive properties may be transported without an "EXPLOSIVE" subsidiary risk label when the substance as packaged (maximum 50 kg) for transport cannot detonate or deflagrate rapidly or undergo a thermal explosion (will be defined as organic peroxide TYPE C, exit box C of Figure 20.1);
- (d) Any organic peroxide formulation which in laboratory testing:
 - (i) detonates partially, does not deflagrate rapidly and shows no violent effect when heated under confinement; or
 - (ii) does not detonate at all, deflagrates slowly and shows no violent effect when heated under confinement; or
 - (iii) does not detonate or deflagrate at all and shows a medium effect when heated under confinementis acceptable for transport in packages of not more than 50 kg net mass (will be defined as organic peroxide TYPE D, exit box D of Figure 20.1);
- (e) Any organic peroxide formulation which, in laboratory testing, neither detonates nor deflagrates at all and shows low or no effect when heated under confinement is acceptable for transport in packages of not more than 400 kg/450 litres (will be defined as organic peroxide TYPE E, exit box E of Figure 20.1);
- (f) Any organic peroxide formulation which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows only a low or no effect when heated under confinement as well as low or no explosive power may be considered for transport in IBCs or tanks (will be defined as organic peroxide TYPE F, exit box F of Figure 20.1); for additional

³ For transport, these following principles should be applied to the classification of organic peroxide formulations not listed in Table of paragraph 2.5.3.2.4 of the Model Regulations

provisions, see Model Regulations, sub-section 4.1.7.2 and packing instruction IBC520, sub-section 4.2.1.13 and portable tank instruction T23;

- (g) Any organic peroxide ~~formulation~~ which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows no effect when heated under confinement nor any explosive power ~~should be exempted from Division 5.2~~, provided that ~~the formulation~~ it is thermally stable (self-accelerating decomposition temperature is 60 °C or higher for a 50 kg package) and, for liquid ~~formulations-mixtures~~, a diluent having a boiling point of not less than 150 °C type A is used for desensitization, ~~will be~~ (defined as organic peroxide TYPE G, ~~exit box G of Figure 20.1~~). If the ~~formulation-organic peroxide~~ is not thermally stable or a diluent having a boiling point less than 150 °C other than type A is used for desensitization, ~~the formulation should~~ it shall be defined as organic peroxide TYPE F.

20.4.4 *Test types*

20.4.4.1 Paragraphs 20.4.2 and 20.4.3 refer only to those properties of self-reactive substances and organic peroxides which are decisive for their classification. These properties should be determined experimentally.

20.4.4.2 The test methods for determining the type of self-reactive substance or organic peroxide are grouped into eight series, lettered A to H, designed to provide the information necessary to answer the questions in the flow chart given in Figure 20.1 and to apply the principles for classification.

20.4.4.3 Test series A comprises laboratory tests and criteria concerning propagation of detonation as requested in box 1 of the flow chart.

20.4.4.4 Test series B comprises a test and criteria concerning the propagation of detonation of the substance as packaged for transport, as requested in box 2 of the flow chart.

20.4.4.5 Test series C comprises laboratory tests and criteria concerning propagation of deflagration as requested in boxes 3, 4 and 5 of the flow chart.

20.4.4.6 Test series D comprises a test and criteria concerning the propagation of a rapid deflagration of the substance as packaged for transport classification, as requested in box 6 of the flow chart.

20.4.4.7 Test series E comprises laboratory tests and criteria concerning the determination of the effect of heating under defined confinement, as requested in boxes 7, 8, 9 and 13 of the flow chart.

20.4.4.8 Test series F comprises laboratory tests and criteria concerning the explosive power of substances which are considered for transport-containment in Intermediate Bulk Containers (IBCs) or tanks, or for exemption (see box 11 of the flow chart), as requested in box 12 of the flow chart.

20.4.4.9 Test series G comprises tests and criteria concerning the determination of the effect of a thermal explosion of the substance as packaged for transport classification, as requested in box 10 of the flow chart.

20.4.4.10 Test series H comprises tests and criteria concerning the determination of the self-accelerating decomposition temperature of organic peroxides and self-reactive, or potentially self-reactive substances.

20.4.5 *Application of the test methods*

20.4.5.1 The ordering of test series A to H relates more to the sequence of assessing results than to the order in which tests are conducted. The recommended sequence of laboratory scale testing is test series E, H, F, C and then A. Some tests may not be required – see the introduction to each test series.

20.4.5.2 The package tests of test series B, D and G need be performed only if indicated by the results from the corresponding tests in test series A, C and E.

20.5 Example of a test report

20.5.1 Examples of a test report and a classification are illustrated in figures 20.2 and 20.3 respectively.

20.5.2 To allow for analytical uncertainties, the concentration of the substance to be ~~transported~~ classified may be up 2% higher than the concentration tested. If an organic peroxide is tested, the available oxygen content should be given in the general data section of the report. Similarly, if a self-reactive substance is tested, the activator type and concentration, if any, should be given.

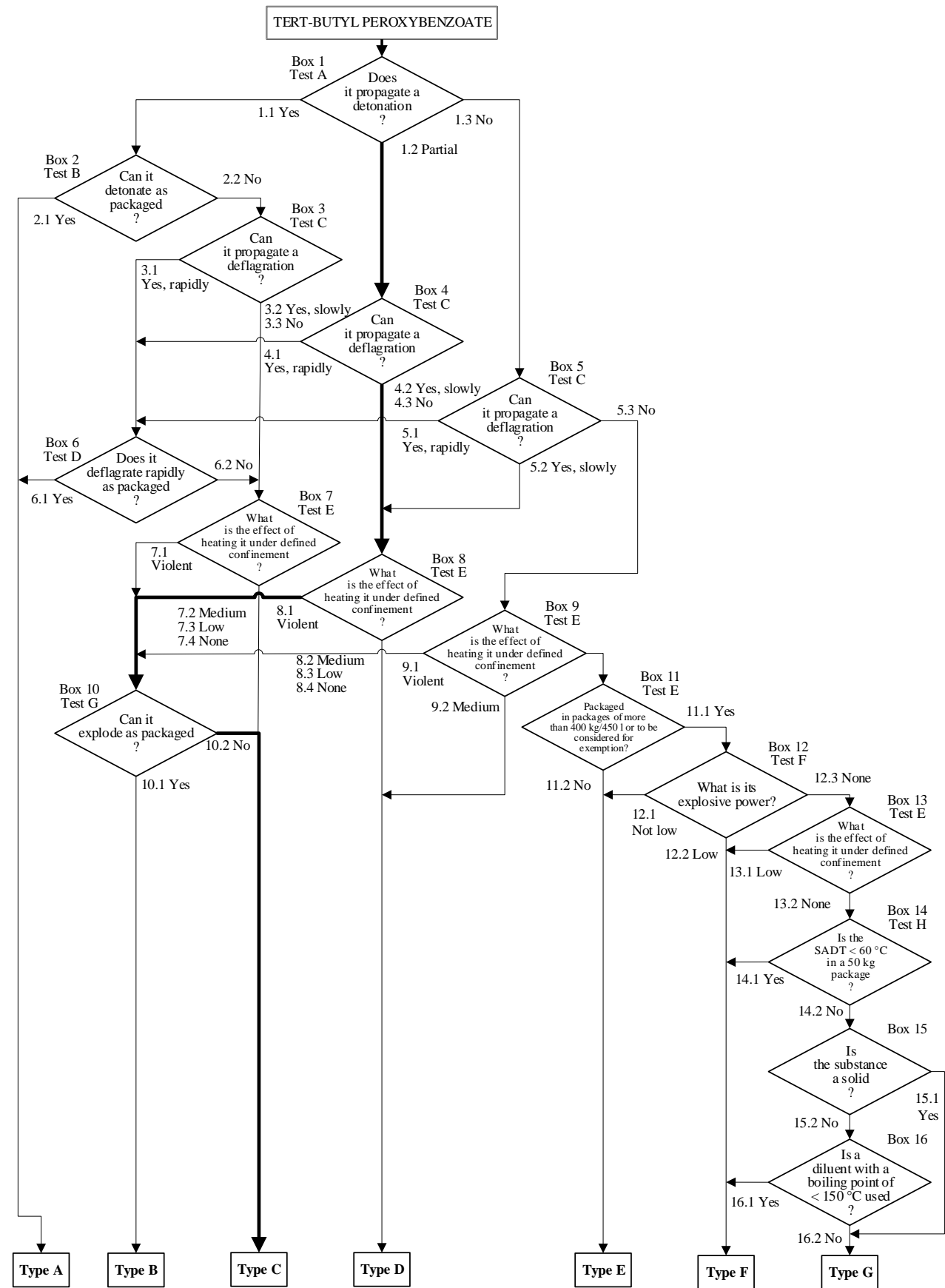
20.5.3 If the preliminary test results indicate that the substance is very sensitive to initiation (e.g. by impact, friction or sparks), the results should be recorded in the report.

Figure 20.2: EXAMPLE OF A TEST REPORT

1.	Name of substance	:	tert-BUTYL PEROXYBENZOATE, technically pure
2.	General data		
2.1	Composition	:	98% tert-butyl peroxybenzoate
2.2	Molecular formula	:	C ₁₁ H ₁₄ O ₃
2.3	Available oxygen content	:	8.24%
2.4	Activator content	:	Not applicable
2.5	Physical form	:	Liquid
2.6	Colour	:	Colourless
2.7	Apparent density	:	1 040 kg/m ³
2.8	Particle size	:	Not applicable
3.	Detonation (test series A)		
	Box 1 of the flow chart	:	Does the substance <u>it</u> propagate a detonation?
3.1	Method	:	BAM 50/60 steel tube test (test A.1)
3.2	Sample conditions	:	Ambient temperature
3.3	Observations	:	30 cm of tube fragmented, unreacted substance remained in the tube
3.4	Result	:	Partial
3.5	Exit	:	1.2
4.	Deflagration (test series C)		
	Box 4 of the flow chart	:	Does the substance <u>Can it</u> propagate a deflagration?
4.1	Method 1	:	Time/pressure test (test C.1)
4.2	Sample conditions	:	Ambient temperature
4.3	Observations	:	Time 2.5 s
4.4	Result	:	Yes, slowly
4.5	Method 2	:	Deflagration test (test C.2)
4.6	Sample conditions	:	Temperature 50 °C
4.7	Observations	:	Deflagration rate 0.65 mm/s
4.8	Result	:	Yes, slowly
4.9	Overall result	:	Yes, slowly
4.10	Exit	:	4.2
5.	Heating under confinement (test series E)		
	Box 8 of the flow chart	:	What is the effect of heating it under defined confinement?
5.1	Method 1	:	Koenen test (test E.1)
5.2	Sample conditions	:	Mass 26.0 g
5.3	Observations	:	Limiting diameter 3.5 mm (time to reaction 19 s, duration of reaction 22 s)
5.4	Result	:	Violent
5.5	Method 2	:	Dutch pressure vessel test (test E.2)
5.6	Sample conditions	:	10.0 g

5.7	Observations	:	Limiting diameter 10.0 mm (time to reaction 110 s, duration of reaction 4 s)
5.8	Result	:	Violent
5.9	Overall result	:	Violent
5.10	Exit	:	8.1
6.	Explosion in package (test series E)		
	Box 10 of the flow chart	:	Can the substance it explode as packaged for transport ?
6.1	Method	:	Thermal explosion test in the package (test G.1)
6.2	Sample conditions	:	25 kg of substance in packaging type 6HG2 with a capacity of 30 litres
6.3	Observations	:	Fume off only, no fragmentation of the package
6.4	Result	:	No explosion (packing method OP5)
6.5	Exit	:	10.2
7.	Thermal stability (test series H)		
7.1	Method	:	United States SADT test (test H.1)
7.2	Sample conditions	:	20 litres of substance in packaging type 6HG2 with a capacity of 25 litres
7.3	Observations	:	Auto-accelerating decomposition at 63 °C, no auto-accelerating decomposition at 58 °C, self-accelerating decomposition temperature 63 °C
7.4	Result	:	No temperature control required
8.	Additional data (see 20.5.3)		
8.1	Method	:	BAM fallhammer test (test 3 (a) (ii))
8.2	Sample conditions	:	Ambient temperature
8.3	Observations	:	Limiting impact energy 5 J
8.4	Result	:	Sensitive to impact
9.	Proposed assignment		
9.1	Proper shipping name	:	ORGANIC PEROXIDE TYPE C, LIQUID
9.2	UN number	:	3103
9.3	Division	:	5.2
9.4	Technical name	:	tert-Butyl peroxybenzoate
9.5	Concentration	:	≤ 100%
9.6	Diluent(s)	:	None
9.7	Subsidiary hazards	:	None
9.8	Packing group	:	II
9.9	Packing method	:	OP5
9.10	Control temperature	:	Not required
9.11	Emergency temperature	:	Not required

Figure 20.3: CLASSIFICATION OF TERT-BUTYL PEROXYBENZOATE



SECTION 21

TEST SERIES A

21.1 Introduction

20.1.1 Test series A comprises laboratory tests and criteria concerning propagation of detonation as requested in box 1 of Figure 20.1.

21.2 Test methods

21.2.1 The question "Does it propagate a detonation?" (box 1 of Figure 20.1) is answered on the basis of the results of one of the test methods in Table 21.1. If a liquid is being considered for ~~transport~~ containment in tank containers or IBCs with a capacity exceeding 450 litres, a cavitated version of a Series A test should be performed (see Appendix 3).

Table 21.1: TEST METHODS FOR TEST SERIES A

Test code	Name of test	Section
A.1	BAM 50/60 steel tube test	21.4.1
A.5	UN gap test	21.4.3
A.6	UN detonation test ^a	21.4.4

^a *Recommended test*

All tests are considered to be equivalent and only one test method has to be used.

21.2.2 For organic peroxides and self-reactive substances, a combination of a test for explosive power (any test of series F except test F.5 for peroxides, and any test of series F except tests F.4 and F.5 for self-reactive substances) with two tests for the effects of heating under confinement may be used as a screening procedure for assessing the ability to propagate a detonation. A test of series A need not be performed if:

- (a) A "No" result is obtained from the explosive power test; and
- (b) A "No" or "Low" result is obtained from test E.2 and either test E.1 or E.3.

~~For transport in packages (excluding IBCs),~~ if the screening procedure indicates that a Series A test is not needed, the question in box 1 is answered with a "No". However, if the substance is being considered for transport ~~containment~~ in tank containers or IBCs, or for exemption, then a series A test is required unless the result of a series A test on a formulation of the substance with a higher concentration and the same physical state is "No".

21.3 Test conditions

21.3.1 As the apparent density of the substance has an important effect on the results from series A tests, it should always be recorded. The apparent density of solids should be determined from measurement of the tube volume and sample mass.

21.3.2 If a mixture can separate out ~~during transport~~, the test should be performed with the initiator in contact with the potentially most explosive part, if known.

21.3.3 The tests should be performed at ambient temperature unless the substance is likely to encounter ~~be transported under~~ conditions where it may change its physical state or density. Organic peroxides and self-reactive substances which require temperature control should be tested at the control temperature if below ambient temperature.

21.3.4 *The preliminary procedure should be performed before performing these tests (see section 20.3).*

21.3.5 When a fresh batch of steel tubes is used, calibration tests using water (for tests on liquids) and an inert, organic solid (for tests on solids) should be performed to determine the average blank fragmentation length. The "No" / "Partial" criteria should be set to 1.5 times the average blank fragmentation length.

21.4 Series A test prescriptions

21.4.1 Test A.1: BAM 50/60 steel tube test

21.4.1.1 Introduction

This test is used to measure the ability of a substance to propagate a detonation by subjecting it to a detonating booster charge under confinement in a steel tube. It may be used to answer the question in box 1 of Figure 20.1.

21.4.1.2 Apparatus and materials

A seamless drawn steel tube of 500 mm length, 60 mm external diameter and 5 mm wall-thickness (e.g. according to DIN 2448) should be used, made from steel St 37.0 with tensile strength of 350 to 480 N.mm⁻² (e.g. according to DIN 1629). The tube is closed by a malleable cast iron screwing cap or by an appropriate plastic cap, put over the open end of the tube. The booster consists of a cylindrical pellet of 50 g RDX/wax (95/5) compressed to a pressure of 1 500 bar and with dimensions shown in Figure 21.4.1.1. The upper part of the booster has an axial recess of 7 mm diameter and 20 mm depth which accepts a detonator of sufficient strength to initiate the booster reliably. Substances which may react dangerously with steel St. 37.0 are tested in tubes with an internal polythene coating¹.

21.4.1.3 Procedure

21.4.1.3.1 Normally, the steel tube is filled with the substance as received, the sample mass determined and, if solid, the apparent density calculated using the measured internal tube volume. However, lumps are crushed and paste-like or gel-type substances are carefully packed to eliminate voids. In all cases, the final density of the substance in the tube should be as close as possible to its shipping density. The booster is placed centrally in the upper end of the tube, so that it is surrounded by the substance. When liquids are tested, the booster is separated from the liquid by wrapping it in a thin foil of aluminium or an appropriate plastic material. The wrapped booster is then attached to the malleable iron cap by means of thin wires passing through four additional drillings in the cap. The cap is carefully screwed onto the tube and the detonator inserted into the booster through the central hole in the screw cap. The detonator is then initiated.

21.4.1.3.2 At least two tests, which may be instrumented (e.g. by a continuous velocity probe), are performed unless detonation of the substance is observed. An instrumented third test may be necessary if no conclusion can be drawn from two uninstrumented tests.

21.4.1.4 Test criteria and method of assessing results

21.4.1.4.1 The test results are assessed on the basis of:

- (a) The type of fragmentation of the tube;
- (b) The completeness of the reaction of the substance; and
- (c) If the occasion arises, the measured rate of propagation in the substance.

The test giving the most severe assessment should be used for classification.

¹ In special cases, pure aluminium or steel 1.4571 according to DIN 17440 may be used as tube material.

21.4.1.4.2 The test criteria are as follows:

- "Yes":
- The tube is fragmented completely; or
 - The tube is fragmented at both ends; or
 - A velocity measurement shows that the rate of propagation in the non-fragmented part of the tube is constant and above the velocity of sound in the substance.
- "Partial":
- The tube is fragmented only at the initiator end and the average tube fragmentation length (average over two tests) is greater than 1.5 times the average fragmentation length found with an inert material having the same physical state; and
 - A significant portion of unreacted substance remains or a velocity measurement shows that the rate of propagation in the non-fragmented part of the tube is lower than the velocity of sound in the substance.
- "No":
- The tube is fragmented only at the initiator end and the average fragmentation length (average of two tests) not more than 1.5 times the average fragmentation length found with an inert material having the same physical state; and
 - A significant portion of unreacted substance remains or a velocity measurement shows that the rate of propagation in the non-fragmented part of the tube is lower than the velocity of sound in the substance.

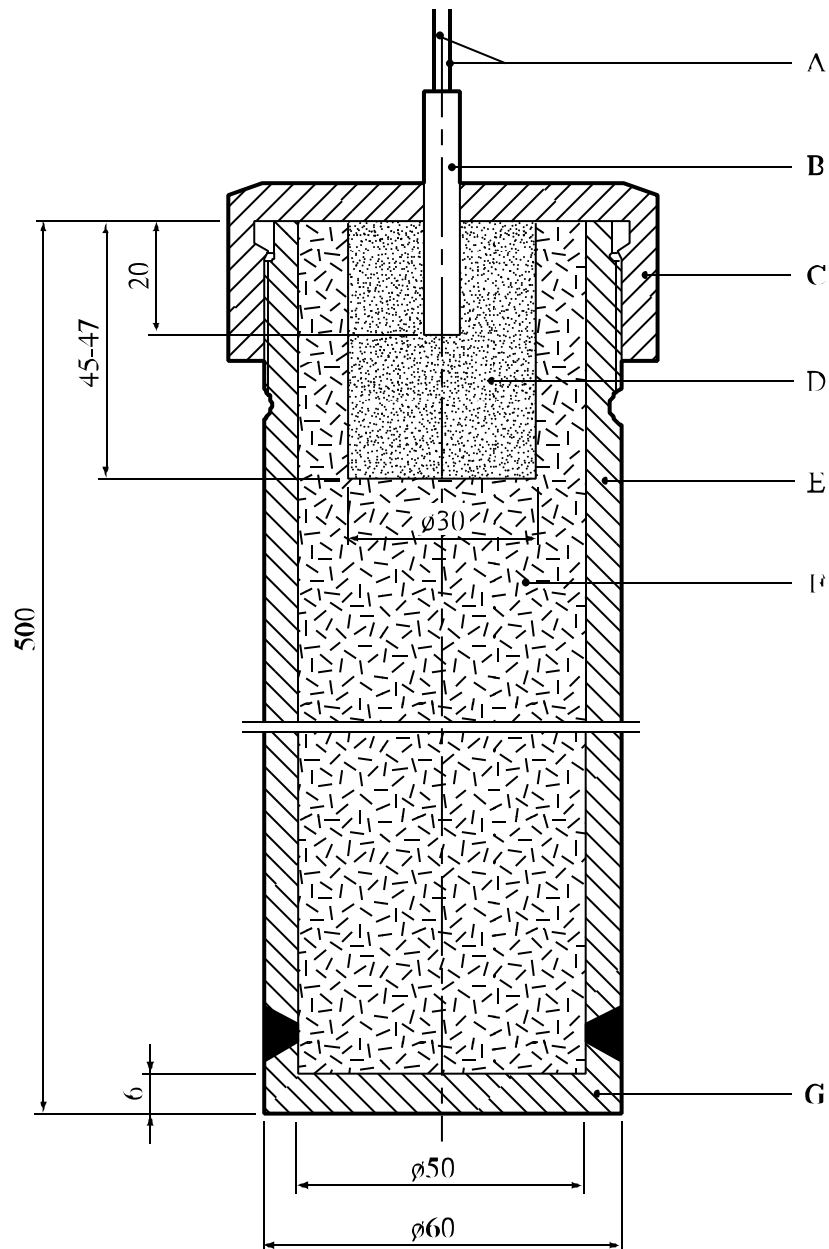
21.4.1.5 *Examples of results*

Substances	Apparent density (kg/m^3)	Fragmented length (cm)	Result
Azodicarbonamide	627	15	No
2,2'-Azodi(2,4-dimethylvaleronitrile)	793	16	No
Benzene-1,3-disulphohydrazide	640	50	Yes
Benzene sulphohydrazide	630	17	No
tert-Butyl peroxybenzoate	-	30	Partial
tert-Butyl peroxy-2-ethylhexanoate	-	18	No
3-Chloroperoxybenzoic acid, not more than 86% with 3-chlorobenzoic acid	610	24, 6 ^a	Yes
Cumyl hydroperoxide, 84% in cumene	-	15	No
Cyclohexanone peroxide(s)	620	50	Yes
2-Diazo-1-naphthol-5-sulphochloride	690	20	No ^b
Dibenzoyl peroxide	730	30, 12 ^a	Yes
Dibenzoyl peroxide, 75% with water	740	20	No
Di-tert-butyl peroxide	-	16	No
Dicetyl peroxydicarbonate	590	13	No
Dicumyl peroxide	520	14	No
Diisopropyl peroxydicarbonate	790	50	Yes
Dilauroyl peroxide	580	25	Partial
Dimyristyl peroxydicarbonate	460	20	No
Dimyristyl peroxydicarbonate, 42% stable dispersion in water	-	15	No
N,N'-Dinitrosopentamethylene tetramine, 90% with mineral oil	590	50	Yes ^c
N,N'-Dinitrosopentamethylene tetramine, 80% with 17% inorganic solid and 3% mineral oil	500	50	Yes
N,N'-Dinitrosopentamethylene tetramine, 75% with 15% calcium carbonate and 10% mineral oil	-	26	Partial
<i>Inert substances:</i>			
Air		8	
Dimethyl phthalate		13	
Icing sugar	682	14	
Sand		13	
Water		14	

^a *Both ends fragmented.*

^b *Substance completely reacted by deflagration.*

^c *Detonation velocity 3 040 m/s.*



- (A) Detonator wires
- (B) Detonator inserted 20 mm into the booster charge
- (C) Screw cap of malleable cast iron or a plastics cap
- (D) Booster charge of RDX/wax (95/5) with 30 mm diameter and length of approximately 46 mm
- (E) Steel tube 500 mm long with internal diameter 50 mm, external diameter 60 mm
- (F) Substance under test
- (G) Welded steel based 6 mm thick

Figure 21.4.1.1: BAM 50/60 STEEL TUBE TEST

~~21.4.2 Test A.2: TNO 50/70 steel tube test~~

~~21.4.2.1 Introduction~~

~~This test is used to measure the ability of a substance to propagate a detonation by subjecting it to a detonating booster charge under confinement in a steel tube. It may be used to answer the question in box 1 of Figure 20.1.~~

~~21.4.2.2 Apparatus and materials~~

~~21.4.2.2.1 Solids~~

~~The apparatus consists of a seamless steel tube (e.g. material St. 35 in accordance with DIN 1629/P3), inner diameter 50 mm, wall thickness 10 mm, and length 1 160 mm (tube type A). At one end (which will be called the bottom), it is closed by welding a 20 mm thick steel plate to the tube (see Figure 21.4.2.1). The tube is instrumented, e.g. by a continuous wire velocity probe, to measure the velocity of propagation in the substance. The booster charge consists of four RDX/wax (95/5) booster charges of 50 mm diameter, mass 50 g and length 16.4 mm.~~

~~21.4.2.2.2 Liquids~~

~~The detonability of liquids is determined with the aid of a tube similar to the tube used for solids but with a length of 750 mm. One end of the tube (called the bottom) is closed by a 0.5 mm metal plate under which the four boosters are positioned (tube type B), see Figure 21.4.2.2. The tube is held upright by means of a holder or three supports welded onto the tube. For corrosive liquids and liquids which decompose on contact with St. 35, a tube of stainless steel 316 (passivated if necessary) is used with a length of 750 mm, an internal diameter of 50 mm and an external diameter of 63 mm (tube type C).~~

~~21.4.2.3 Procedure~~

~~21.4.2.3.1 Solids~~

~~The substance should be tested at ambient temperature or at the control temperature, if below ambient. After fitting the velocity probe, the solid substance under investigation is introduced via the open end of the tube while the tube is continuously tapped. After filling up to 60 mm below the upper rim of the tube, the sample mass is determined and the apparent density calculated using the measured internal tube volume. The four booster charges are inserted, the final booster charge provided with a detonator and the charge detonated. Two tests are performed unless detonation of the substance is observed.~~

~~21.4.2.3.2 Liquids~~

~~For tests on liquids the booster charge, which is identical to that used for solids, should be positioned under the metal plate after which the tube is completely filled with the liquid and its mass determined. Subsequently, the procedures used for solids and liquids are the same.~~

~~21.4.2.4 Test criteria and method of assessing results~~

~~21.4.2.4.1 The test results are assessed on the basis of the fragmentation pattern of the tube and, in some cases, on the measured propagation velocity. The test giving the most severe assessment should be used for classification.~~

~~21.4.2.4.2 The test criteria are as follows:~~

~~"Yes": The tube is fragmented completely; or~~

~~A velocity measurement shows that the rate of propagation in the non-fragmented part of the tube is constant and above the velocity of sound in the substance.~~

~~"Partial": In all tests, the substance failed to detonate but the average fragmentation length (average over two tests) is greater than 1.5 times the average fragmentation length found with an inert material with the same physical state.~~

"No": In all tests, the substance failed to detonate and the average fragmentation length (average over two tests) is not more than 1.5 times the average fragmentation length found with an inert material with the same physical state.

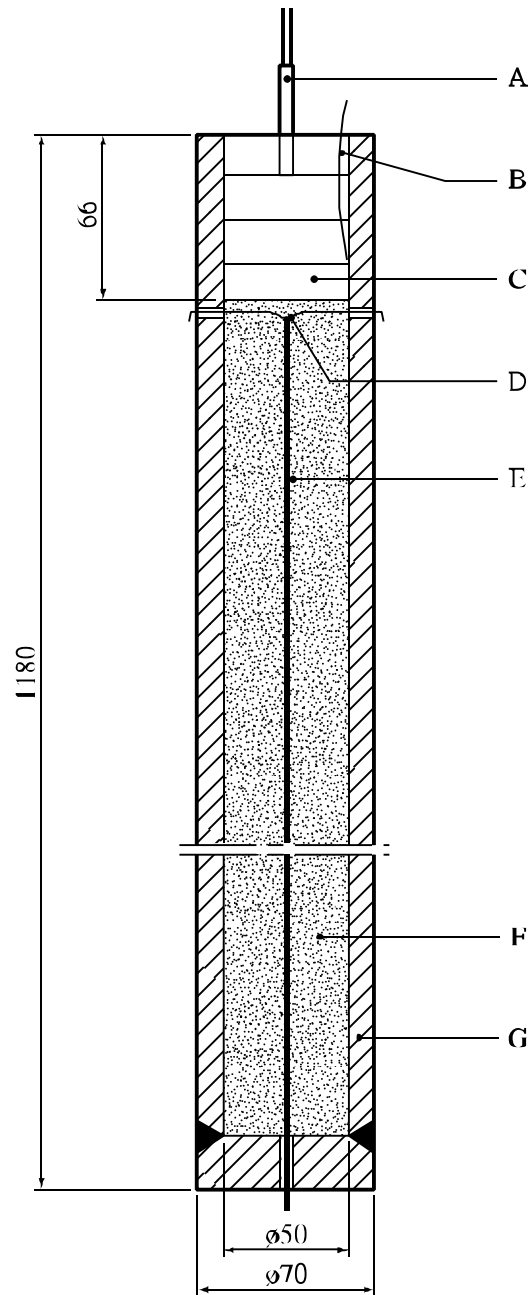
21.4.2.5 Examples of results

Substance	Tube type	Apparent density (kg/m ³)	Fragmented length (cm)	Result
tert-Butyl peroxybenzoate			0	Partial
tert-Butyl peroxy-2-ethylhexanoate		70	7.4	Ø
tert-Butyl peroxy isopropyl carbonate			7	Partial
Dibenzoyl peroxide, 75% with water			6.0	Partial
1,1-Di-(tert-butylperoxy)-3,3,5-trimethylcyclohexane		30	6	Ø
Dicyclohexyl peroxydicarbonate ^a		40	3 ^b	Yes
Dicyclohexyl peroxydicarbonate, with 10% water ^a			3 ^e	Yes
2,5-Diethoxy-4-morpholinobenzene-diazonium zinc chloride, 90%		10	6.7	Ø
2,5-Diethoxy-4-(phenylsulphonyl)-benzenediazonium zinc chloride, 67%			5	Ø
Dilauroyl peroxide			4	Partial
3-Methyl-4-(pyrrolidin-1-yl)benzene-diazonium tetrafluoroborate, 95%			9	Ø
Di-n-octanoyl peroxide (liquid)			0	Ø

^a Performed at the control temperature.

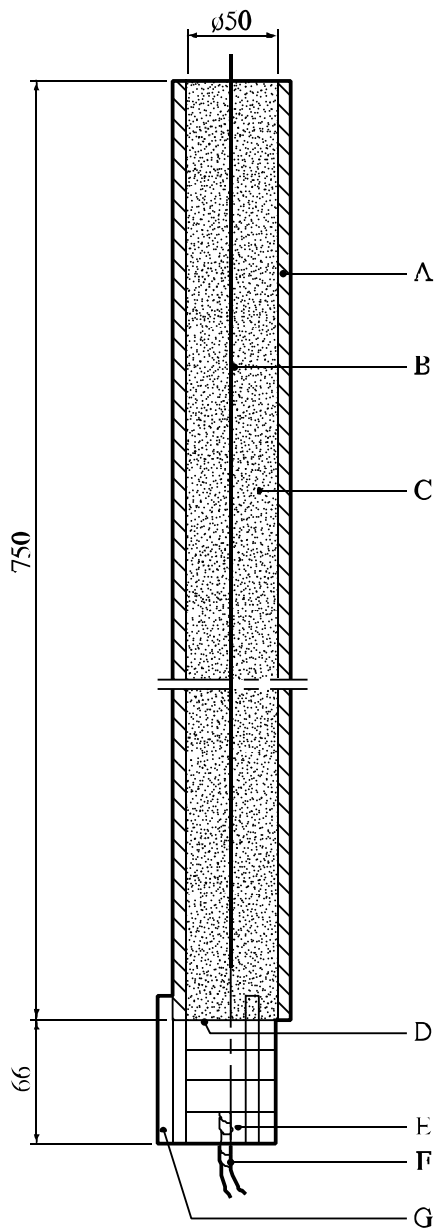
^b Propagation velocity, 660 m/s, greater than the sound velocity in the substance.

^c Propagation velocity, 690 m/s, greater than the sound velocity in the substance.



- | | |
|--------------------------|-----------------------------------|
| (A) Detonator | (B) Ionization probe |
| (C) 4 RDX/wax cartridges | (D) Eye |
| (E) Velocity probe | (F) Substance under investigation |
| (G) Tube, steel | |

Figure 21.4.2.1: TNO 50/70 STEEL TUBE TEST FOR SOLIDS (TUBE TYPE A)



- | | |
|---|--------------------|
| (A) 63.5 (C) or 70 mm (B) outer diameter steel tube | (B) Velocity probe |
| (C) Substance under investigation | (D) Steel disc |
| (E) 4 RDX/wax cartridges | (F) Detonator |
| (G) Supports | |

Figure 21.4.2.2: TNO 50/70 STEEL TUBE TEST FOR LIQUIDS (TUBE TYPES B AND C)

21.4.32 *Test A.5: UN gap test*

21.4.32.1 *Introduction*

This test is used to measure the ability of a substance to propagate a detonation by subjecting it to a detonating booster charge under confinement in a steel tube. It may be used to answer the question in box 1 of Figure 20.1.

21.4.32.2 *Apparatus and materials*

The apparatus is shown in Figure 21.4.32.1. The test sample is contained in an annealed, seamless, carbon steel tube with an external diameter of 48 ± 2 mm, a wall thickness of 4 mm and a length of 400 ± 5 mm. If the test substance may react with the steel, the inside of the tube may be coated with fluorocarbon resin. The bottom of the tube is closed with a plastics sheet pulled tightly (so that it plastically deforms) over the bottom of the tube and held tightly in place. The plastics sheet shall be compatible with the substance under test. The booster charge consists of 160 g RDX/wax (95/5) or PETN/TNT that has a minimum of 50% PETN in the mixture, 50 ± 1 mm in diameter with a density of $1\,600 \pm 50$ kg/m³. The charges may be pressed in one or more pieces, as long as the total charge is within the specifications, and the PETN/TNT charge is cast. A mild steel witness plate, 150 ± 10 mm square and 3 mm thick, may be mounted at the upper end of the steel tube and separated from it by spacers 1.6 ± 0.2 mm thick.

21.4.32.3 *Procedure*

21.4.32.3.1 The sample is loaded to the top of the steel tube. Solid samples are loaded to the density attained by tapping the tube until further settling becomes imperceptible. The sample mass is determined and, if solid, the apparent density calculated using the measured internal volume of the tube.

21.4.32.3.2 The tube is placed in a vertical position and the booster charge is placed in direct contact with the sheet which seals the bottom of the tube. The detonator is fixed in place against the booster charge and initiated. Two tests should be performed unless detonation of the substance is observed.

21.4.32.4 *Test criteria and method of assessing results*

21.4.32.4.1 The test results are assessed on the basis of the fragmentation pattern of the tube. The witness plate is used only to provide supplemental information on the violence of the reaction. The test giving the most severe assessment should be used for classification.

21.4.32.4.2 The test criteria are as follows:

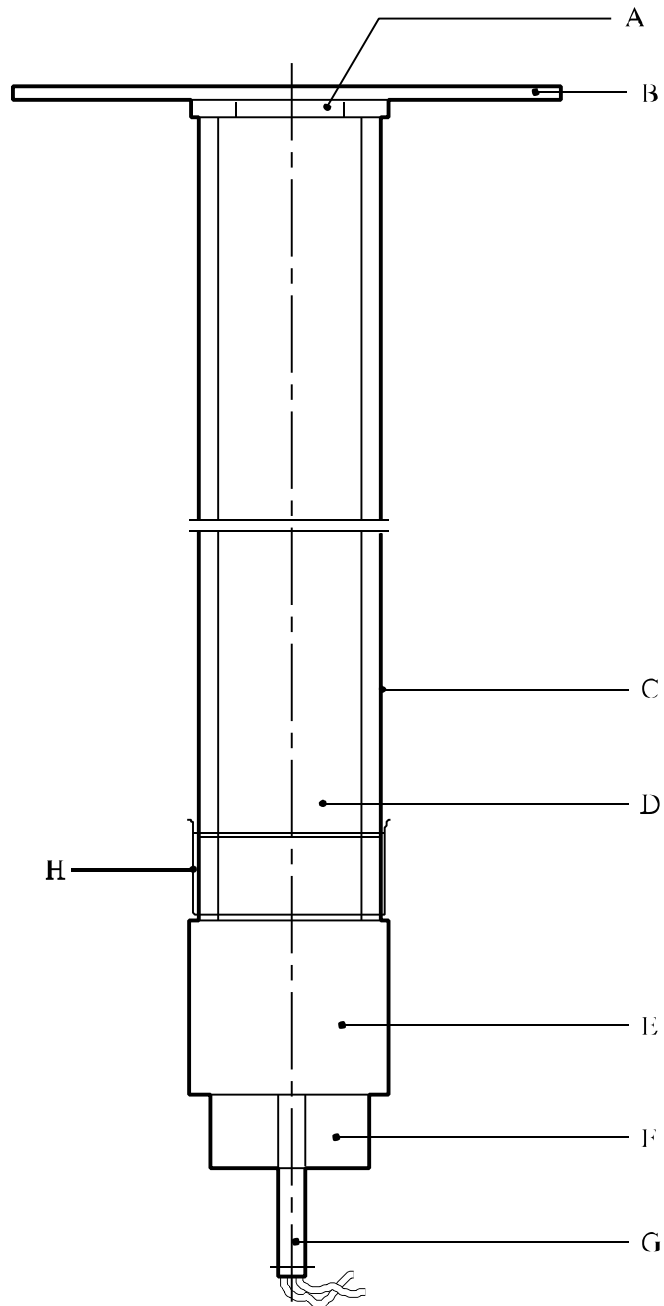
"Yes": - The tube is fragmented over its entire length.

"Partial": - The tube is not fragmented over its entire length but the average tube fragmentation (average over the two tests) is greater than 1.5 times the average fragmentation length found with an inert material with the same physical state.

"No": - The tube is not fragmented over its entire length and the average tube fragmentation (average over the two tests) is not more than 1.5 times the average fragmentation length found with an inert material with the same physical state.

21.4.32.5 *Examples of results*

Substance	Apparent density (kg/m ³)	Fragmented length (cm)	Result
2,2'-Azodi(isobutyronitrile)	366	40	Yes
tert-Butyl peroxybenzoate		25	Partial
tert-Butyl peroxy-2-ethylhexanoate		25	Partial
Dibenzoyl peroxide, 75% with water	685	40	Yes
2,5-Di-(tert-butylperoxy)-2,5-dimethylhexyne-3		34	Partial
Dilauroyl peroxide	564	28	No



- | | | | |
|-----|------------------------------------|-----|----------------------|
| (A) | Spacers | (B) | Witness plate |
| (C) | Steel tube | (D) | Substance under test |
| (E) | RDX/wax or PETN/TNT booster charge | (F) | Detonator holder |
| (G) | Detonator | (H) | Plastics sheet |

Figure 21.4.32.1: UN GAP TEST

21.4.43 *Test A.6: UN detonation test*

21.4.43.1 *Introduction*

This test is used to measure the ability of a substance to propagate a detonation by subjecting it to a detonating booster charge under confinement in a steel tube. It may be used to answer the question in box 1 of Figure 20.1.

21.4.43.2 *Apparatus and materials*

The apparatus is shown in Figure 21.4.43.1 and is identical for solids and liquids. The test sample is contained in an annealed, seamless, carbon steel tube with an external diameter of 60 ± 1 mm, a wall thickness of 5 ± 1 mm and a length of 500 ± 5 mm. If the test substance may react with the steel, the inside of the tube may be coated with fluorocarbon resin. The bottom of the tube is closed with a plastics sheet held tightly in place. The plastics sheet shall be compatible with the substance under test. The booster charge is a 200 g RDX/wax (95/5) or PETN/TNT that has a minimum of 50% PETN in the mixture, 60 ± 1 mm in diameter with a density of $1\,600 \pm 50$ kg/m³. The charges may be pressed in one or more pieces as long as the total charge is within the specifications and the PETN/TNT charge is cast. The tube may be instrumented, e.g. by a continuous wire velocity probe, to measure the velocity of propagation in the substance. Additional information on the explosive behaviour of the test sample can be gained by the use of a witness plate or of a velocity probe, as shown in Figure 21.4.43.1. The mild steel witness plate, 150 mm square and 3 mm thick, may be mounted at the upper end of the tube and separated from it by spacers 1.6 mm thick.

21.4.43.3 *Procedure*

The sample is loaded to the top of the steel tube. Solid samples are loaded to the density attained by tapping the tube until further settling becomes imperceptible. The sample mass is determined and, if solid, the apparent density calculated. The tube is placed in a vertical position and the booster charge is placed in direct contact with the sheet which seals the bottom of the tube. The detonator is fixed in place against the booster charge and initiated. Two tests should be performed unless detonation of the substance is observed.

21.4.43.4 *Test criteria and method of assessing results*

21.4.43.4.1 The test results are assessed on the basis of:

- (a) The type of fragmentation of the tube; and
- (b) If the occasion arises, the measured rate of propagation in the substance.

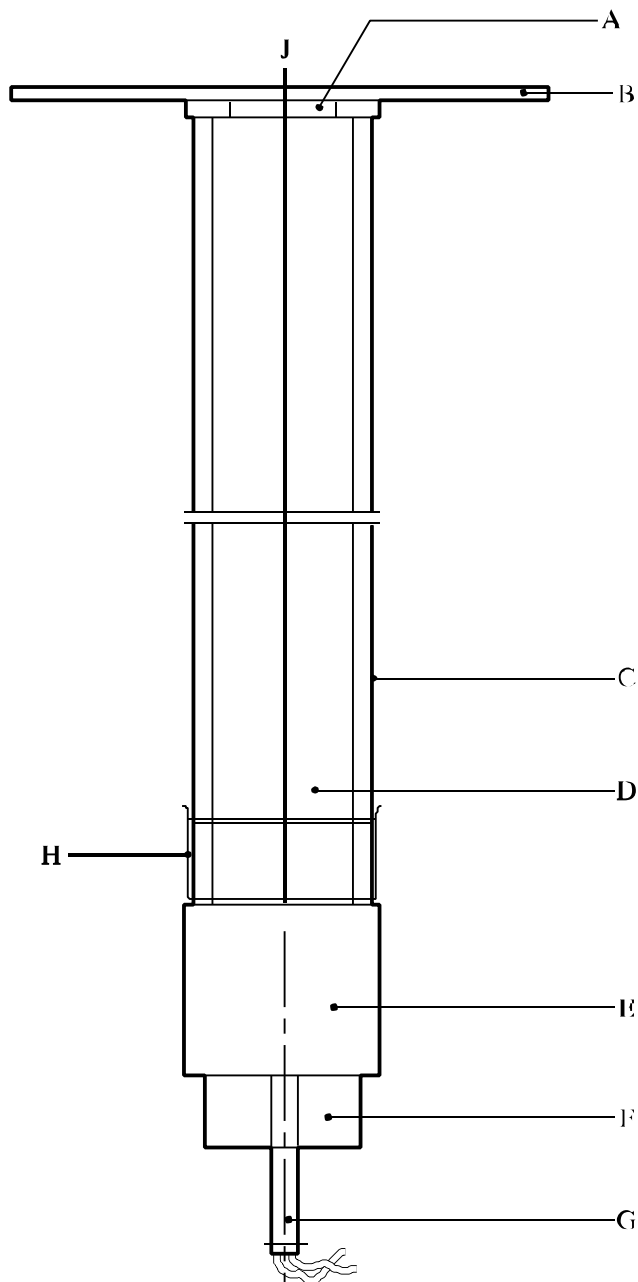
The test giving the most severe assessment should be used for classification.

21.4.43.4.2 The test criteria are as follows:

- "Yes": - The tube is fragmented completely.
- "Partial": - The tube is not fragmented over its entire length but the average tube fragmentation (average over the two tests) is greater than 1.5 times the average fragmentation length found with an inert material with the same physical state.
- "No": - The tube is not fragmented over its entire length and the average tube fragmentation (average over the two tests) is not more than 1.5 times the average fragmentation length found with an inert material with the same physical state.

21.4.43.5 *Examples of results*

Substance	Apparent density (kg/m³)	Fragmented length (cm)	Result
2,2'-Azodi(isobutyronitrile)	346	50	Yes
tert-Butyl peroxybenzoate		28	Partial
tert-Butyl peroxy-2-ethylhexanoate		23	No
Dibenzoyl peroxide, 75% with water	697	22	No
2,5-Di-(tert-butylperoxy)-2,5-dimethylhexyne-3	870	30	Partial
Dilauroyl peroxide	580	32	Partial



-
- | | | | |
|-----|------------------------------------|-----|----------------------|
| (A) | Spacers | (B) | Witness plate |
| (C) | Steel tube | (D) | Substance under test |
| (E) | RDX/wax or PETN/TNT booster charge | (F) | Detonator holder |
| (G) | Detonator | (H) | Plastics sheet |
| (J) | Velocity probe | | |
-

Figure 21.4.43.1: UN DETONATION TEST

SECTION 22

TEST SERIES B

22.1 Introduction

Test series B comprises a test and criteria concerning the propagation of detonation of a substance as packaged ~~for transport~~. The test is required only for substances which propagate detonation (box 1 of Figure 20.1).

22.2 Test methods

The question "Can it detonate as packaged ~~for transport~~?" (box 2 of Figure 20.1) is answered on the basis of the results of the test method in Table 22.1.

Table 22.1: TEST METHOD FOR TEST SERIES B

Test code	Name of test	Section
B.1	Detonation test in package ^a	22.4.1

^a *Recommended test.*

22.2.2 The test is required only for substances for which the answer to the question in box 1 of Figure 20.1 is "Yes".

22.3 Test conditions

22.3.1 The test from series B should be applied to **substances in packages** (not larger than 50 kg) ~~of substance~~ in the condition and form in which they are offered for ~~transport~~**classification**.

22.3.2 *The preliminary procedure should be performed before performing these tests (see section 20.3).*

22.4 Series B test prescription**22.4.1 Test B.1: Detonation test in package****22.4.1.1 Introduction**

This test is used to measure the ability of a substance to propagate a detonation when packaged ~~as for transport~~. It involves subjecting the substance in a package to the shock from a detonating booster charge. It is used to answer the question in box 2 of Figure 20.1.

22.4.1.2 Apparatus and materials

A detonator, detonating cord, plastic explosive and suitable confining material are required. A mild steel sheet of about 1 mm thickness, with a minimum size in each direction of 0.2 m larger than that of the bottom dimensions of the package, serves as a witness plate beneath the package.

22.4.1.3 Procedure

The test is applied to packed substances in the condition and form in which they are offered for ~~transport~~**classification**. The package is placed on the steel witness plate from which the edges are supported by bricks or other suitable material so that there is sufficient free air space below the witness plate that puncture is not impeded. Two charges of plastic explosive (each maximum 100 g but in total not more than 1% by mass of the substance in the package) are placed on top of the substance in the package. For liquids, metal-wire support may be needed to ensure

that the two explosive charges are located correctly in the middle of each of the two semicircular or triangular parts of the top surface (see Figure 22.4.1.1). Each charge is initiated by the detonator through a detonating cord. Both pieces of detonating cord should be of equal length. The preferred method of confinement is loose sand placed around the test package with a minimum thickness of 0.5 m in every direction. Alternative methods of confinement are to use boxes, bags or drums filled with earth or sand placed around and on top of the package with the same minimum thickness. The test is performed in duplicate unless a detonation is observed. An instrumented third test may be necessary if no conclusion can be drawn from two uninstrumented tests.

22.4.1.4 *Test criteria and method of assessing results*

22.4.1.4.1 The test results are assessed on the basis of evidence of a detonation of the substance under investigation by:

- (a) A crater at the test site;
- (b) Damage to the witness plate beneath the product;
- (c) Disruption and scattering of most of the confining material; and
- (d) When appropriate, the measured rate of propagation in the substance.

22.4.1.4.2 The test criteria are as follows:

"Yes": - Formation of a crater at the test site or perforation of the witness plate beneath the product; both in combination with a disruption and scattering of most of the confining material; or the propagation velocity in the lower half of the package is constant and is above the velocity of sound in the substance.

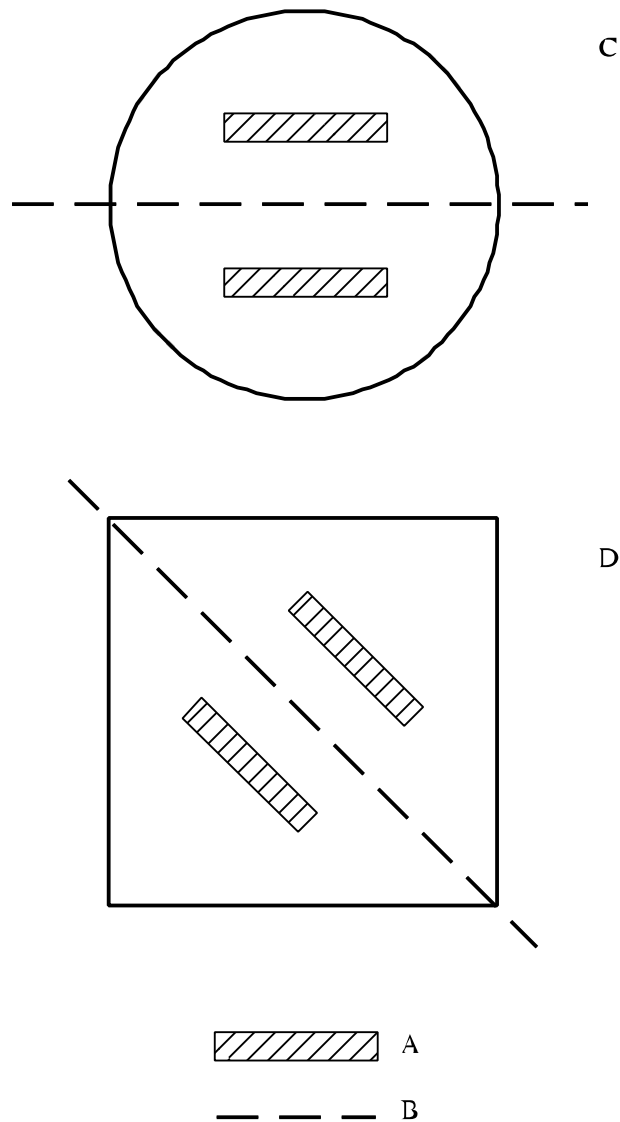
"No": - No formation of a crater at the test site, no perforation of the witness plate beneath the product, a velocity measurement (if made) shows that the rate of propagation is lower than the velocity of sound in the substance and, for solids, retrieval of unreacted substance after the test.

22.4.1.5 *Examples of results*

Substance	Apparent density (kg/m ³)	Packaging	Result
Dibenzoyl peroxide	730	1G, 25 kg	Yes ^a
Dicyclohexyl peroxydicarbonate	600	1G, 5 kg	No ^b
Dicyclohexyl peroxydicarbonate, with 10% water	600	1G, 5 kg	No ^b

^a Performed in duplicate. Detection of detonation by formation of crater.

^b Tests performed in duplicate. Propagation velocity measured instead of using a witness plate.



- (A) Explosive charges
- (B) Line of symmetry
- (C) Top view of cylindrical package
- (D) Top view of rectangular package

Figure 22.4.1.1: DETONATION TEST IN PACKAGE

SECTION 23**TEST SERIES C****23.1 Introduction**

Test series C comprises laboratory tests and criteria concerning propagation of deflagration as requested in boxes 3, 4 and 5 of Figure 20.1.

23.2 Test methods

23.2.1 The question "Can it propagate a deflagration?" (boxes 3, 4 and 5 of Figure 20.1) is answered on the basis of the results of one, or if necessary both, of the test methods in Table 23.1.

Table 23.1: TEST METHODS FOR TEST SERIES C

Test code	Name of test	Section
C.1	Time/pressure test ^a	23.4.1
C.2	Deflagration test ^a	23.4.2

^a *Recommended test.*

23.2.2 The answer is "Yes, rapidly" if shown to be so by either test. The answer is "Yes, slowly" if the deflagration test result is "Yes, slowly" and the time/pressure test result is not "Yes, rapidly". The answer is "No" if the deflagration test result is "No" and the time/pressure test is not "Yes, rapidly".

23.3 Test conditions

23.3.1 The preliminary procedure (see section 20.3) should be carried out before performing these tests.

23.4 Series C test prescriptions**23.4.1 Test C.1: Time/pressure test****23.4.1.1 Introduction**

This test is used to measure the ability of a substance¹ under confinement to propagate a deflagration. It may be used to answer the question in boxes 3, 4 and 5 of Figure 20.1.

23.4.1.2 Apparatus and materials

23.4.1.2.1 The time/pressure apparatus (Figure 23.4.1.1) consists of a cylindrical steel pressure vessel 89 mm in length and 60 mm in external diameter. Two flats are machined on opposite sides (reducing the cross-section of the vessel to 50 mm) to facilitate holding whilst fitting the firing plug and vent plug. The vessel, which has a bore of 20 mm diameter, is internally rebated at either end to a depth of 19 mm and threaded to accept 1" British Standard Pipe (BSP). A pressure take-off, in the form of a side-arm, is screwed into the curved face of the pressure vessel 35 mm from one end and at 90° to the machined flats. The socket for this is bored to a depth of 12 mm and threaded to accept the 1/2" BSP thread on the end of the side-arm. A washer is fitted to ensure a gas-tight seal. The side-arm extends 59 mm beyond the pressure vessel body and has a bore of 6 mm. The end of the side-arm is rebated and threaded to accept a diaphragm type pressure transducer. Any pressure-measuring device may be used provided that it is not affected by the hot gases or decomposition products and is capable of responding to rates of pressure rise of 690 to 2 070 kPa in not more than 5 ms.

¹ *When testing liquids, variable results may be obtained because the substance may give two pressure peaks.*

23.4.1.2.2 The end of the pressure vessel furthest from the side-arm is closed with a firing plug which is fitted with two electrodes, one insulated from and the other earthed to the plug body. The other end of the pressure vessel is closed by an aluminium bursting disc 0.2 mm thick (bursting pressure approximately 2 200 kPa) held in place with a retaining plug which has a 20 mm bore. A suitable deformable washer or rubber ring is used with both plugs to ensure a good seal. A support stand (Figure 23.4.1.2) holds the assembly in the correct attitude during use. This comprises a mild steel base plate measuring 235 mm × 184 mm × 6 mm and a 185 mm length of square hollow section (S.H.S.) 70 × 70 × 4 mm.

23.4.1.2.3 A section is cut from each of two opposite sides at one end of the length of S.H.S. so that a structure having two flat sided legs surmounted by an 86 mm length of intact box section results. The ends of these flat sides are cut at an angle of 60° to the horizontal and welded to the base plate.

23.4.1.2.4 A slot measuring 22 mm wide × 46 mm deep is machined in one side of the upper end of the base section such that when the pressure vessel assembly is lowered, firing plug end first, into the box section support, the side-arm is accommodated in this slot. A packing piece of steel 30 mm wide and 6 mm thick is welded to the lower internal face of the box section to act as a spacer. Two 7 mm thumb screws, tapped into the opposite face, serve to hold the pressure vessel firmly in place. Two 12 mm wide strips of 6 mm thick steel, welded to the side pieces abutting the base of the box section, support the pressure vessel from beneath.

23.4.1.2.5 The ignition system consists of an electric fusehead of the type commonly used in low tension detonators, together with a 13 mm square piece of primed cambric. Fuseheads with equivalent properties may be used. Primed cambric consists of a linen fabric coated on both sides with a potassium nitrate/silicon/sulphurless gunpowder pyrotechnic composition².

23.4.1.2.6 The procedure for the preparation of the ignition assembly for solids starts with separation of the brass foil contacts of an electric fusehead from its insulator, (see Figure 23.4.1.3). The exposed portion of insulation is then cut off. The fusehead is then fixed onto the terminals of the firing plug by means of the brass contacts such that the tip of the fusehead is 13 mm above the surface of the firing plug. An approximately 13 mm square piece of primed cambric is pierced through the centre and positioned over the attached fusehead around which it is then folded and secured with fine cotton thread.

23.4.1.2.7 For liquids samples, a single piece of thin PVC sheathing, or equivalent, is used to cover the primed cambric in such a way that the primed cambric is not in contact with the liquid sample. The leads of the resistance wire are then fixed onto the terminals of the firing plug such that the tip of the primed cambric is above the surface of the firing plug.

23.4.1.3 Procedure

23.4.1.3.1 The apparatus assembled, complete with pressure transducer but without the aluminium bursting disc in position, is supported firing plug end down. 5.0 g³ of the substance is introduced into the apparatus so as to be in contact with the ignition system. Normally no tamping is carried out when filling the apparatus unless it is necessary to use light tamping in order to get the 5.0 g charge into the vessel. If, even with light tamping, it is impossible to get all the 5.0 g of sample in, then the charge is fired after filling the vessel to capacity. Note should be taken of the charge weight used. The washer or rubber ring and aluminium bursting disc are placed in position and the retaining plug is screwed in tightly. The charged vessel is transferred to the firing support stand, bursting disc uppermost, which should be contained in a suitable, armoured fume cupboard or firing cell. A power source is connected to the external terminals of the firing plug and the charge is fired. The signal produced by the pressure transducer is recorded on a suitable data acquisition system which allows both evaluation and a permanent record of the time/pressure profile to be achieved.

² Obtainable from the national contact for test details in United Kingdom (see Appendix 4).

³ **If preliminary safety-in-handling tests (e.g. heating in a flame) or burning tests (e.g. a series 3 type (d) test) indicate that a rapid reaction is likely to occur, then the sample size should be reduced to 0.5 g until the severity of the confined reaction is known. If it is necessary to use a 0.5 g sample size, the sample size is gradually increased until either a "Yes, rapidly" result is obtained or the test is performed with a 5.0 g sample.**

23.4.1.3.2 The test is carried out three times. The time taken for the pressure to rise from 690 kPa to 2 070 kPa above atmospheric is noted. The shortest time interval should be used for classification.

23.4.1.4 *Test criteria and method of assessing results*

23.4.1.4.1 The test results are interpreted in terms of whether a gauge pressure of 2 070 kPa is reached and, if so, the time taken for the pressure to rise from 690 kPa to 2 070 kPa gauge.

23.4.1.4.2 The test criteria are as follows:

"Yes, rapidly": - The time for a pressure rise from 690 kPa to 2 070 kPa is less than 30 ms.

"Yes, slowly": - The time for a pressure rise from 690 kPa to 2 070 kPa is greater than or equal to 30 ms.

"No": - A pressure rise to 2 070 kPa above atmospheric is not achieved.

NOTE: If necessary, the deflagration test, Test C.2, should be performed to distinguish between "Yes, slowly" and "No".

23.4.1.5 *Examples of results*

Substance	Maximum pressure (kPa)	Time for a pressure rise from 690 to 2 070 kPa (ms)	Result
Azodicarbonamide	> 2 070	63	Yes, slowly
Azodicarbonamide, 67% with zinc oxide	> 2 070	21	Yes, rapidly
2,2'-Azodi(isobutyronitrile)	> 2 070	68	Yes, slowly
2,2'-Azodi(2-methylbutyronitrile)	> 2 070	384	Yes, slowly
tert-Butyl hydroperoxide, 70% with water	1 380	-	No
tert-Butyl peroxybenzoate	> 2 070	2 500	Yes, slowly
tert-Butyl peroxy-2-ethylhexanoate	> 2 070	4 000	Yes, slowly
Cumyl hydroperoxide, 80% with cumene	< 690 ^a	-	No
2-Diazo-1-naphthol-5-sulphohydrazide	> 2 070	14	Yes, rapidly
Dibenzoyl peroxide	> 2 070	1	Yes, rapidly
Di-tert-butyl peroxide	> 2 070	100	Yes, slowly
Dicetyl peroxydicarbonate	< 690	-	No
Dicumyl peroxide	< 690 ^a	-	No
Dicumyl peroxide, with 60% inert solid	< 690 ^a	-	No
2,5-Diethoxy-4-morpholinobenzene-diazonium tetrafluoroborate, 97%	> 2 070	308	Yes, slowly
Dilauroyl peroxide	990	-	No
2,5-Dimethyl-2,5-di-(tert-butylperoxy)-hexyne-3	> 2 070	70	Yes, slowly
Magnesium monoperoxyphthalate hexahydrate, 85% with magnesium phthalate	900	-	No
4-Nitrosophenol	> 2 070	498	Yes, slowly

^a No ignition.

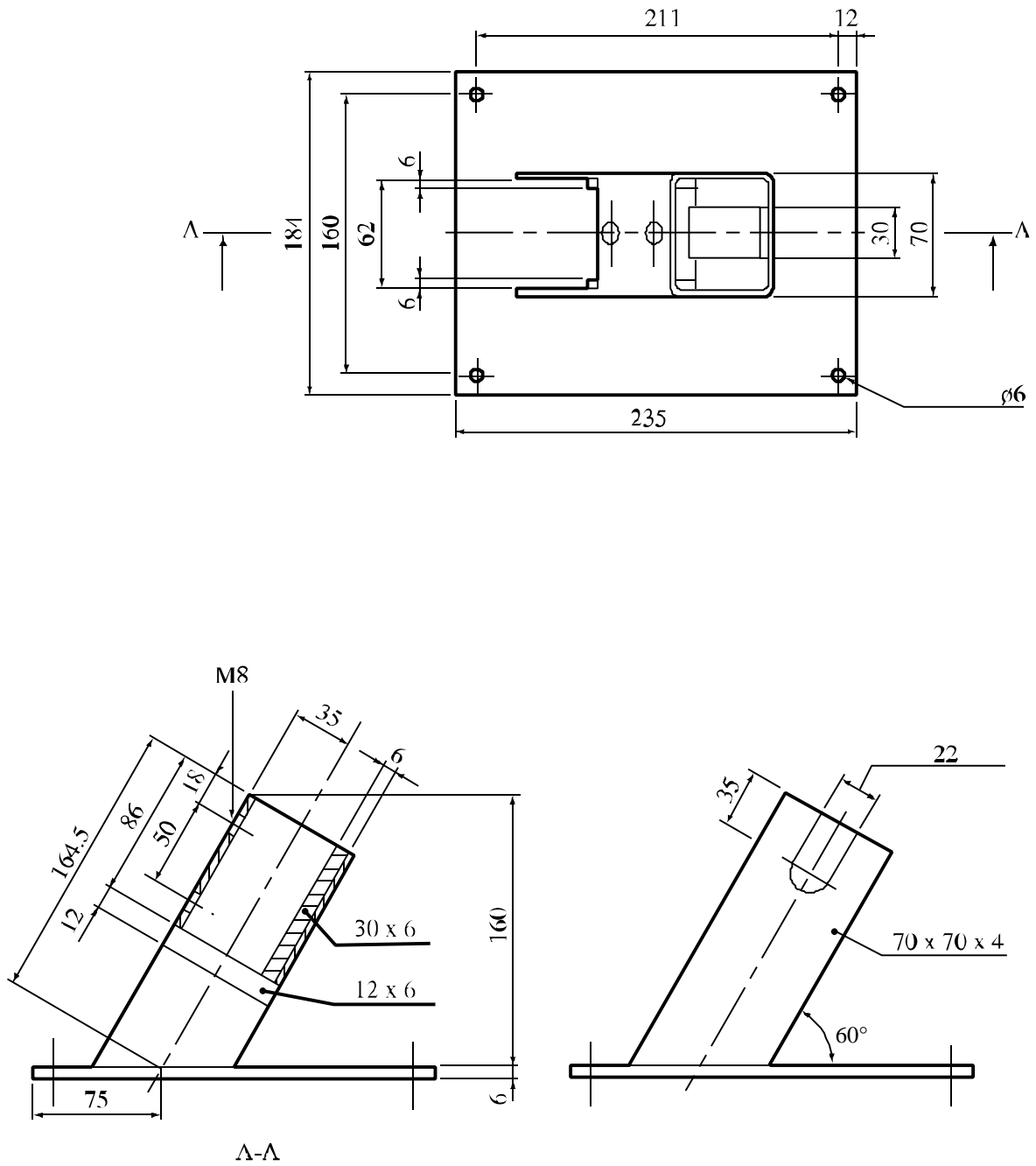
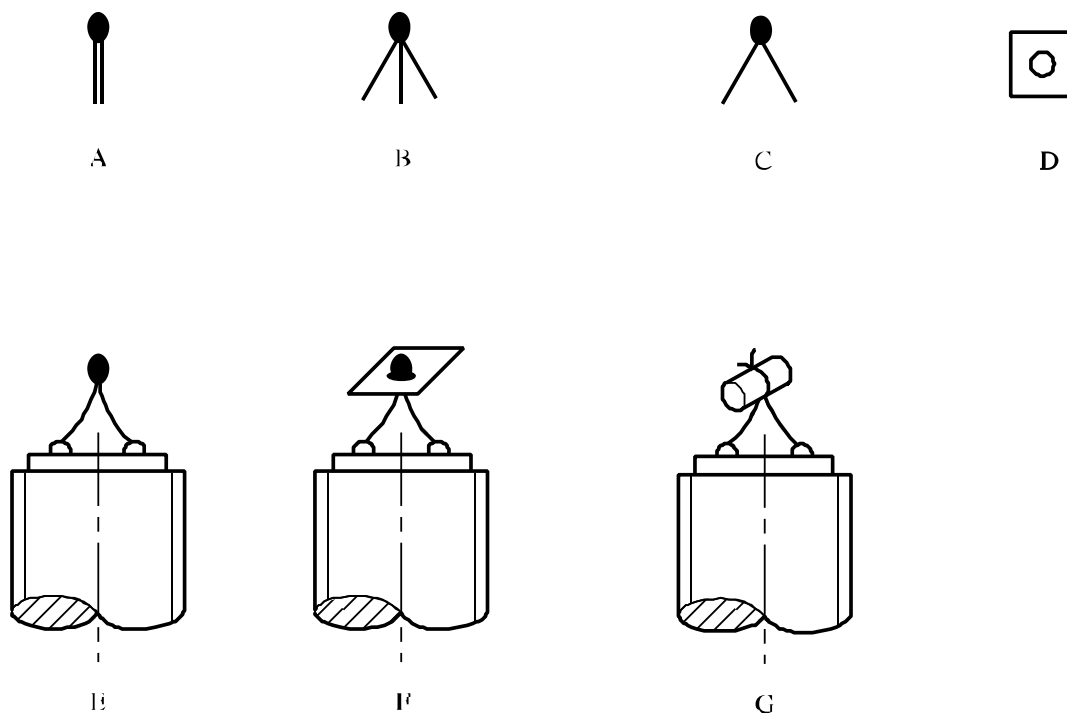
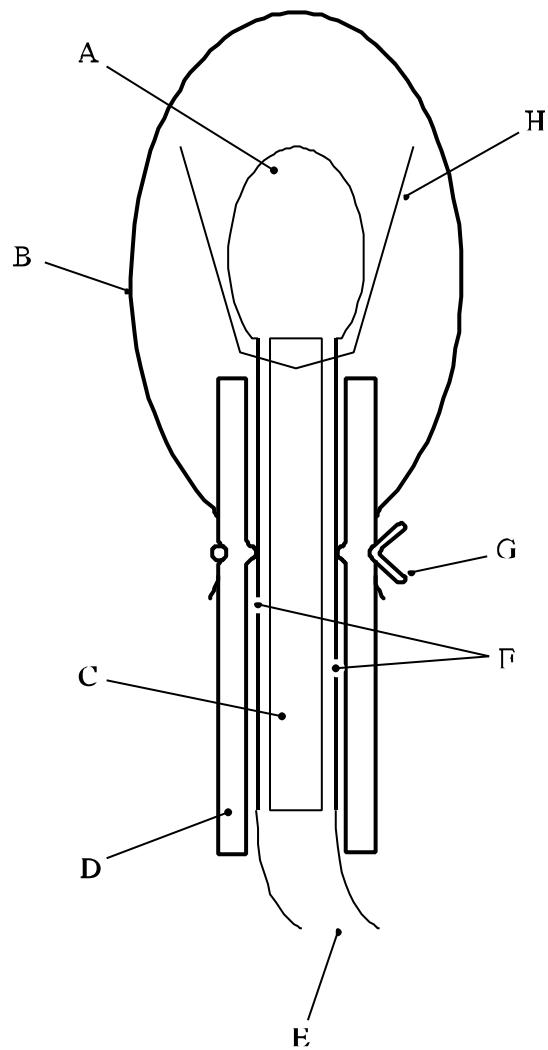


Figure 23.4.1.2: SUPPORT STAND



-
- (A) Electrically ignited fusehead as manufactured
 - (B) Brass foil contacts parted from card insulator
 - (C) Insulating card cut off
 - (D) Primed cambric SR252 13 mm square with centre hole
 - (E) Fusehead fixed to pins on firing plug
 - (F) Cambric positioned on fusehead
 - (G) Cambric folded around and tied with thread
-

Figure 23.4.1.3: IGNITION SYSTEM FOR SOLIDS



- (A) Fusehead
- (B) PVC sheath
- (C) Insulating card
- (D) Silicone rubber tubing
- (E) Firing leads
- (F) Foil contacts
- (G) Wire to make liquid-tight seal
- (H) Primed cambric

Figure 23.4.1.4: IGNITION SYSTEM FOR LIQUIDS

23.4.2 *Test C.2: Deflagration test*

23.4.2.1 *Introduction*

This test is used to measure the ability of a substance to propagate a deflagration. It may be used to answer the question in boxes 3, 4 and 5 of Figure 20.1.

23.4.2.2 *Apparatus and materials*

23.4.2.2.1 The test is performed with a Dewar vessel (see Figure 23.4.2.1) which is provided with vertical observation windows on opposite sides. The windows are not necessary when using thermocouples to measure the deflagration rate. A timer with an accuracy of 1 second is used to measure the deflagration rate.

23.4.2.2.2 The Dewar vessel has a volume of about 300 cm³, an internal diameter of 48 ± 1 mm, an external diameter of 60 mm and a length between 180 and 200 mm. The half-time of cooling with water or other suitable material filled to a height of 20 mm below the rim (i.e. 265 cm³) of Dewar vessel, closed by a tight fitting cork, should be longer than 5 hours. Horizontal graduation marks are drawn at 50 and 100 mm from the top of the Dewar vessel. The time it takes for the decomposition front to propagate from the 50 mm mark to the 100 mm mark yields the deflagration rate. A glass thermometer with an accuracy of 0.1 °C is used to measure the temperature of the test substance prior to ignition. Alternatively, the deflagration rate and sample temperature may be determined by using two thermocouples at distances of 50 mm and 100 mm from the top of the Dewar vessel.

23.4.2.2.3 Any gas flame with a flame length of at least 20 mm can be used for igniting the substance.

23.4.2.2.4 For personal protection, the test is performed in an explosion-proof fume-chamber or in a well-ventilated test-cell. The capacity of the exhaust fan shall be large enough to dilute the decomposition products to the extent that no explosive mixtures with air can be obtained. A shield is placed between the observer and the Dewar vessel.

23.4.2.3 *Procedure*

23.4.2.3.1 ***If preliminary safety-in-handling tests (e.g. heating in a flame) or a small scale burning test (e.g. the series 3 type (d) test) indicate that a rapid reaction is likely to occur, exploratory tests in borosilicate glass tubes should be performed, with suitable safety precautions, prior to the Dewar vessel test.*** In this case, it is recommended that the test be performed in a 14 mm diameter tube first and subsequently in a 28 mm diameter tube. If the deflagration rate in any of these exploratory tests exceeds 5 mm/s, the substance can forthwith be classified as a rapidly deflagrating substance and the main test, using a Dewar vessel, can be omitted.

23.4.2.3.2 The Dewar vessel and the substance are brought to the emergency temperature as defined in the Model Regulations. If the substance is sufficiently stable as to require no emergency temperature, a test temperature of 50 °C is used. The Dewar vessel is filled to a height of 20 mm below the rim with the substance. Granular substances are filled into the Dewar vessel in such a way that the bulk density of the substance will be comparable with that in [transport the package](#) and there are no lumps.

23.4.2.3.3 Pasty materials are introduced into the Dewar vessel in such a way that no air pockets will be present in the sample to be tested. The height of filling shall be about 20 mm below the rim of the Dewar vessel. The mass and the temperature of the substance are recorded. The Dewar vessel is placed in the test-cell or fume-chamber behind a shield, after which the substance is heated at the top by means of a gas burner. At the moment when ignition is observed or, alternatively, if no ignition occurs within five minutes, the gas burner is removed and extinguished. The period of time that is required for the reaction zone to pass the distance between the two marks is measured with the timer. If the reaction stops before reaching the lower mark, the substance is considered to be non-deflagrative. The test is performed in duplicate and the shortest time interval is used for the calculation of the deflagration rate. Alternatively, the rate may be determined by locating thermocouples down the centre of the Dewar at distances 50 mm and 100 mm from the top of the Dewar vessel. The thermocouple outputs are monitored continuously. The passage of the reaction front causes a steep increase in output. The time between the increases in output is determined.

23.4.2.4 *Test criteria and method of assessing results*

23.4.2.4.1 The test results are interpreted in terms of whether a reaction zone will propagate downwards through the substance and, if so, the rate of propagation. The participation of oxygen from the air in the reaction at the sample surface is negligible after the reaction zone has propagated over a distance of 30 mm. The reaction zone will extinguish if the substance does not deflagrate under the test conditions. The propagation velocity of the reaction zone (deflagration rate) is a measure of the susceptibility of the substance to deflagration under atmospheric pressure.

23.4.2.4.2 The test criteria are as follows:

"Yes, rapidly": - the deflagration rate is greater than 5.0 mm/s.

"Yes, slowly": - the deflagration rate is less than or equal to 5.0 mm/s and greater than or equal to 0.35 mm/s.

"No": - the deflagration rate is less than 0.35 mm/s or the reaction stops before reaching the lower mark.

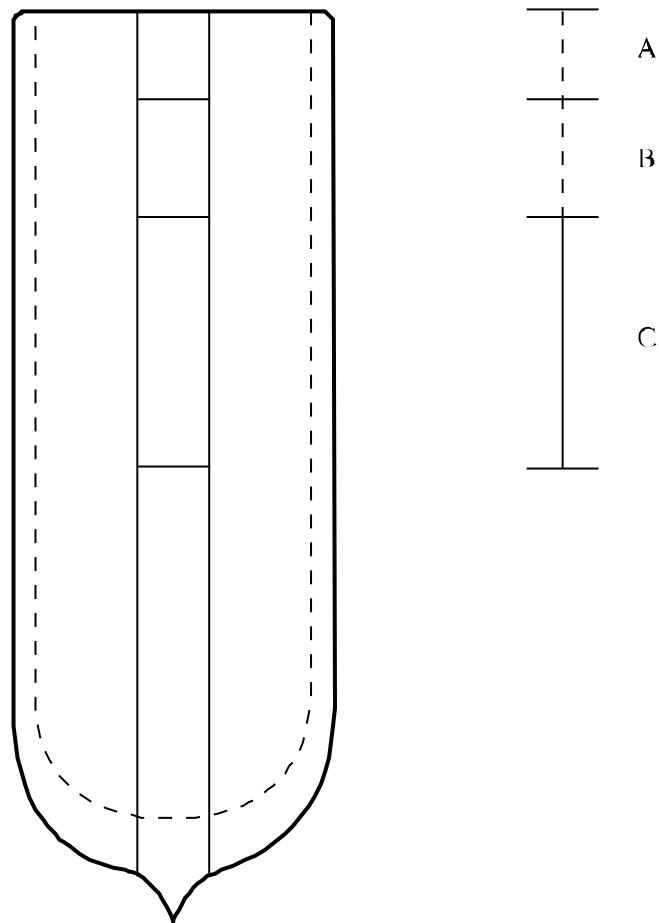
NOTE: The time/pressure test, test C.1, is carried out if "Yes, rapidly" is not obtained.

23.4.2.5 *Examples of results*

Substance	Sample mass (g)	Temperature (°C)	Propagation rate (mm/s)	Result
Azodicarbonamide	174	50	0.35	Yes, slowly
2,2'-Azodi(isobutyronitrile)	101	45	^a	No
tert-Butyl peroxybenzoate	276	50	0.65	Yes, slowly
tert-Butyl peroxy-2-ethylhexanoate	237	25	0.74	Yes, slowly
tert-Butyl peroxy-3,5,5-trimethylhexanoate, 75% in solvent	238	50	0.27	No
Cumyl hydroperoxide, 80% with cumene	273	50	0.12	No
Dibenzoyl peroxide	158	20	100 ^b	Yes, rapidly
Di-tert-butyl peroxide	212	50	0.27	No
Di-(4-tert-butylcyclohexyl) peroxydicarbonate	123	35	4.3	Yes, slowly
Dicetyl peroxydicarbonate	159	35	No ignition	No
Dicumyl peroxide	292	50	No ignition	No
Dicyclohexyl peroxydicarbonate	-	26	26	Yes, rapidly
Dicyclohexyl peroxydicarbonate, 90% with water	-	15	13	Yes, rapidly
Dilauroyl peroxide	130	45	No ignition	No
Dilauroyl peroxide, 42% stable dispersion in water	265	45	No ignition	No
2,5-Dimethyl-2,5-di-(tert-butylperoxy)-hexyne-3	235	50	2.9	Yes, slowly
2,5-Dimethyl-2,5-di-(benzoylperoxy)-hexane	231	50	6.9	Yes, rapidly
4-Nitrosophenol	130	35	0.90	Yes, slowly

^a Pulsating flame followed by extinguishing of flame; no stable propagation under test conditions.

^b Performed with an exploratory test using a glass tube with a diameter of 14 mm at 20 °C instead of 50 °C.



-
- (A) Height of filling 20 mm below rim
(B) 30 mm region for deflagration to be established
(C) 50 mm region for measuring the deflagration rate
-

Figure 23.4.2.1: DEWAR VESSEL WITH OBSERVATION WINDOWS

SECTION 24

TEST SERIES D

24.1 Introduction

Test series D comprises a test and criteria concerning the propagation of a rapid deflagration of a substance as packaged ~~for transport~~. The test is required for substances which deflagrate rapidly in a series C test.

24.2 Test method

24.2.1 The question "Does it deflagrate rapidly in package?" (box 6 of Figure 20.1) is answered on the basis of the results of the test method in Table 24.1.

Table 24.1: TEST METHOD FOR TEST SERIES D

Test code	Name of test	Section
D.1	Deflagration test in package ^a	24.4.1

^a *Recommended test.*

24.2.2 The test is only required for substances for which the answer from the series C test is "Yes, rapidly".

24.3 Test conditions

24.3.1 The test of series D should be applied to packages (not larger than 50 kg) of substance in the condition and form in which they are offered for ~~transport~~classification.

24.3.2 *The preliminary procedure (see section 20.3) should be carried out before performing these tests.*

24.4 Series D test prescription**24.4.1 Test D.1: Deflagration test in the package****24.4.1.1 Introduction**

This test is used to measure the ability of a substance to rapidly propagate a deflagration when packaged ~~as for transport~~. It may be used to answer the question in box 6 of Figure 20.1.

24.4.1.2 Apparatus and materials

An igniter just sufficient to ensure ignition of the substance (e.g. a squib with maximum 2 g of a slow burning pyrotechnic composition wrapped in thin plastics foil) and suitable confining material are required.

24.4.1.3 Procedure

The test is applied to packaged substances in the condition and form in which they are offered for ~~transport~~classification. The package is placed on the ground and the igniter is placed in the centre of the substance. For liquids, a support of metal wires may be needed to fix the igniter in the desired place. The igniter should be protected against the liquid. The test is performed under confinement. The preferred method of confinement is loose sand placed around the test package with a minimum of 0.5 m in every direction. Alternative methods of confinement are to use boxes, bags or drums filled with earth or sand placed around and on top of the package with the same minimum thickness. The test is performed in triplicate, unless an explosion is observed. *If no deflagration is observed after*

ignition, the package should not be approached for at least 30 minutes. It is recommended that a thermocouple be inserted near the igniter to allow monitoring of its operation and to check when it is safe to approach the package.

24.4.1.4 *Test criteria and method of assessing results*

24.4.1.4.1 The test results are assessed on the basis of the evidence of a rapid deflagration of the substance under investigation by:

- (a) Fragmentation of the packaging; and
- (b) Disruption and scattering of most of the confining material.

24.4.1.4.2 The test criteria are as follows:

"Yes" : - Fragmentation of inner or outer packaging into more than three pieces (excluding the bottom and top parts of the packaging) shows that the substance under investigation deflagrated rapidly in that package.

"No" : - No fragmentation or a fragmentation of the inner or outer packaging into not more than three pieces (excluding the bottom and top parts of the packaging) shows that the substance under investigation did not deflagrate rapidly in that package.

24.4.1.5 *Examples of results*

Substance	Packaging	Number of fragments	Result
Dibenzoyl peroxide	1A2, 25 kg	>40	Yes
Dibenzoyl peroxide	4G, 25 kg	>40	Yes
Dibenzoyl peroxide, 94% with water	1A2, 25 kg	>40	Yes
Dibenzoyl peroxide, 75% with water	4G, 25 kg	No fragmentation	No

SECTION 25**TEST SERIES E****25.1 Introduction**

25.1.1 Test series E comprises laboratory tests and criteria concerning the determination of the effect of heating under defined confinement as requested in boxes 7, 8, 9 and 13 of Figure 20.1.

25.2 Test methods

25.2.1 The question "What is the effect of heating it under defined confinement?" (boxes 7, 8, 9 and 13 of Figure 20.1) is answered on the basis of combinations of the results from the test methods in Table 25.1.

Table 25.1: TEST METHODS FOR TEST SERIES E

Test code	Name of test	Section
E.1	Koenen test ^a	25.4.1
E.2	Dutch pressure vessel test ^b	25.4.2
E.3	USA pressure vessel test	25.4.3

^a Recommended test for self-reactive substances in combination with one of the other tests.

^b Recommended test for organic peroxides in combination with one of the other tests.

25.2.2 The combination of the Koenen test and either the Dutch pressure vessel or USA pressure vessel test should be used for self-reactive substances. The combination of the Dutch pressure vessel test and either the Koenen test or the USA pressure vessel test should be used for organic peroxides. For classification, the highest hazard rating should be applied.

25.3 Test conditions

25.3.1 *The preliminary procedure (see section 20.3) should be carried out before performing these tests.*

25.4 Series E test prescriptions**25.4.1 Test E.1: Koenen test****25.4.1.1 Introduction**

This test is used to determine the sensitiveness of substances to the effect of intense heat under high confinement. It may be used, in conjunction with an additional heating under confinement test, to answer the question in boxes 7, 8, 9 and 13 of Figure 20.1.

25.4.1.2 Apparatus and materials

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 SPCEN (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. For classification the following diameter holes shall be used: 1.0 - 1.5 - 2.0 - 2.5 - 3.0 - 5.0 - 8.0 - 12.0 - 20.0 mm. In addition, other diameters can be used for hazard assessment. 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 29 ± 4 MPa.

25.4.1.2.2 Heating is provided by propane, from an industrial cylinder fitted with pressure regulator, via a flow meter and distributed by a manifold to the four burners. Other fuel gases may be used provided 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 cm³ of dibutyl phthalate or equivalent. 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 135 °C to 285 °C is recorded and the heating rate calculated.

25.4.1.2.3 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 25.4.1.2. 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 25.4.1.2. The burners are lit simultaneously by a pilot flame or an electrical ignition device. ***The test apparatus is placed in a protected area.*** Measures should be taken to ensure that the burner flames are not affected by any draughts. Provision should be made for extracting any gases or smoke resulting from the test.

25.4.1.3 Procedure

25.4.1.3.1 The tube is filled to a height of 60 mm from the bottom of the tube. Cast solids should be cast to the internal dimensions of the steel tube with a height of 60 mm and then placed inside the tube. Powders are filled in approximately three equal increments with tamping¹ to 80 N force between each increment. Liquids and gels are loaded into the tube to a height of 60 mm taking particular care with gels to prevent the formation of voids. Determine the total mass used to fill the tube to this level and use this amount of solid for each trial filling being performed. 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.

25.4.1.3.2 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.

25.4.1.3.3 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 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.

25.4.1.3.4 The following effects are differentiated:

- "O": Tube unchanged;
- "A": Bottom of tube bulged out;

¹ ***For reasons of safety, e.g. the substance is friction sensitive, the substance need not be tamped. In cases where the physical form of the sample can be changed by compression or compression of the sample is not related to the transport/packing conditions, e.g. for fibrous materials, more representative filling procedures may be used.***

-
- "B": Bottom and wall of the tube bulged out;
"C": Bottom of tube split;
"D": Wall of tube split;
"E": Tube split into two² fragments;
"F": Tube fragmented into three² 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 25.4.1.3. 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".

25.4.1.3.5 The series of trials is started with a single trial using an orifice plate with a certain diameter mm. If, in this trial, the result "explosion" is observed, the series is continued with single trials at increasing diameters until only negative results in three tests are obtained at the same level. If in the first trial "no explosion" occurs, the series is continued with single trials using plates with the decreasing diameters and finally 1.0 mm until, at one of these diameters, the result "explosion" is obtained. Subsequently, trials are carried out at increasing diameters, until only negative results in three tests are obtained at the same diameter. 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.

25.4.1.4 *Test criteria and method of assessing results*

25.4.1.4.1 The test criteria are as follows:

- "Violent": The limiting diameter is greater than or equal to 2.0 mm.
- "Medium": The limiting diameter is equal to 1.5 mm.
- "Low": The limiting diameter is equal to or less than 1.0 mm and the effect in any test is different from type "O".
- "No": The limiting diameter is less than 1.0 mm and the effect in all tests is of type "O".

² *The upper part of the tube remained in the closing device is counted as one fragment.*

Substance	Sample mass (g)	Limiting diameter (mm)	Type of fragmentation ^a	Result
Azodicarbonamide	20.0	1.5	"F"	Medium
Azodicarbonamide, 67% with zinc oxide	24.0	1.5	"F"	Medium
2,2'-Azodi(2,4-dimethylvaleronitrile)	17.5	< 1.0	"O"	No
2,2'-Azodi(isobutyronitrile)	15.0	3.0	"F"	Violent
Benzene-1,3-disulphohydrazide		12.0	"F"	Violent
Benzene-1,3-disulphohydrazide, 70% with mineral oil		2.0	"F"	Violent
Benzene sulphohydrazide	18.5	1.0	"F"	Low
tert-Butyl peroxybenzoate	26.0	3.5	"F"	Violent
tert-Butyl peroxy-2-ethylhexanoate	24.2	2.0	"F"	Violent
Cumyl hydroperoxide, 84.1% in cumene	27.5	1.0	"F"	Low
2-Diazo-1-naphthol-5-sulphochloride	19.0	2.5	"F"	Violent
Dibenzoyl peroxide	17.5	10.0	"F"	Violent
Dibenzoyl peroxide, 75% with water	20.0	2.5	"F"	Violent
Di-tert-butyl peroxide,	21.5	<1.0	"O"	No
Dicetyl peroxydicarbonate	16.0	<1.0	"O"	No
2,4-Dichlorobenzoyl peroxide	21.0	6.0 ^b	"F"	Violent
Dicumyl peroxide	18.0	<1.0	"O"	No
Diisopropyl peroxydicarbonate	21.0	8.0	"F"	Violent
Dilauroyl peroxide	14.0	<1.0	"O"	No
2,5-Dimethyl-2,5-di(tert-butylperoxy)-hexane	23.0	1.5	"F"	Medium
Dimyristyl peroxydicarbonate	16.0	<1.0	"O"	No
N,N'-Dinitroso-N,N'-dimethyl-terephthalamide 70%, with mineral oil	18.0	4.0	"F"	Violent
Diperoxy isophthalic acid	18.0	24.0	"H"	Violent
Disuccinic acid peroxide	18.0	6.0	"F"	Violent
4-Nitrosophenol	17.0	< 1.0	"A"	Low

^a *At the limiting diameter.*

^b *With a sample mass of 13 g the limiting diameter is < 1.0 mm*

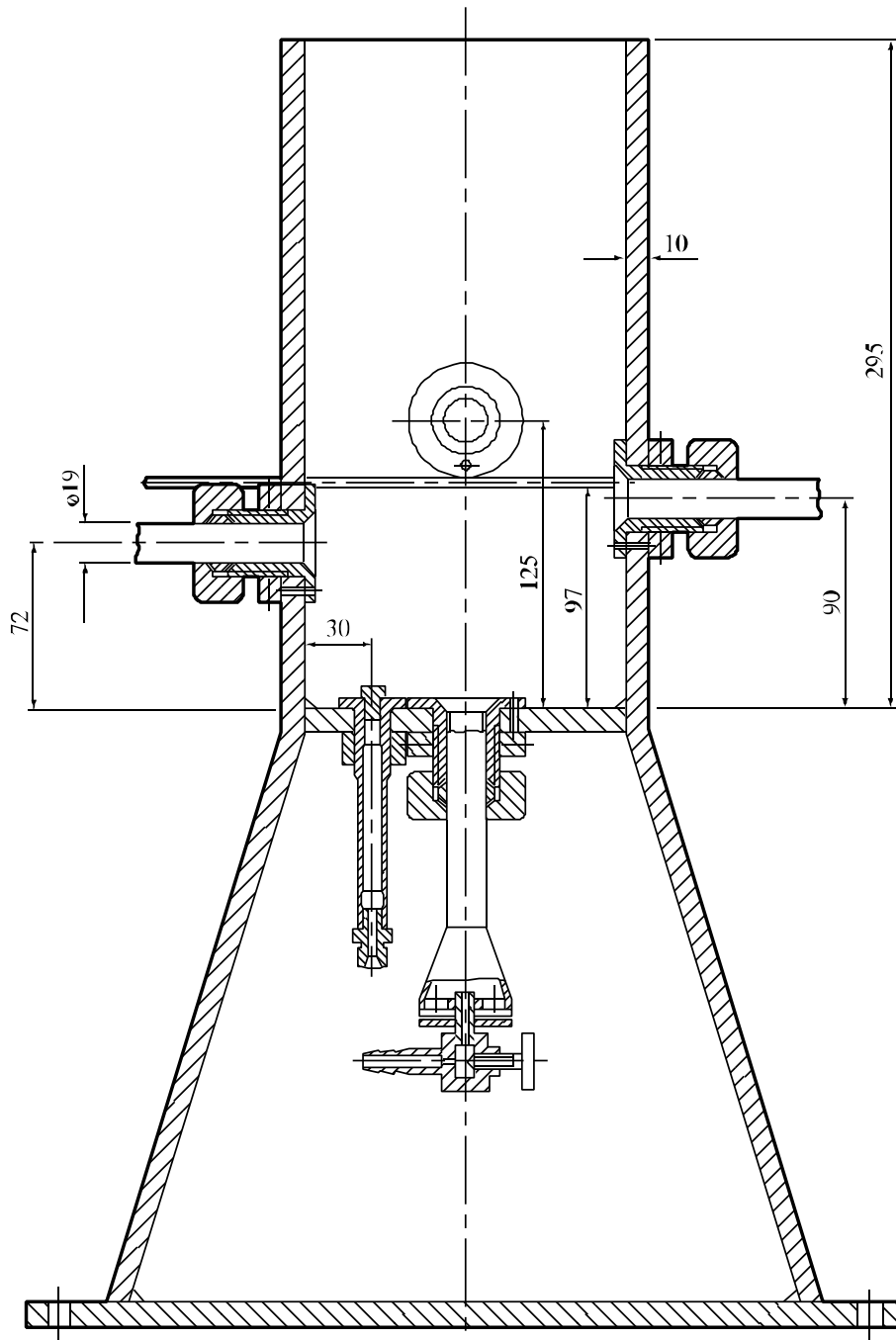


Figure 25.4.1.2: HEATING AND PROTECTIVE DEVICE

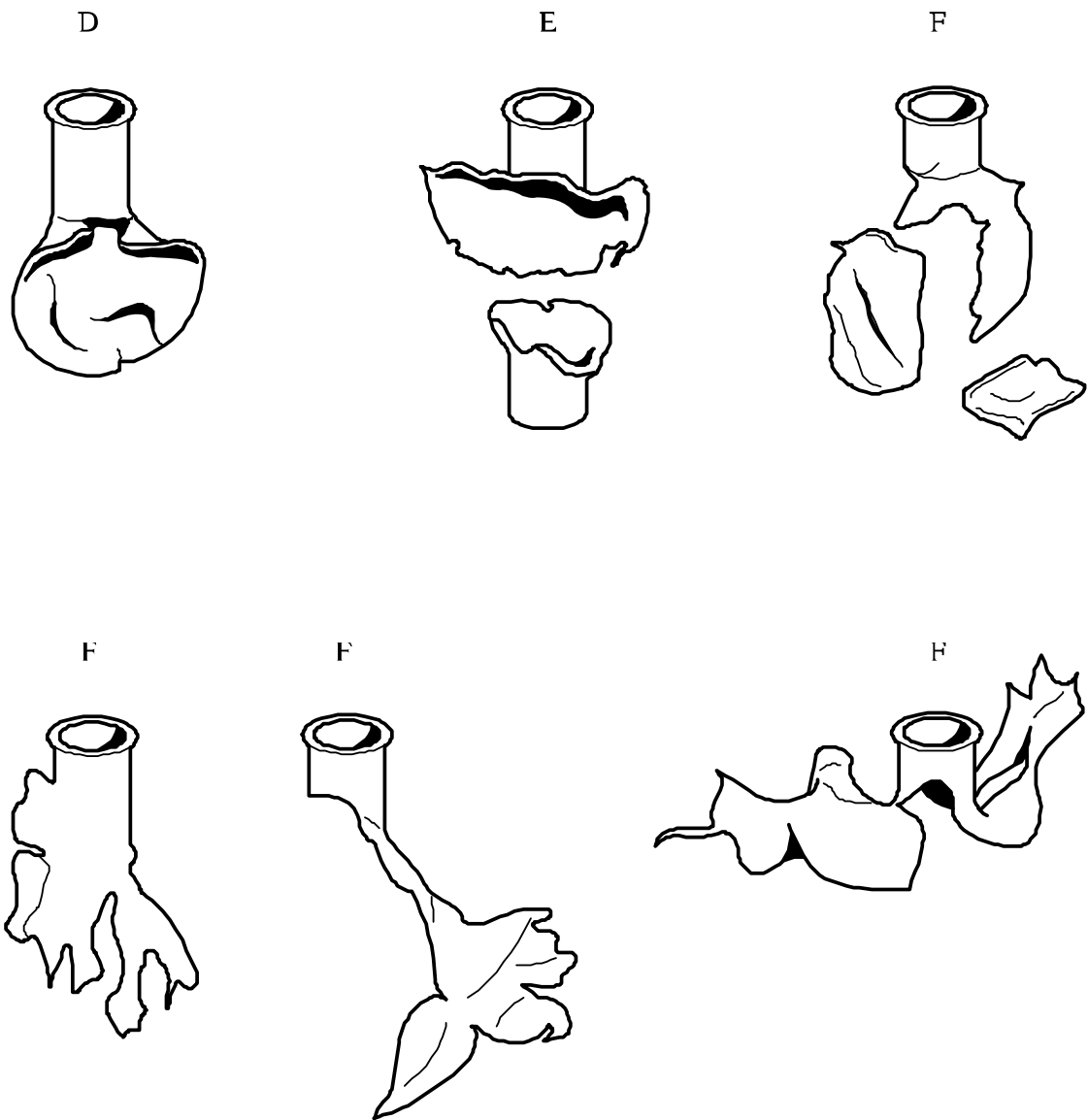


Figure 25.4.1.3: EXAMPLES OF EFFECT TYPES D, E AND F

25.4.2 *Test E.2: Dutch pressure vessel test*

25.4.2.1 *Introduction*

This test is used to determine the sensitiveness of substances to the effect of intense heat under defined confinement. It may be used, in conjunction with an additional heating under confinement test, to answer the question in boxes 7, 8, 9 and 13 of Figure 20.1.

25.4.2.2 *Apparatus and materials*

25.4.2.2.1 Description of the pressure vessel

Figure 25.4.2.1 shows the apparatus used. The vessel is made of stainless steel, type AISI 316. Eight aperture discs are used, the diameters of the orifices being: 1.0 - 2.0 - 3.5 - 6.0 - 9.0 - 12.0 - 16.0 and 24.0 mm. In addition other diameters may be used for hazard assessment. These discs have a thickness of $2.0 \text{ mm} \pm 0.2 \text{ mm}$. The bursting discs are 38 mm diameter aluminium discs rated to burst at $620 \pm 60 \text{ kPa}$ at $22 \text{ }^\circ\text{C}$ (see Figure 25.4.2.2).

25.4.2.2.2 Heating device

The pressure vessel is heated by technical-grade butane taken from a cylinder fitted with a pressure regulator. A Teclu burner is used. Other gases may be used, with a suitable burner, provided that a heating rate of $3.5 \pm 0.3 \text{ K/s}$ is obtained. The heating rate should be checked by heating 10 g of dibutyl phthalate or equivalent in the pressure vessel and measuring its temperature. The time taken for the temperature of the oil to rise from $50 \text{ }^\circ\text{C}$ to $200 \text{ }^\circ\text{C}$ is recorded and the heating rate calculated.

25.4.2.3 *Procedure*

25.4.2.3.1 For a normal test, 10.0 g of the substance should be placed in the vessel. The bottom of the vessel should be evenly covered with the substance. The bursting disc, the selected orifice plate and retaining ring are then put in place. The wing nuts are tightened by hand and the box nut with a spanner. The bursting disc is covered by enough water to keep it at a low temperature. The pressure vessel is placed on a tripod (with an inside ring diameter of 67 mm) which may be placed inside a protective cylinder. The ring at the middle of the vessel rests on the tripod.

25.4.2.3.2 The burner is lit, the flow of gas is set to the required rate and the flow of air adjusted so that the colour of the flame is blue and the inner cone of the flame light blue. The tripod should be of such a height that the inner cone just touches the bottom of the vessel. The burner is then placed under the vessel through an opening in the protective casing. ***The test area should be very well ventilated and entry prohibited during the test.*** The vessel is observed from outside the test area either by mirrors or by an aperture in the wall fitted with armoured glass. The time to reaction and duration of reaction can provide additional information useful in interpreting the results. Finally the receptacle is cooled in water and cleaned.

25.4.2.3.3 The series of trials is started with a single trial using an orifice plate with a certain diameter. If there is no rupture of the disc with this orifice, experiments are performed with single trial using plates with decreasing diameters until rupture of the disc occurs. In cases where no disc rupture is observed with an orifice of 1.0 mm, the next test with an orifice of 1.0 mm is carried out with 50.0 g of the substance instead of 10.0 g. If still no rupture of the disc is observed the experiment is repeated until three successive experiments without rupture are obtained. In the event of rupture of the disc, the experiments are repeated at the next higher level (10 g instead of 50 g or next higher diameter of the orifice) until the level is found at which there are no ruptures in three successive experiments.

25.4.2.4 *Test criteria and method of assessing results*

25.4.2.4.1 The relative degree of sensitivity of a substance to heating in a pressure vessel is expressed by the limiting diameter. This being the orifice with the largest diameter in millimetres with which, in three tests, the bursting disc is broken at least once, while having remained unbroken during three tests with the next larger diameter.

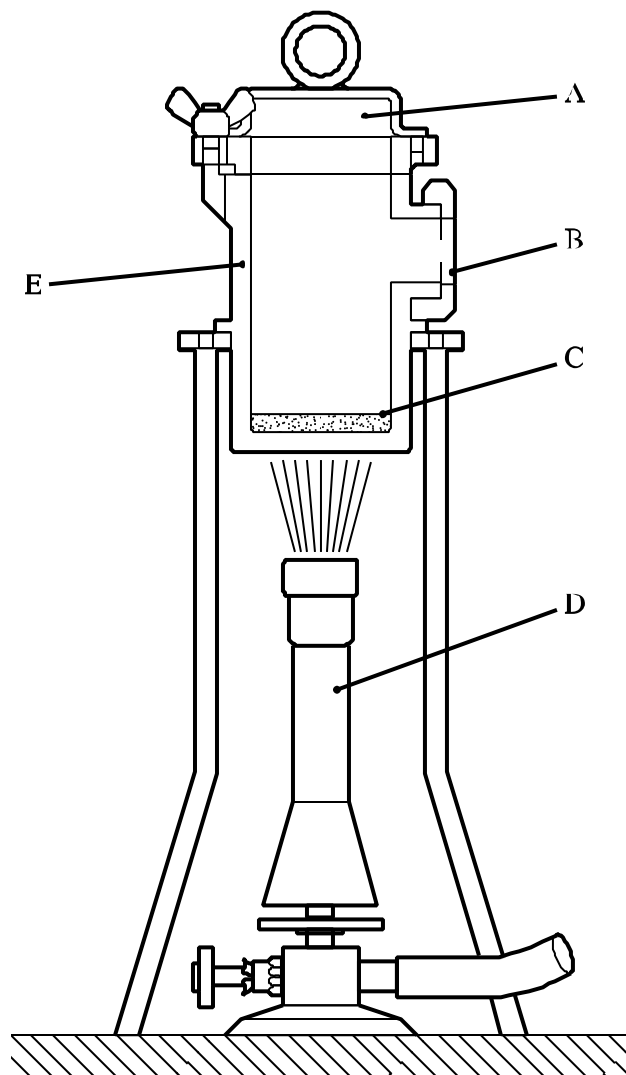
25.4.2.4.2 The test criteria are as follows:

- "Violent": - Rupture of the disc with an orifice of 9.0 mm or greater and a sample mass of 10.0 g.
- "Medium": - No rupture of the disc with an orifice of 9.0 mm but rupture of the disc with an orifice of 3.5 mm or larger but smaller than 9.0 mm and a sample mass of 10.0 g.
- "Low": - No rupture of the disc with an orifice of 3.5 mm and a sample mass of 10.0 g but rupture of the disc with an orifice of 1.0 mm or larger but smaller than 3.5 mm and a sample mass of 10.0 g or rupture of the disc with an orifice of 1.0 mm and a sample mass of 50.0 g.
- "No": - No rupture of the disc with an orifice of 1.0 mm and a sample mass of 50.0 g.

25.4.2.5 *Examples of results*

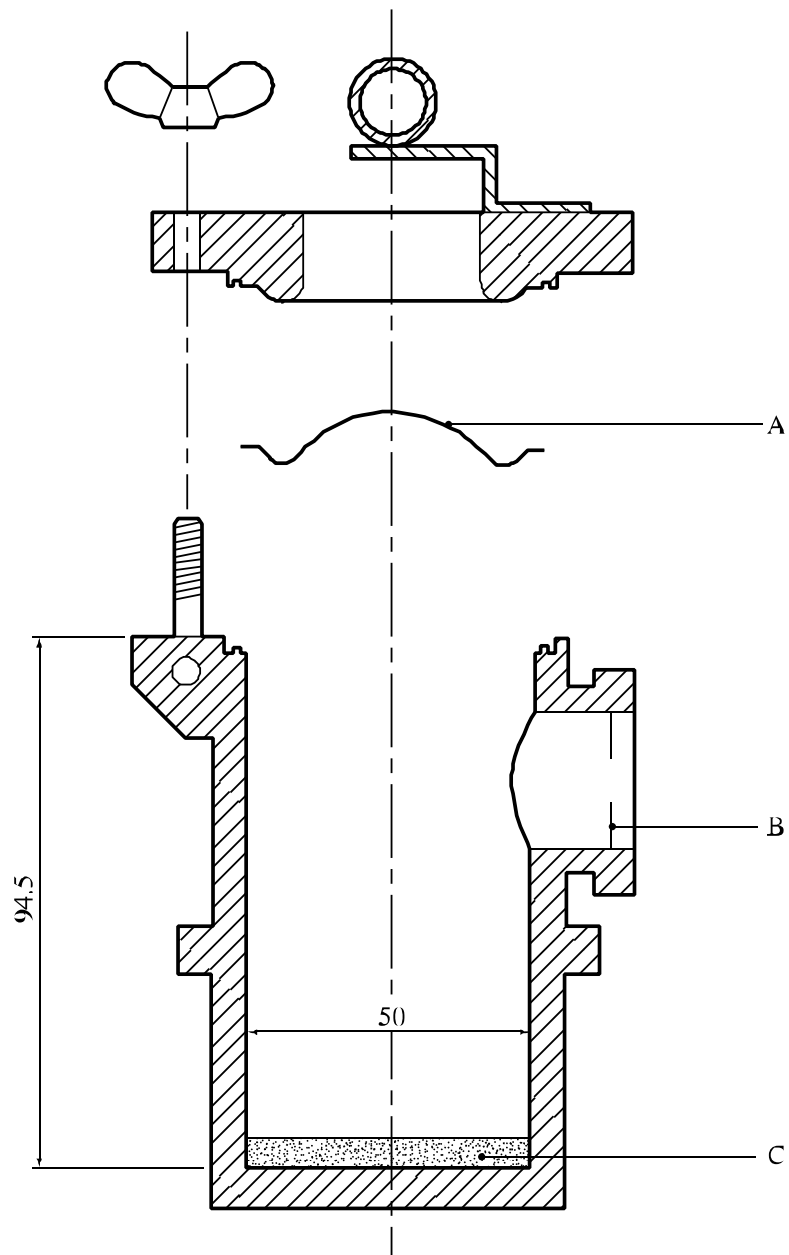
Substance	Limiting diameter (mm)	Result
Azodicarbonamide	1.5	Low
2,2'-Azodi-(2,4-dimethylvaleronitrile)	6.0	Medium
2,2'-Azodi(isobutyronitrile)	5.5	Medium
2,2'-Azodi(2-methylbutyronitrile)	6.0	Medium
tert-Butyl peroxybenzoate	9.0	Violent
tert-Butyl peroxy-2-ethylhexanoate	6.0	Medium
Cumyl hydroperoxide, 80% with cumene	1.0	Low
Dibenzoyl peroxide, 75% with water	6.0	Medium
Di-tert-butyl peroxide	3.5	Medium
Dicetyl peroxydicarbonate	1.0	Low
Dicumyl peroxide	3.5	Medium
2,5-Diethoxy-4-morpholinobenzenediazonium zinc chloride, 90%	< 1.0 ^a	No
2,5-Diethoxy-4-morpholinobenzenediazonium tetrafluoroborate, 97%	< 1.0	No
2,5-Diethoxy-4-(phenylsulphonyl)-benzenediazonium zinc chloride, 67%	< 1.0 ^a	No
Dilauroyl peroxide	2.0	Low
Dilauroyl peroxide, 42%, stable dispersion in water	< 1.0 ^a	No
3-Methyl-4-(pyrrolidin-1-yl)benzene-diazonium tetrafluoroborate, 95%	< 1.0 ^a	No
4-Nitrosophenol	1.0 ^a	Low

^a *Test carried out with a 50 g sample.*



-
- (A) Bursting disc
 - (B) Orifice plate
 - (C) Test sample (10 g or 50 g)
 - (D) Teclu burner
 - (E) Pressure vessel with an internal diameter of 50 mm and internal height of 94.5 mm
-

Figure 25.4.2.1: DUTCH PRESSURE VESSEL TEST



- (A) Bursting disc
- (B) Orifice plate
- (C) Test sample

Figure 25.4.2.2: BURSTING DISC ASSEMBLY

25.4.3 *Test E.3: United States pressure vessel test*

25.4.3.1 *Introduction*

This test is used to determine the sensitiveness of substances to the effect of intense heat under defined confinement. It may be used, in conjunction with an additional heating under confinement test, to answer the question in boxes 7, 8, 9 and 13 of Figure 20.1.

25.4.3.2 *Apparatus and materials*

The following apparatus and materials are used:

- (a) Test-vessel: 316 stainless steel cylindrical pressure vessel (see Figure 25.4.3.1);
- (b) Pressure vessel holder (see Figure 25.4.3.2);
- (c) Electrical heater (e.g. 700 W);
- (d) Sample holder: aluminium cup 28 mm × 30 mm;
- (e) Rupture discs: 38 mm aluminium rupture discs rated 620 ± 50 kPa at 22 °C;
- (f) 2 mm thick orifice plates with the following orifice diameters (mm): 1.0, 1.2, 2.0, 3.0, 3.5, 5.0, 6.0, 8.0, 9.0, 12.0, 16.0 and 24.0.

25.4.3.3 *Procedure*

25.4.3.3.1 The general assembly of the apparatus is shown in Figure 25.4.3.1. The heating rate should be checked by heating 5.0 g of dibutyl phthalate in a sample cup in the pressure vessel and measuring the temperature of the dibutyl phthalate. The time taken for the temperature of the dibutyl phthalate to rise from 50 °C to 200 °C is recorded and the heating rate calculated. The heating rate should be 0.5 ± 0.1 K/s. An orifice plate, with an orifice diameter larger than the expected vent needed to cause rupture, is selected and inserted into the side port.

25.4.3.3.2 A 5.0 g sample of the substance to be tested is weighed accurately into an aluminium cup. The cup is then lowered and positioned with the aid of forceps in the centre of the pressure vessel. The rupture disc is positioned and secured tightly by the flange bolts. Water is poured over the rupture disc to keep the disc relatively cool. The heating is switched on to the correct setting at least 30 minutes prior to the start of the test. The test-vessel is inserted into the pressure vessel holder onto the heater. This plate holder prevents the test-vessel from falling over. It also prevents escaping vent vapours from reaching the hot plate. The time to decomposition is noted.

25.4.3.3.3 If the disc does not rupture, the experiment is repeated using a smaller orifice diameter until rupture of the disc occurs. In the event of a rupture of the disc, the experiment is repeated at the next higher diameter of the orifice until the level is found at which there are no ruptures in three successive experiments.

25.4.3.4 *Test criteria and method of assessing results*

25.4.3.4.1 The smallest orifice diameter which does not cause a rupture disc to burst during decomposition is designated as the USA-PVT number. This value is used as a measure of the effects of heating a substance under defined confinement. USA-PVT ratings for all substances are based on the same test conditions and heating rate.

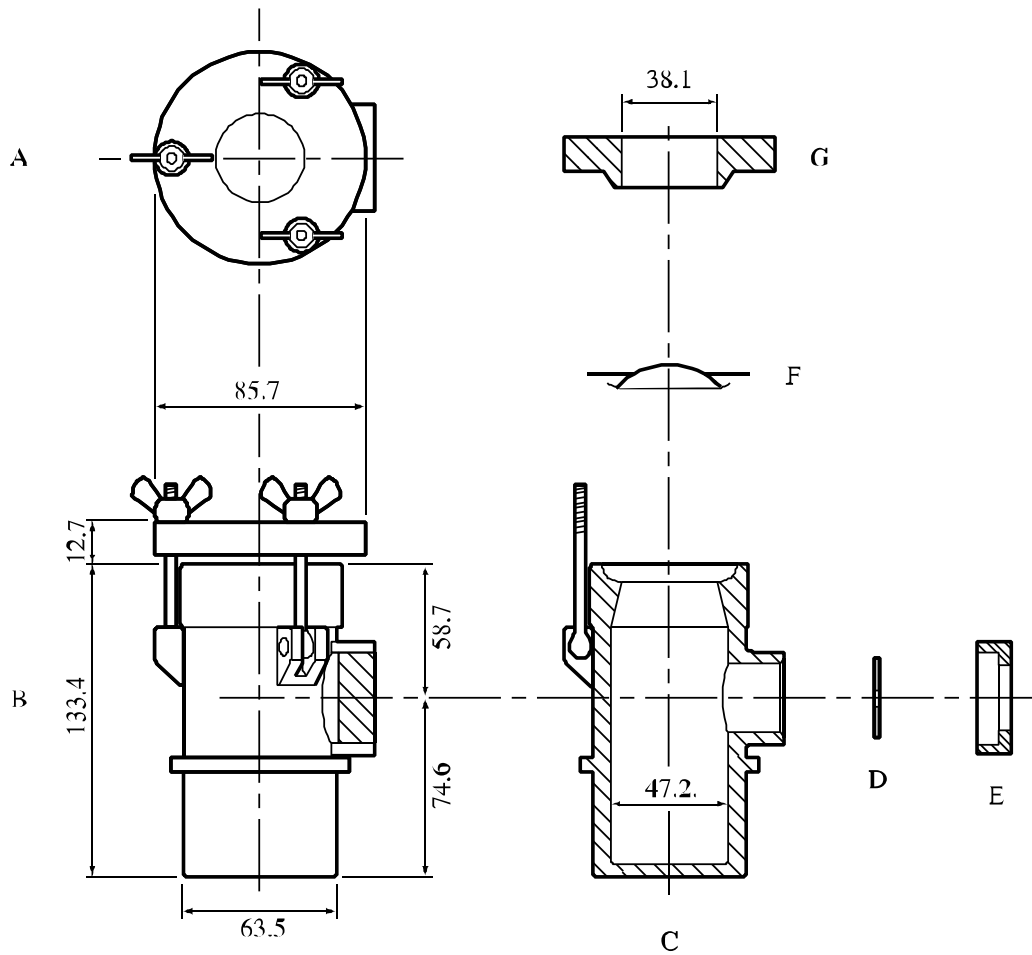
25.4.3.4.2 The effect of heating under confinement of the substance is defined by the following criteria:

- "Violent": - Substances having USA-PVT numbers 9.0 to 24.0.
- "Medium": - Substances having USA-PVT numbers 3.5 to 8.0.
- "Low": - Substances having USA-PVT numbers 1.2 to 3.0.
- "No": - Substances having USA-PVT number 1.0.

25.4.3.5 *Examples of results*

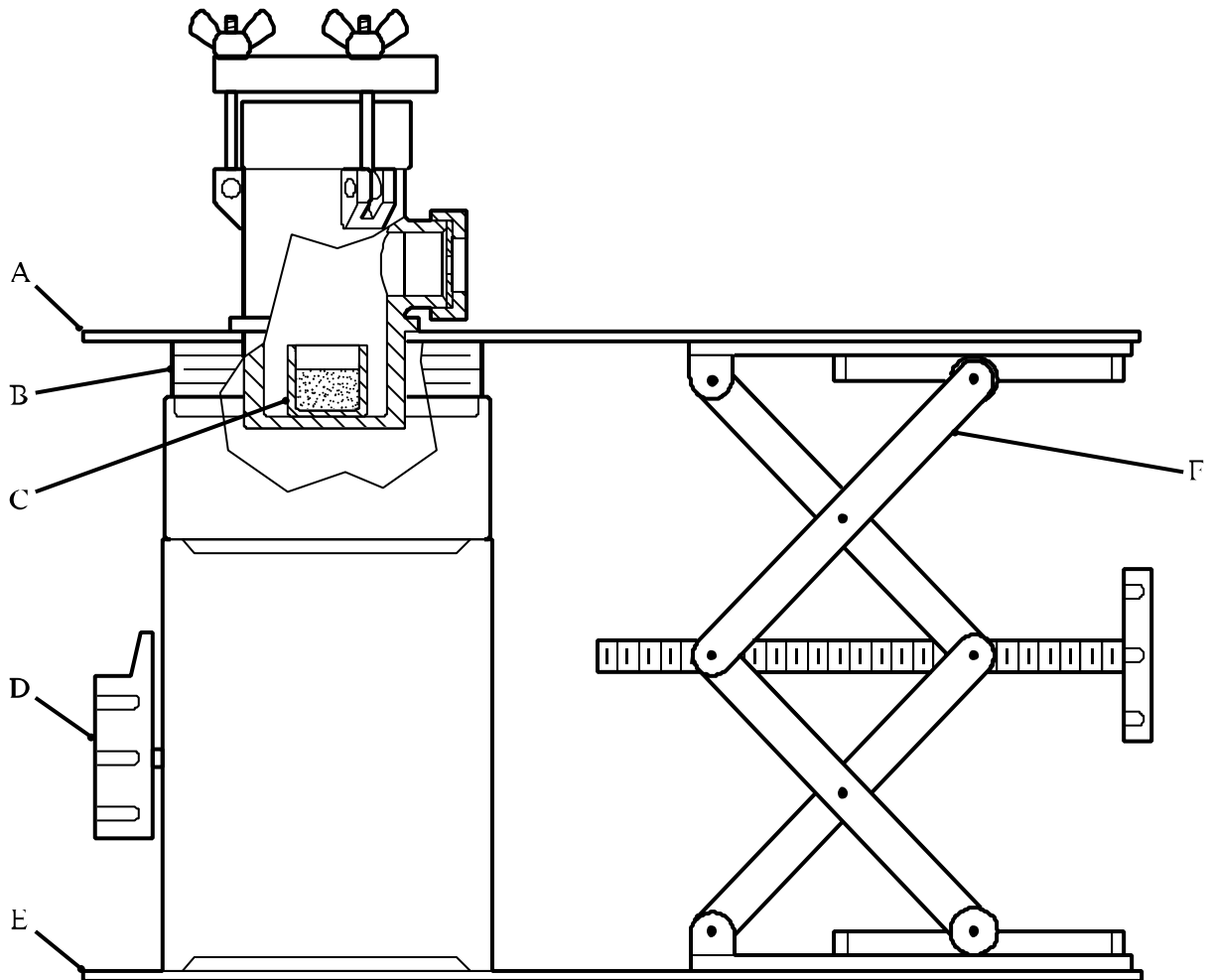
Substance	USA-PVT No	Result
tert-Butyl hydroperoxide, 70% with water	1.0	No
tert-Butyl peroxy acetate, 75% in solution	8.0	Medium
tert-Butyl peroxybenzoate	8.0	Medium
tert-Butyl peroxy isopropyl carbonate, 75% in solution	2.0	Low
tert-Butyl peroxy pivalate, 75% in solution	4.5 ^a	Medium
Cumyl hydroperoxide, 85% with cumene	1.0	No
Dibenzoyl peroxide	18.0 ^a	Violent
Di-tert-butyl peroxide	1.0	No
Dicumyl peroxide	2.0	Low
Dicumyl peroxide, with 60% inert solid	1.0	No
Dilauroyl peroxide	6.0	Medium
2,5-Dimethyl-2,5-di-(tert-butylperoxy) hexyne-3	9.0	Violent

^a *Intermediate diameters, no longer used.*



-
- (A) Top view of lid
 - (B) Side view of assembly
 - (C) Body of pressure vessel
 - (D) Orifice plate
 - (E) Orifice plate retaining nut
 - (F) Bursting disc
 - (G) Cap
-

Figure 25.4.3.1: UNITED STATES PRESSURE VESSEL TEST



- (A) Shield
- (B) Thermal insulation
- (C) Sample cup
- (D) Electrical heater
- (E) Base
- (F) Laboratory jack

Figure 25.4.3.2: TEST APPARATUS AND STAND (side view)

SECTION 26

TEST SERIES F

26.1 Introduction

26.1.1 Test series F comprises laboratory tests and criteria concerning the explosive power of substances as requested in box 12 of Figure 20.1. It is applicable to those substances which are being considered for ~~transport containment~~ in intermediate bulk containers (IBCs) or tank-containers or for exemption from the provisions for self-reactive substances ~~of Division 4.1~~ or organic peroxides ~~of Division 5.2~~ (see box 11 of Figure 20.1). Substances not being considered for these may be assigned to type E without further testing.

26.1.2 All the tests, except test F.5, may also be used for those substances which are being screened for their ability to propagate detonation (see 21.2.2).

26.2 Test methods

The question "What is its explosive power?" (box 12 of Figure 20.1) is answered on the basis of the results of one of the test methods in Table 26.1.

Table 26.1: TEST METHODS FOR TEST SERIES F

Test code	Name of test	Section
F.1	Ballistic mortar Mk.IIIId test	26.4.1
F.2	Ballistic mortar test	26.4.2
F.3	BAM Trauzl test	26.4.3
F.4	Modified Trauzl test ^a	26.4.4
F.5	High-pressure autoclave	26.4.5

^a *Recommended test.*

26.3 Test conditions

26.3.1 *The preliminary procedure (see section 20.3) should be performed before carrying out these tests.*

26.3.2 The results obtained in tests F.1 to F.4 depend on the sensitivity to detonative shock of the substance and the strength of the detonator used. If the results are much lower than those obtained with similar substances, a more powerful initiation system may be used with a suitable adjustment (e.g. by firing with inert samples) to the test criteria.

26.3.3 The tests should be performed at ambient temperature. However, if the control temperature is below ambient temperature, adequate safety precautions should be taken. If the substance is ~~transported~~ under temperature control ~~as~~ a solid but is liquid at ambient temperature then the test should be performed just below the melting point.

26.4 Series F test prescriptions

26.4.1 Test F.1: Ballistic mortar Mk.III d test

26.4.1.1 Introduction

This test is used to measure the explosive power of a substance. A detonator is initiated in the substance whilst the substance is confined in the bore of a mortar. The recoil (swing) of the mortar is measured and, after allowing for the effect of the detonator, the power is calculated as a percentage equivalence of picric acid - the explosive standard. The test may be used to answer the question in box 12 of Figure 20.1.

26.4.1.2 Apparatus and materials

26.4.1.2.1 The mortar consists of a steel tube 457 mm long by 203 mm external diameter, closed at one end and having a bore 229 mm long with an internal diameter of 25 mm, flaring out at the open end. The mortar is suspended by 4 stainless steel cables attached at either end by bottle screws and pivots, thus allowing it to swing freely. The total weight is approximately 113.2 kg and the suspension length is 2,080 mm. A pen, secured at the extremity of a hinged trailing arm attached to the mortar, scribes on a horizontal table a line equal to the horizontal swing of the mortar. The mortar body is made in two pieces, an outer casing of mild steel and an inner cylinder of Vibrac V30 steel heat-treated to a proof stress of 772 MPa. This cylinder is held in place by a retaining annular plate (Figure 26.4.1.1).

26.4.1.2.2 The sand used for stemming is clean, dry, quartz sand sieved to pass a BS 600 micron sieve and to be retained on a BS 250 micron sieve. The picric acid is in the form of pure, dry crystals sieved in the same manner. Boric Acid (analytical grade) is sieved to pass a BS 500 micron sieve. Charge bags are cylindrical, 25 mm in diameter and made of thin paper. The inner charge bag is 90 mm long and the outer charge bag 200 mm long.

26.4.1.2.3 The detonator used is a flat-based aluminium sheathed detonator containing 0.6 g PETN.

26.4.1.3 Procedure

26.4.1.3.1 Impact, friction and electric spark tests are normally carried out on the substance before it is tested in the mortar. 10.00 ± 0.01 g of the substance is tamped into the inner charge bag. The detonator is inserted into a 6 mm cavity made in the substance with a phosphor-bronze rod and the neck of the bag is twisted around the detonator. The charge is then inserted in the outer bag and pressed down to the bottom with a special tool. 57 g of sieved sand is poured into the outer bag and gently compacted by tapping. The neck of the outer bag is twisted around the detonator wires and the whole charge is inserted into the bore of the mortar and rammed with the special tool. The detonator is fired and the total horizontal swing (S) is measured. The test is performed three times and the average swing (S_m) for the substance calculated.

26.4.1.3.2 Liquids are tested by using a cylindrical glass vessel¹ of approximately 16 ml volume instead of the paper charge bag. The open end of the vessel is reduced to a narrow tube 8 mm in diameter and 8 mm in length. The standard detonator sheathed in a suitable length of polythene tubing makes a push fit seal in the neck of the vessel. The vessel is then inserted into the outer charge bag, as for solids.

26.4.1.3.3 The picric acid standard value and the detonator standard value established with paper charge bags may be employed in the power equivalence calculation for liquids fired in glass vessels.

26.4.1.3.4 When a new inner cylinder is inserted into the outer casing of the mortar, the mean swing (average of 10 shots) given by boric acid (B_m) and picric acid (P_m) are found.

¹ The use of glass vessels with powerful explosives can damage the mortar liner. Test firings with picric acid in glass vessels caused severe wear but produced the same results as picric acid fired in paper charge bags.

26.4.1.4 *Test criteria and method of assessing results*

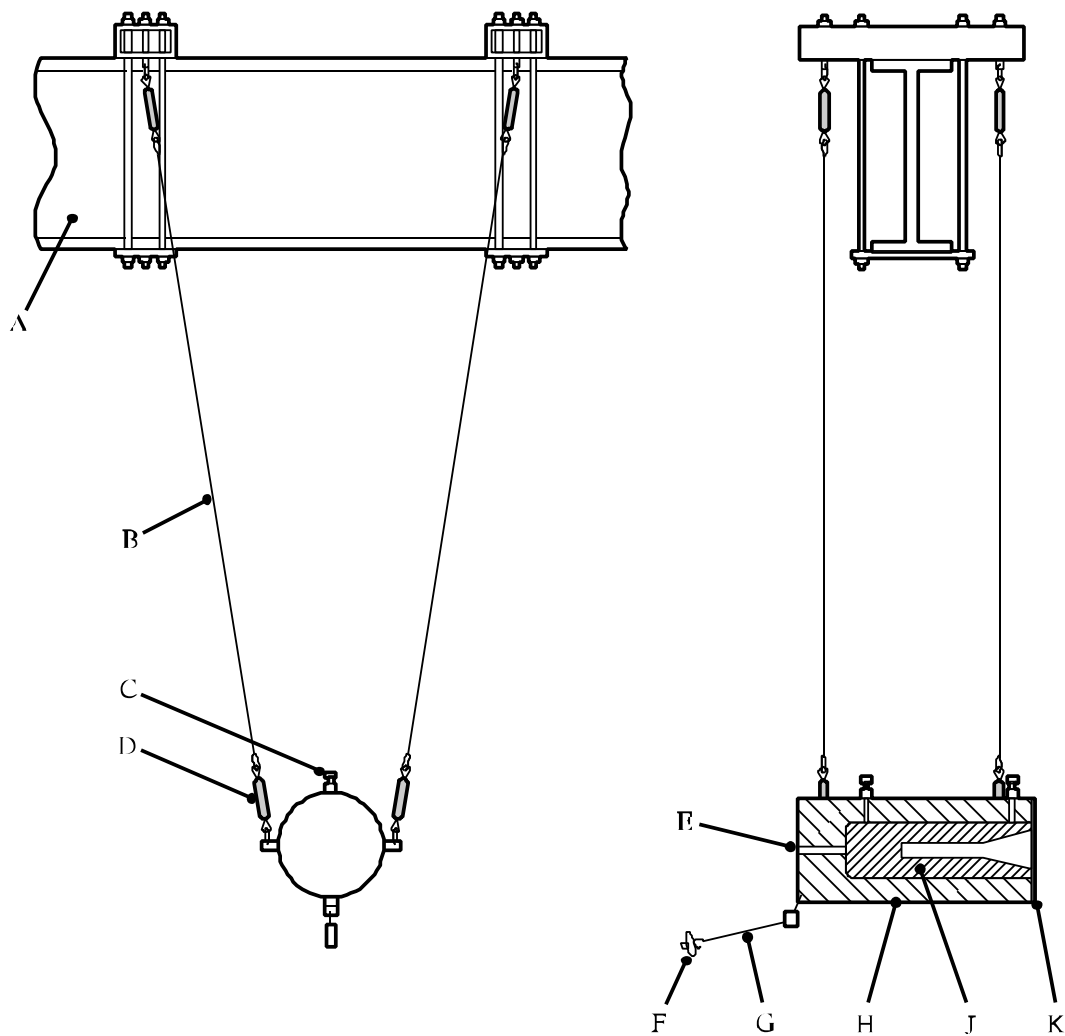
26.4.1.4.1 The explosive power (P) is calculated from $P = 100 \times \frac{(S_m^2 - B_m^2)}{(P_m^2 - B_m^2)}$ as a percentage (rounded to the nearest whole number) of the value given by picric acid.

26.4.1.4.2 The test criteria are as follows:

- "Not Low": - Explosive power values of 7% or greater of that given by picric acid.
- "Low": - Explosive power values of less than 7% of that given by picric acid but more than 1% of that given by picric acid.
- "No": - Explosive power values of 1% or less of that given by picric acid.

26.4.1.5 *Examples of results*

Substance	Mean % of picric acid	Result
tert-Butyl hydroperoxide, 70% with water	2	Low
tert-Butyl peroxybenzoate	13	Not low
tert-Butyl peroxy-2-ethylhexanoate	8	Not low
Cumyl hydroperoxide, 80% in cumene	4	Low
Dibenzoyl peroxide	8	Not low
Dibenzoyl peroxide, 75% with water	6	Low
Di-tert-butyl peroxide	8	Not low
Dicetyl peroxydicarbonate	1	No
Dicumyl peroxide, with 60% inert solid	1	No
Dilauroyl peroxide	1	No
2,5-Dimethyl-2,5-di-(tert-butylperoxy)hexyne-3	17	Not low
Magnesium monoperoxyphthalate hexahydrate, 85% with magnesium sulphate	1	No



- | | | | |
|-----|----------------------------|-----|--------------------------|
| (A) | Suspension beam | (B) | Suspension wire |
| (C) | Liner set-screws | (D) | Bottle screws |
| (E) | Hole to aid liner removal | (F) | Stylus holder |
| (G) | Hinged trailing stylus arm | (H) | Mortar body outer casing |
| (J) | Inner liner | (K) | Annular retaining plate |

Figure 26.4.1.1: BALLISTIC MORTAR MK.IIID

26.4.2 Test F.2: Ballistic mortar test26.4.2.1 *Introduction*

This test is used to measure the explosive power of a substance. A detonator is initiated in the substance whilst the substance is confined in the bore of a mortar by a steel projectile. The recoil of the mortar is measured and the power is calculated as a percentage equivalence of picric acid - the explosive standard. The test may be used to answer the question in box 12 of Figure 20.1.

26.4.2.2 *Apparatus and materials*

26.4.2.2.1 Mortar

The mortar is made of chrome-nickel steel with a mass of 248.50 ± 0.25 kg. It is cylindrical and the axial cavity consists, from front to rear, of the projectile holder, the firing chamber and access for the detonator lead wires. The dimensions of the mortar will change during use (in particular, the firing chamber is enlarged) resulting in diminished recoil with the firing of a given charge. The reference charge used is 10.00 g picric acid (see 26.4.2.2.7). The used mortar is replaced by a new one when the average energy released in the last 10 firings is less than 90 per cent of the average energy produced in the first 10 firings (for similar temperatures and using a projectile in good condition).

26.4.2.2.2 Ballistic Pendulum

The mortar is suspended by steel arms from a roller-bearing mounted horizontal axis. The mortar pendulum is rendered ballistic by attaching a steel weight underneath it. Figure 26.4.2.1 is a representation of the ballistic mortar-pendulum, which has the following principal characteristics:

oscillation period	3.47 s
oscillating mass	479 kg
distance between axis of rotation and axis of mortar	2.99 m

A cursor on the graduated sector displaced by a lateral arm attached to the mortar is used to measure the recoil. The scale marked on the sector is proportional to $(1 - \cos A)$, A being the angle of recoil of the pendulum, i.e. proportional to the work performed.

26.4.2.2.3 Projectile

The projectile is a steel cylinder. The diameters (diameter 127 mm, length 162 mm) are in practice adjusted to meet the following conditions:

- (a) The gap between the projectile, when new, and its housing in the mortar should be less than 0.1 mm;
- (b) The mass of the projectile, when new, should be 16.00 ± 0.01 kg.

A worn projectile should be replaced when the gap between it and its housing in the mortar exceeds 0.25 mm. On firing, the projectile is normally expelled at a speed of between 100 and 200 km/h. The use of a receptacle lined with shock absorbing material enables it to be stopped without being damaged.

26.4.2.2.4 Sample vessels

When liquids are tested, glass ampoules of 16 g mass with a filling orifice and a recess to take the detonator (see Figure 26.4.2.3) are used to contain the test samples. Other substances (solid, granular, pastes, etc.) are loaded in cylindrical sample vessels, 20 mm in diameter, made of tinfoil of thickness 0.03 mm and mass about 2 g. This applies, for instance, to picric acid charges.

26.4.2.2.5 Supports

A steel-wire ring support with three feet, shown in Figure 26.4.2.2, is used to centre the charge in the firing chamber (to reduce wear on the mortar).

26.4.2.2.6 Detonators

These are European standard detonators charged with 0.6 g PETN, as shown in Appendix 1.

26.4.2.2.7 Picric acid (reference substance)

This is pure crushed picric acid, grain size less than 0.5 mm, dried at 100 °C and kept in a tightly-stoppered flask.

26.4.2.3 *Procedure*

26.4.2.3.1 Preparation of charge

26.4.2.3.1.1 Compact solids have to be tested in the form of cylindrical blocks, diameter $20 \text{ mm} \pm 1 \text{ mm}$, with at one end an axial cavity (diameter $7.3 \pm 0.2 \text{ mm}$, depth 12 mm) to accommodate the detonator. The mass of the block should be $10.0 \pm 0.1 \text{ g}$. To prepare the charge, the block is wrapped in tinfoil, thickness 0.03 mm, mass approximately 2 g. The detonator is placed in its housing and the end of the foil wrapping pressed around the head of the detonator (see Figure 26.4.2.3).

26.4.2.3.1.2 Substances other than liquids are packed at normal density in tinfoil wrappings, each test charge weighing $10.0 \pm 0.1 \text{ g}$. The detonator is inserted to a depth of approximately 12 mm in the substance. The end of the wrapping is twisted around the head of the detonator (see Figure 26.4.2.3).

26.4.2.3.1.3 For liquids, a charge of $10.0 \pm 0.1 \text{ g}$ of the test substance is placed in a glass ampoule. The detonator is placed in its housing. If necessary, metal wire can be used to hold it in place (but under no circumstances combustible material).

26.4.2.3.1.4 Charges of $10.0 \pm 0.1 \text{ g}$ of picric acid, at normal density, are also prepared in foil wrappings. The detonator is inserted to a depth of approximately 12 mm in the picric acid. The end of the wrapping is twisted around the head of the detonator.

26.4.2.3.2 Trial run

26.4.2.3.2.1 The charge, placed in a charge holder (see 26.4.2.2.5) is pressed home in the firing chamber, the detonator head being in contact with the rear surface of the chamber (see Figure 26.4.2.3).

26.4.2.3.2.2 The projectile is greased with a consistent quality lubricant, inserted and pushed home in its housing in the mortar. To avoid any scatter in the results, due to possible distortion of the mortar or projectile, the position of the projectile in relation to the mortar housing is checked and recorded.

26.4.2.3.2.3 The cursor (see 26.4.2.2.2) is placed in contact with the moving arm so that the recoil of the pendulum can be measured. After firing, the deviation (D) of the pendulum is noted, i.e. the point at which the cursor remains on the graduated sector at the end of the swing.

26.4.2.3.2.4 The projectile and bore should then be carefully cleaned.

26.4.2.4 *Procedure*

26.4.2.4.1 Four firings are first carried out with picric acid. The average of the four deviations obtained is calculated. This average should have a value around 100, in the arbitrary unit of power adopted for the scale of the sector on which the pendulum recoil is measured. The results of the four firings should not vary by more than one unit, and if that is the case, the value D_0 will be the average of the four deviations measured. If one of the results varies by more than one unit from the average, it is discarded and the value D_0 is the average of the other three results.

26.4.2.4.2 The ambient temperature is recorded.

26.4.2.4.3 The procedure is then repeated with the test substance, for not less than three firings, the deviations obtained being D_1 , D_2 , D_3 etc. The corresponding powers, expressed as a percentage of the finding for picric acid, are calculated by the equation:

$$T_k = 100 \times \frac{D_k}{D_o}, \text{ where } k = 1, 2, 3, \dots,$$

or, for liquids fired in glass ampoules:

$$T_k = 200 \times \frac{D_k}{D_o}, \text{ where } k = 1, 2, 3, \dots$$

26.4.2.4.4 The average value of T_k is then calculated. The result, rounded to the nearest whole number, is called the "ballistic mortar power" (BMP) of the substance.

NOTE: When several substances are to be tested in succession during the same half-day, only one series of four firings with picric acid is made in the half-day.

26.4.2.5 Test criteria and method of assessing results

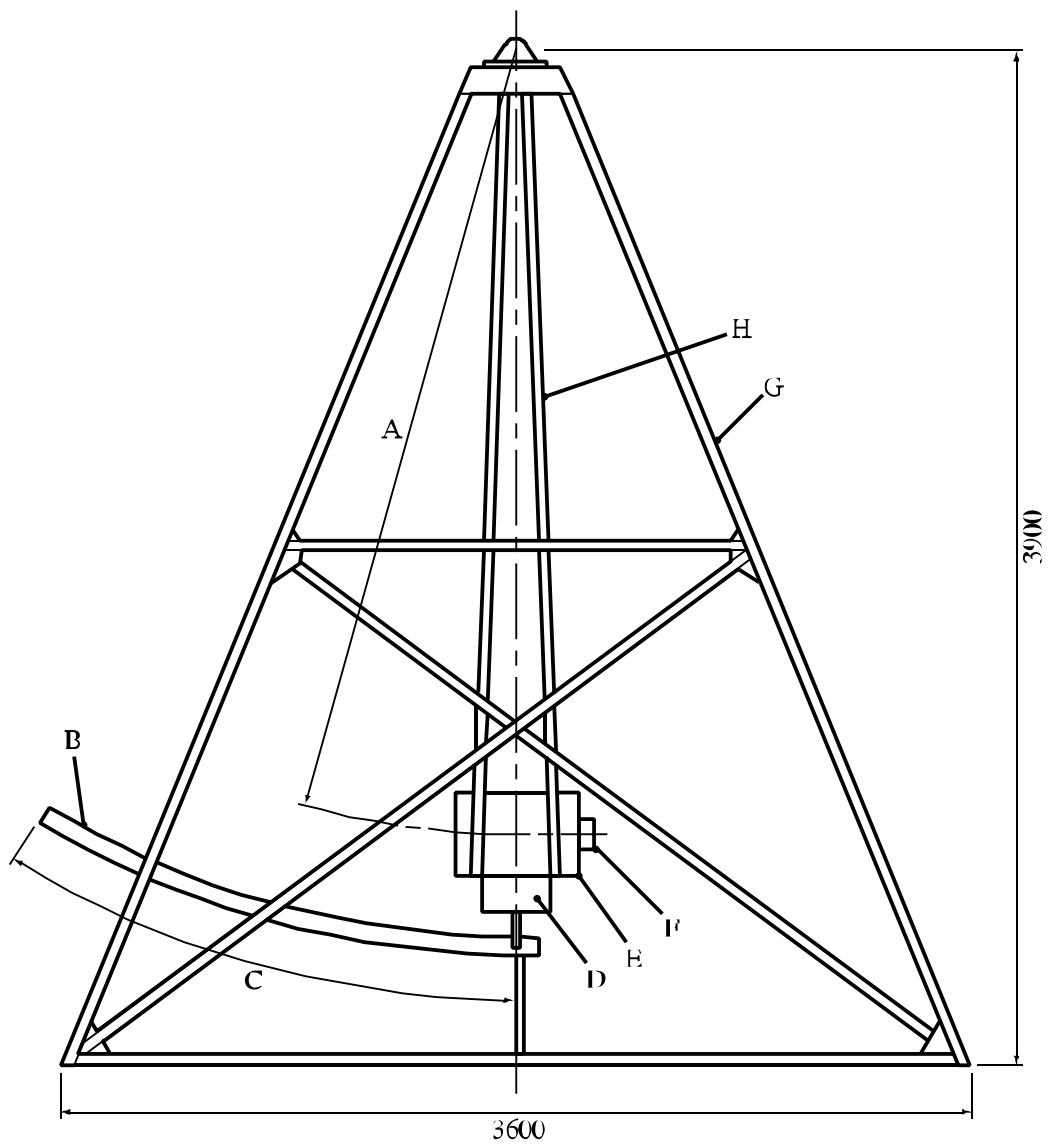
26.4.2.5.1 The result of the test is presented in detail by giving the results T_1 , T_2 , T_3 ... and the value of BMP and the ambient temperature. In summary form, only the BMP value is given.

26.4.2.5.2 The test criteria are as follows:

- "Not Low": - BMP values of 7 or more.
- "Low": - BMP values less than 7 but more than 1.
- "No": - BMP values of 1 or less.

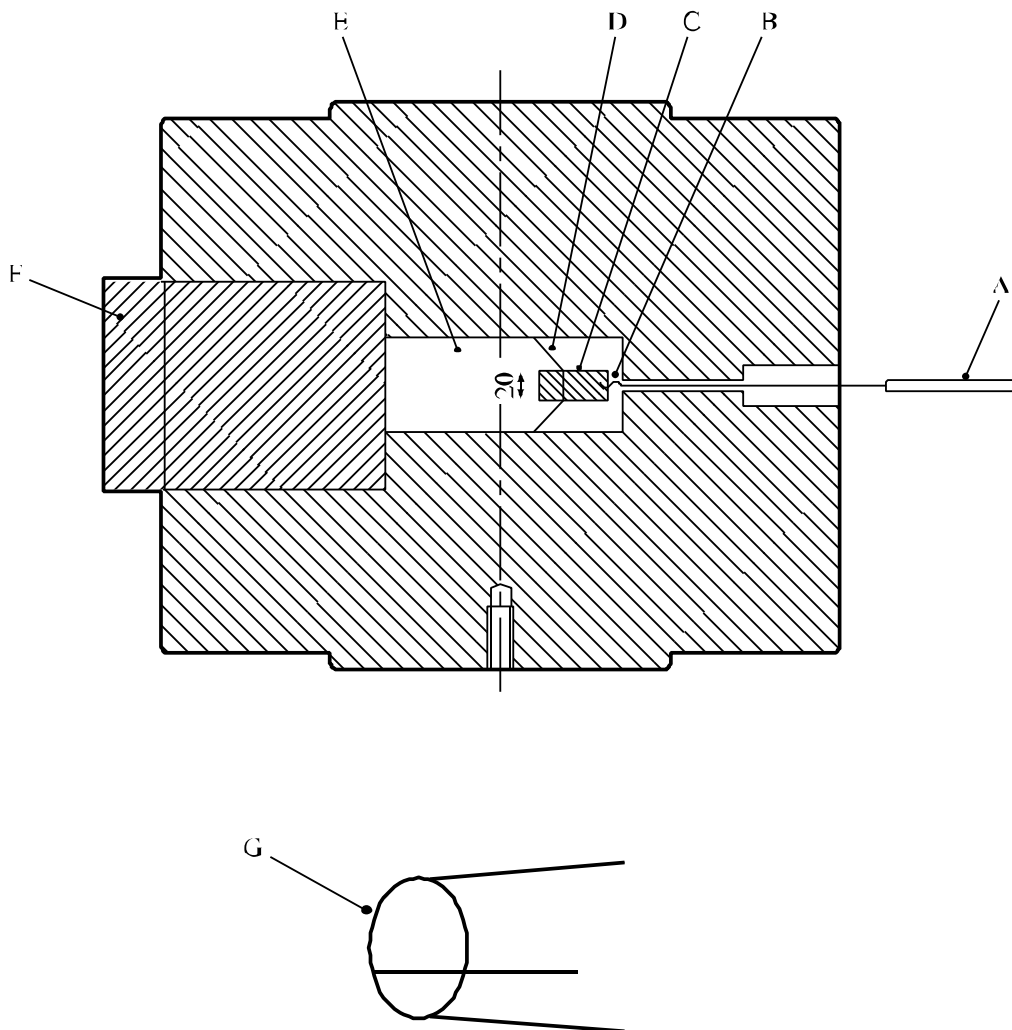
26.4.2.6 Examples of results

Substance	BMP value	Result
2,2'-Azodiisobutyronitrile	13	Not low
tert-Butyl peroxybenzoate	16	Not low
tert-Butyl peroxy-2-ethylhexanoate	7	Not low
Dibenzoyl peroxide	16	Not low
Dibenzoyl peroxide, 75% with water	8	Not low
Di-tert-butyl peroxide	7	Not low
Dilauroyl peroxide	5	Low
p-Menthyl hydroperoxide, 55% in p-menthane	3	Low
Peroxyacetic acid, 36% in a mixture with 19% water, 36% acetic acid and 6% hydrogen peroxide, with stabiliser	27	Not low
Pinanyl hydroperoxide, 54% in pinane	2	Low
Picric acid	100	
Trinitrotoluene	95	
Sand	1	



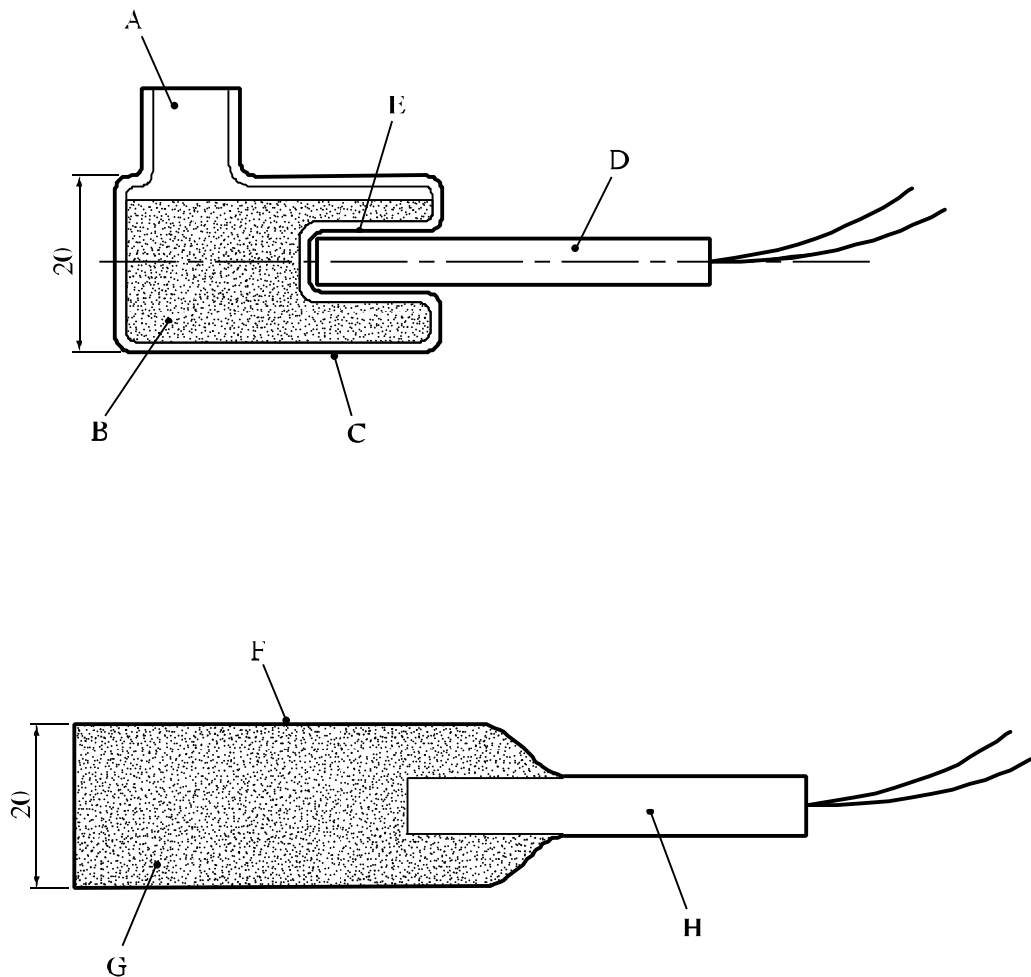
-
- (A) 2 905 mm distance between axes
 - (B) Graduated scale
 - (C) 30° swing angle
 - (D) Weight
 - (E) Mortar
 - (F) Projectile
 - (G) Frame
 - (H) Swinging arm
-

Figure 26.4.2.1: BALLISTIC MORTAR TEST



- (A) To igniter
- (B) Detonator
- (C) 20 mm diameter charge
- (D) Charge holder
- (E) Firing chamber
- (F) Projectile
- (G) Expanded view of charge holder

Figure 26.4.2.2: MORTAR (TOP) AND CHARGE HOLDER (BOTTOM)



-
- (A) Filling orifice
 - (B) 20 mm diameter charge containing 10 g of substance
 - (C) Glass ampoule (16 g)
 - (D) 0.6 g PETN detonator
 - (E) Detonator housing
 - (F) 2 g foil wrapping
 - (G) 20 mm diameter charge containing 10 g of substance
 - (H) 0.6 g PETN detonator
-

Figure 26.4.2.3: CHARGE FOR LIQUIDS (TOP) AND SUBSTANCES OTHER THAN LIQUIDS (BOTTOM)

26.4.3 *Test F3: BAM Trauzl test*26.4.3.1 *Introduction*

This test is used to measure the explosive power of a substance. A detonator is initiated in the substance whilst the substance is confined in a hole in a lead block. The explosive power is expressed in the form of the increase in volume of the cavity in the lead block per 10 g of substance. The test may be used to answer the question in box 12 of Figure 20.1.

26.4.3.2 *Apparatus and materials*

26.4.3.2.1 Initiation of the substance is achieved by a European standard detonator with 0.6 g of PETN (see Appendix 1).

26.4.3.2.2 For the test, standardized Trauzl lead blocks of cylindrical shape are used with a height of 200 mm and a diameter of 200 mm. They have an axial recess of 25 mm diameter and 125 mm depth with a volume of 61 cm³, see Figure 26.4.3.1. The lead blocks are made by casting pure soft lead into moulds at a casting temperature of 390 °C to 400 °C. The quality of a casting series of lead blocks is checked by three test explosions each using 10 cm³ of crystallized picric acid (loading density 1.0 g/cm³). The mean of the three net expansion values obtained should be between 287 cm³ and 300 cm³.

26.4.3.3 *Procedure*

26.4.3.3.1 Solid substances are shaped to cylindrical test charges with a volume of 10 cm³ by wrapping in a weighed piece of tinfoil and the mass of the charge determined. The test charges have an external diameter of 24.5 mm, a height of 22.2 mm, and a coaxial recess of 7 mm diameter and 12 mm depth to take the detonator. The test charge is prepared in a device consisting of a piston, a two-part matrix, a clamping frame and a base piece (Figure 26.4.3.2). For this, a trapezoidal piece of tinfoil (thickness approx. 0.01 mm) 55 mm wide is wound round the piston. The die with its tinfoil sheath is then introduced into the matrix until it reaches the backstop of the base. The matrix is clamped with the aid of the frame and the piston is slowly drawn out of the tinfoil tube after pressing it firmly against the base piece. The bottom of the tinfoil tube is carefully pierced in its centre using a thin wooden rod. From the side of the clamping frame, the standard detonator PETN 0.6 g is inserted into the base piece so that the detonator wires are drawn through the hole in the adjusting screw until the detonator touches the screw. The screw is so adjusted that the detonator projects 12.0 mm from the base piece. The substance to be tested is put into the tinfoil tube, compressing it lightly by means of a wooden rod. The projecting tinfoil edge is folded inwards and the piston is pressed into the matrix up to the collar. After withdrawing the piston, the prepared test charge, in the tinfoil tube, with the inserted detonator, is carefully taken out of the matrix.

26.4.3.3.2 Liquid substances are tested in thin-walled glass cylinders of similar shape and of such a capacity as to take the sample volume of 10 cm³ and that of the detonator, when it is introduced to a depth of 12 mm into the liquid. The neck of the vessel is of such a length that it keeps the detonator in a central position. After having determined the sample mass, the test charge is carefully introduced into the recess of the lead block right to the bottom. The lead blocks are stored in a temperature-controlled room, so that the temperature, measured in the depth of the recess, immediately before introducing the charge, is in the range 10 °C and 20 °C. For the test, the lead block should rest on a flat, massive support of steel laid on the ground. For stemming, the remaining space in the recess is filled with dry quartz sand, passed through a sieve of 144 meshes per cm², with a gravimetric density of 1.35 g/cm³. The lead block is then hit at the side three times with a hammer of 2 kg mass and the excess of sand is removed from the upper surface.

26.4.3.3.3 The detonator is fired and the block emptied of any residues. The volume of the enlarged cavity is measured using water and the expansion which would be caused by a 10 g sample calculated using the expression:

$$10 \times \frac{\text{Volume of enlarged cavity (cm}^3\text{)} - 61}{\text{Sample mass (g)}}$$

26.4.3.3.4 Normally, the test is conducted in duplicate and the highest expansion value obtained used for the assessment.

26.4.3.4 *Test criteria and method of assessing results*

26.4.3.4.1 The explosive power is expressed in the form of the increase in volume of the cavity in the lead block per 10 g of substance. At a given strength of initiation, the explosive power increases with the volume of expansion.

26.4.3.4.2 The test criteria are as follows:

"Not Low": - The expansion of the lead block is 25 cm³ or more per 10 g of sample.

"Low": - The expansion of the lead block is less than 25 cm³ but more than or equal to 10 cm³ per 10 g of sample.

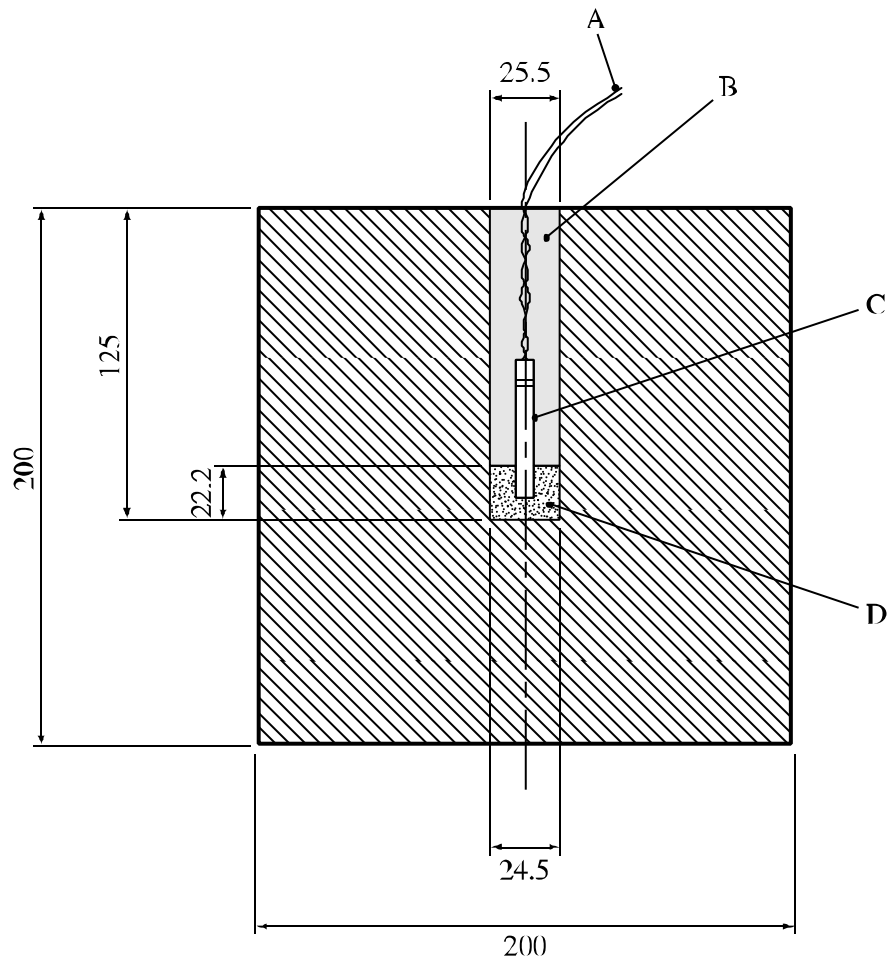
"No": - The expansion of the lead block is less than 10 cm³ per 10 g of sample.

26.4.3.5 *Examples of results*

Substance	Sample mass (g)	Expansion (cm ³ /10g)	Result
Azodicarbonamide		9	No
2,2'-Azodi(isobutyronitrile)		26 ^a	Not low
Benzene-1,3-disulphohydrazide		50 ^a	Not low
Benzene-1,3-disulphohydrazide, 70% with mineral oil		11 ^a	Low
Benzene sulphohydrazide	8.4	8	No
tert-Butyl peroxybenzoate	9.1	32 ^a	Not low
tert-Butylperoxy-2-ethylhexanoate	7.2	28 ^a	Not low
3-Chloroperoxybenzoic acid, not more than 86% with 3-chlorobenzoic acid	7.1	42 ^a	Not low
Cumyl hydroperoxide, 84.1% with cumene	9.3	10	Low
Cyclohexanone peroxide(s)	6.4	50 ^a	Not low
Dibenzoyl peroxide	8.0	31 ^a	Not low
Dibenzoyl peroxide, 75% with water	8.0	21 ^a	Low
Di-tert-butyl peroxide	7.2	28 ^a	Not low
Dicetyl peroxydicarbonate	7.3	5 ^a	No
Dicumyl peroxide	6.9	12 ^a	Low
Diisopropyl peroxydicarbonate	7.8	78 ^a	Not low
Dilauroyl peroxide	8.0	11 ^a	Low
Dimyristyl peroxydicarbonate	7.4	11	Low
Dimyristyl peroxydicarbonate, 42%, stable dispersion in water	7.8	5 ^a	No
N,N'-Dinitrosopentamethylene tetramine		147 ^a	Not low
N,N'-Dinitrosopentamethylene tetramine 80%, with 17% inorganic solid and 3% mineral oil	10.2	7 ^b	No
Diperoxy isophthalic acid	8.7	144	Not low
4-Nitrosophenol	7.3	11	Low
Boric acid		0	
Dimethyl phthalate		5	
Water		6	

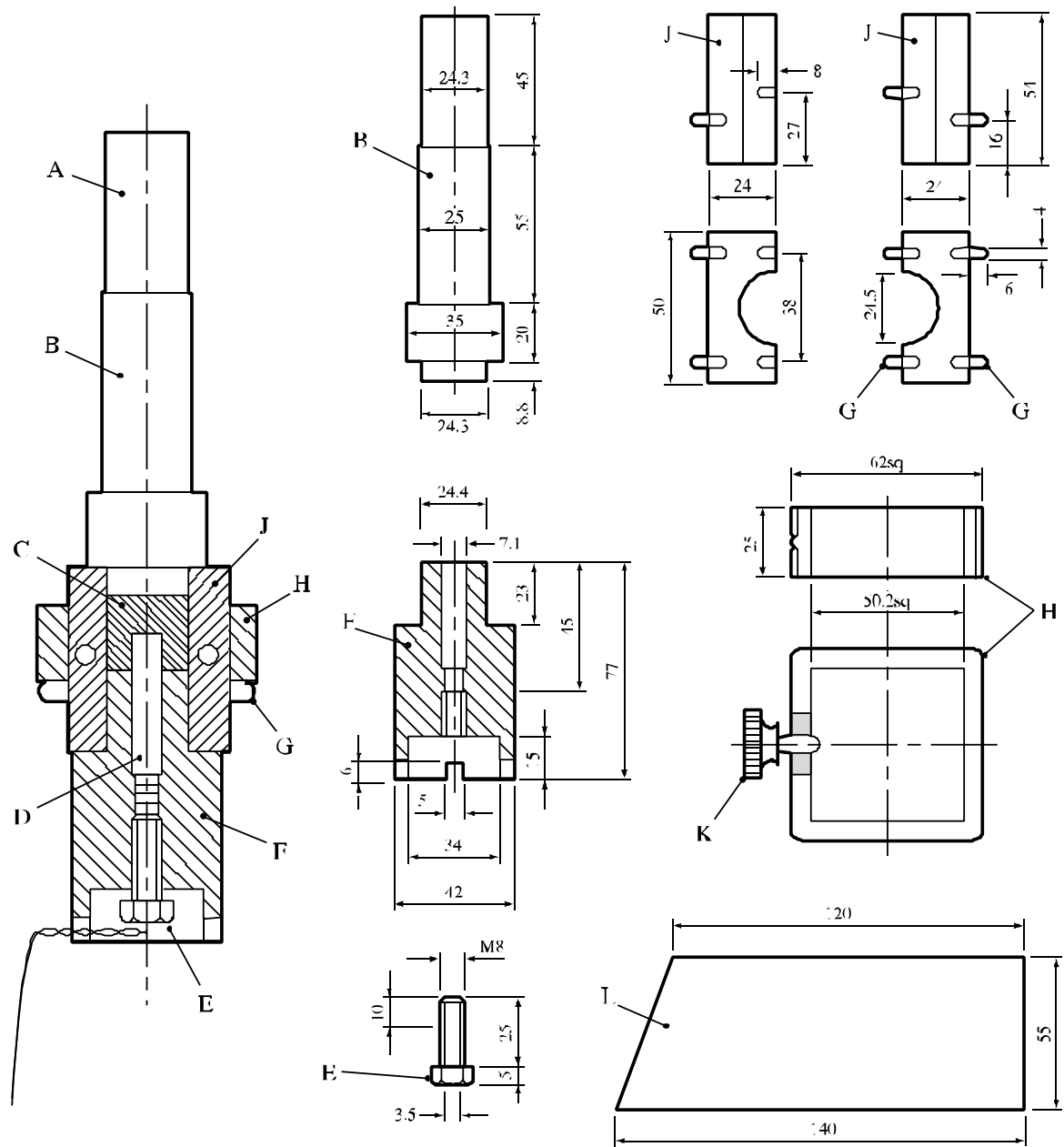
^a Determined by using test charges of 11 cm³ volume and a slightly stronger test blasting cap with a copper tube of 6.85 mm external diameter and 45 mm length, with flat bottom containing 0.5 g PETN with 10% wax, 0.2 g tetryl, and 0.5 g mercury fulminate as explosive charge, all pressed at 400 bar.

^b Initiation with 3 detonators gives 123 cm³/10 g, Not low



- (A) Detonator wires
- (B) Dry sand stemming
- (C) European standard detonator
- (D) Test sample

Figure 26.4.3.1: BAM TRAUZL TEST



- | | |
|---|--------------------|
| (A) End part of piston for preparing the tinfoil tube | (B) Piston |
| (C) Test sample | (D) Detonator |
| (E) Adjusting screw (axial bore 3.5 mm, slot 1 mm, 100 mm long) | (F) Base piece |
| (G) Pins | (H) Clamping frame |
| (J) Matrix | (K) Knurled screw |
| (L) Tin foil | |

Figure 26.4.3.2: DEVICE FOR MAKING THE CHARGES
(10 cm³ volume, 24.6 mm diameter and 22.2 mm height) FOR THE BAM TRAUZL TEST

26.4.4 *Test F.4: Modified Trauzl test*26.4.4.1 *Introduction*

This test is used to measure the explosive power of a substance. A detonator is initiated in the substance whilst the substance is confined in a hole in a lead block. The explosive power is expressed in the form of the average increase in volume of the cavity in the lead block over the value obtained from an inert substance with similar physical properties. The test may be used to answer the question in box 12 of Figure 20.1.

26.4.4.2 *Apparatus and materials*

The lead block is machined from cast or extruded lead rod 50 ± 1 mm diameter by 70 mm long with a cavity 25.4 mm in diameter and 57.2 mm long as shown in Figure 26.4.4.1. The cavity is cut with a flat-tipped drill to prevent puncture of the lead block. The blasting cap used is a standard No. 8 (USA) detonator (see Appendix 1). Assembly A is used for liquids and pastes and assembly B for solids (see Figure 26.4.4.2). The sample vial used for assembly A is a commercial 12 ml, 21 mm outer diameter vial. The sample vial used for assembly B is a commercial 16 ml, 24.9 mm outer diameter vial. The polyethylene stoppers are the standard ones supplied with the vials. The glass tube used to locate the blasting cap in assemblies A and B is a borosilicate glass culture tube. It is 10 mm outer diameter \times 75 mm long. A 10 mm diameter hole drilled in the centre of the polyethylene stopper gives a tight fit which holds the tube secure. Two rubber "O" rings (16.5 mm inner diameter, 2.5 mm diameter cross section) are used to centre the vial in the cavity in the lead block in assembly A.

26.4.4.3 *Procedure*

A 6.0 g sample is placed in the sample vial which is assembled as required and placed in the lead block. The lead block is placed on a solid surface in a protected area, the blasting cap is fully inserted and, when the area is vacated, the cap is fired. The volume of the cavity in the lead block is measured accurately, to the nearest 0.2 ml, using water before and after the test. Three tests are conducted on the substance and on the inert reference substance using the same type of assembly.

26.4.4.4 *Test criteria and method of assessing results*

26.4.4.4.1 The explosive power of the test sample is expressed in terms of the average increase of the volume of the cavity in the lead block over that given by the inert reference substance.

26.4.4.4.2 The test criteria are as follows:

"Not low": - The average net block expansion is equal to or greater than 12 cm^3 .

"Low": - The average net block expansion is less than 12 cm^3 but greater than 3 cm^3 .

"No": - The average net block expansion is 3 cm^3 or less.

Substance	Average net expansion (cm ³)	Result
2,2'-Azodi(isobutyronitrile)	18	Not low
2,2'-Azodi(2-methylbutyronitrile)	14	Not low
tert-Butyl hydroperoxide, 72% with water	7	Low
tert-Butyl peroxyacetate, 75% in solution	25	Not low
tert-Butyl peroxybenzoate	19	Not low
tert-Butyl peroxy-2-ethylhexanoate	10	Low
Cumyl hydroperoxide, 85% with cumene	5	Low
Dibenzoyl peroxide	16	Not low
Di-tert-butyl peroxide	12	Not low
Di-sec-butyl peroxydicarbonate	23 ^a	Not low
Diisopropyl peroxydicarbonate	45 ^a	Not low
2,5-Dimethyl-2,5-di-(tert-butylperoxy)hexyne-3	31	Not low
2,5-Dimethyl-2,5-di-(benzoylperoxy) hexane	9	Low
Di-n-propyl peroxydicarbonate	32 ^a	Not low

Expansion with inert reference substances in assembly A

Air	6
Dimethyl phthalate	10
Mineral spirits	10.5
Paste of 60% CaCO ₃ + 40% dimethyl phthalate	8
Water	10

Expansion with inert reference substances in assembly B

Air	5.5
Benzoic acid	7
Calcium carbonate (powder)	5
Kaolin clay	6

^a *Performed at ambient temperature.*

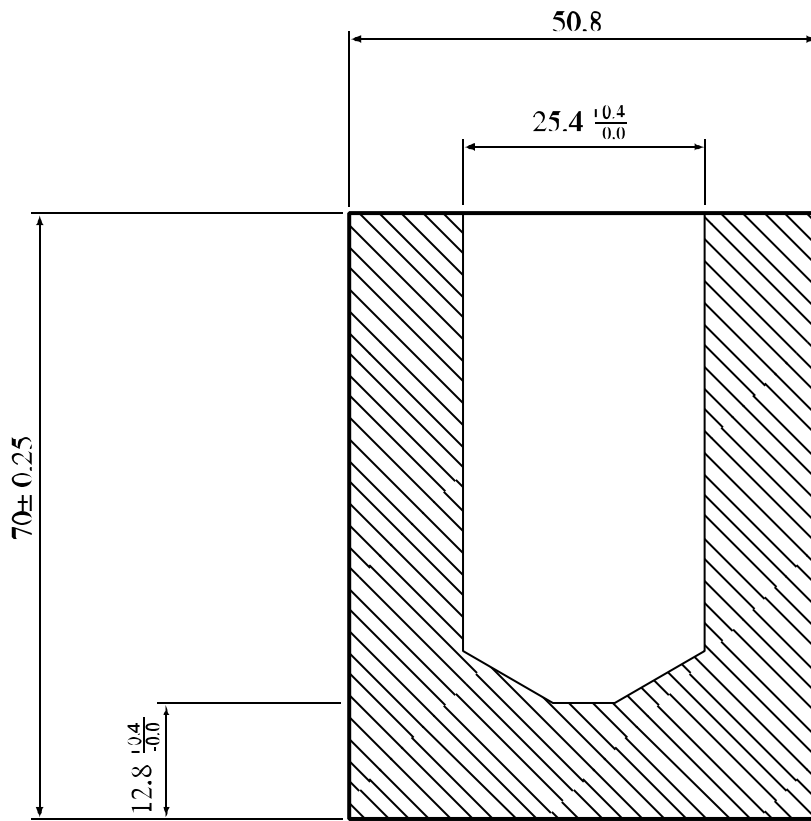
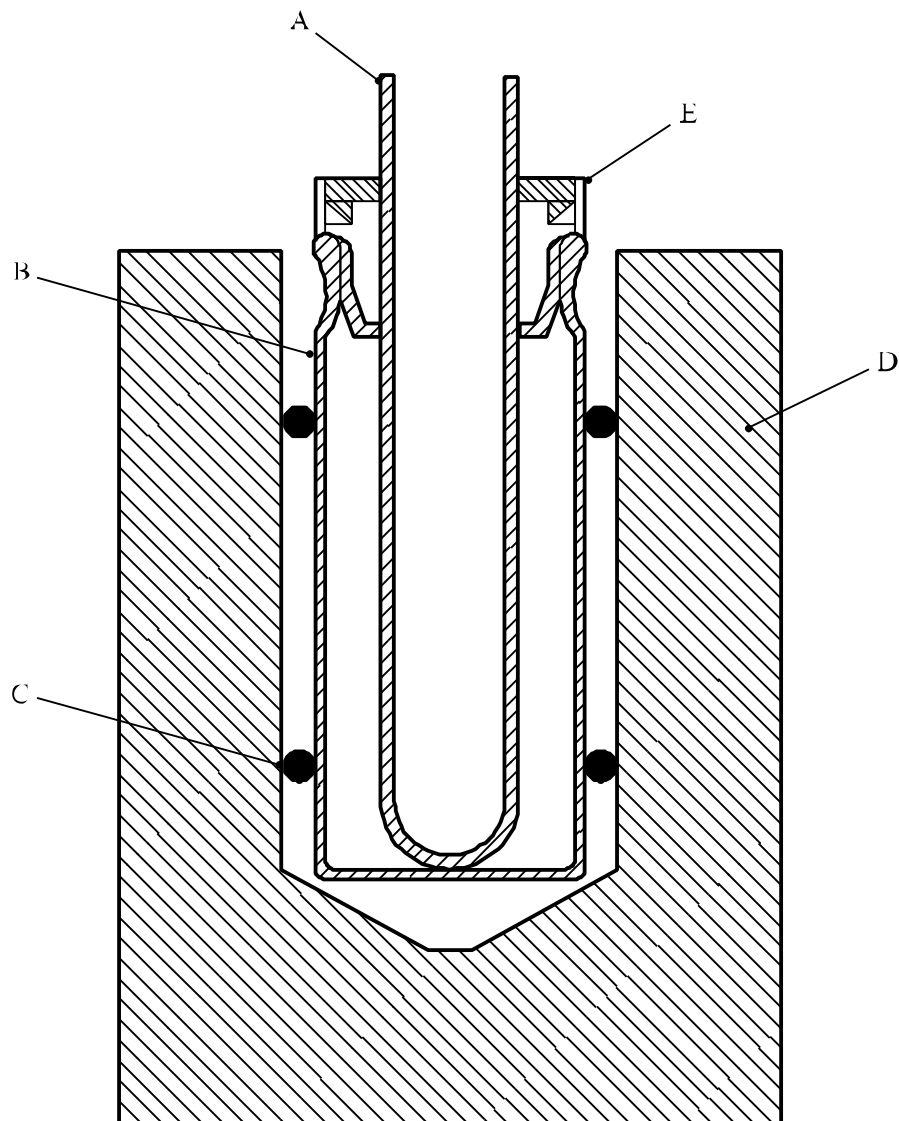


Figure 26.4.4.1: MODIFIED TRAUZL TEST



-
- (A) Glass tube
 - (B) Glass vial (12 ml assembly A, 16 ml assembly B)
 - (C) "O"-ring (assembly A only)
 - (D) Lead block
 - (E) Stopper
-

Figure 26.4.4.2: ASSEMBLIES A AND B

26.4.5 *Test F.5: High pressure autoclave*26.4.5.1 *Introduction*

This test is used to measure the specific energy of a substance. Varying quantities of substance are heated in a sealed vessel and the maximum pressure rise obtained for each sample size measured. The specific energy is a function of the maximum pressure rise. The test may be used to answer the question in box 12 of Figure 20.1.

26.4.5.2 *Apparatus*

The high pressure autoclave (Figure 26.4.5.1) is a cylindrical stainless steel vessel with a capacity of 96 ml and a working pressure of 150 MPa at a temperature of 473 K. The vessel is made from stainless steel type AISI 431, has an internal diameter of 38 mm and an internal height of 84 mm. An inner sample vessel (stainless steel type AISI 316, internal diameter 32 mm and internal height 77 mm) is used inside the autoclave. A coated Ni/Cr resistance wire (specific resistance of approximately 10 ohms/m), skip-wound around a piece of glass tube, is used to heat the sample by means of a constant current supply; a heating power of 50-150 W is supplied. Owing to the use of the inner vessel, the heat transfer from the substance to the autoclave is relatively small compared to the heat transfer that would exist in the situation without inner vessel. Therefore rapid heating will take place which will lead to an exothermic reaction involving self-heating and explosion. The pressure-time history of the explosion is determined. The pressure is registered by means of a piezo-electric transducer.

26.4.5.3 *Procedure*

The required amount of substance is weighed into the sample vessel after which the sample vessel is placed in the autoclave. The heating coil is connected to the lid of the autoclave which is then closed. Provisions are made to ensure that the whole heating coil is completely immersed in the substance. The ends of the heating wire are then connected to the power supply electrodes by low-resistance wire. The sample is then heated until explosion occurs. Experiments are normally performed using 5, 10, 15, 20 and 25 g of substance and the maximum pressure recorded. However, these quantities may need to be varied according to the bulk density and detonability of the substance.

26.4.5.4 *Test criteria and method of assessing results*

26.4.5.4.1 The results are assessed on the basis of the specific energy (F) which is a function of the maximum pressure rise (P_m). The initial sample mass (M_o) and the volume (V) of the reaction vessel are required to calculate the specific energy using the following equation:

$$V/M_o = F/P_m + C$$

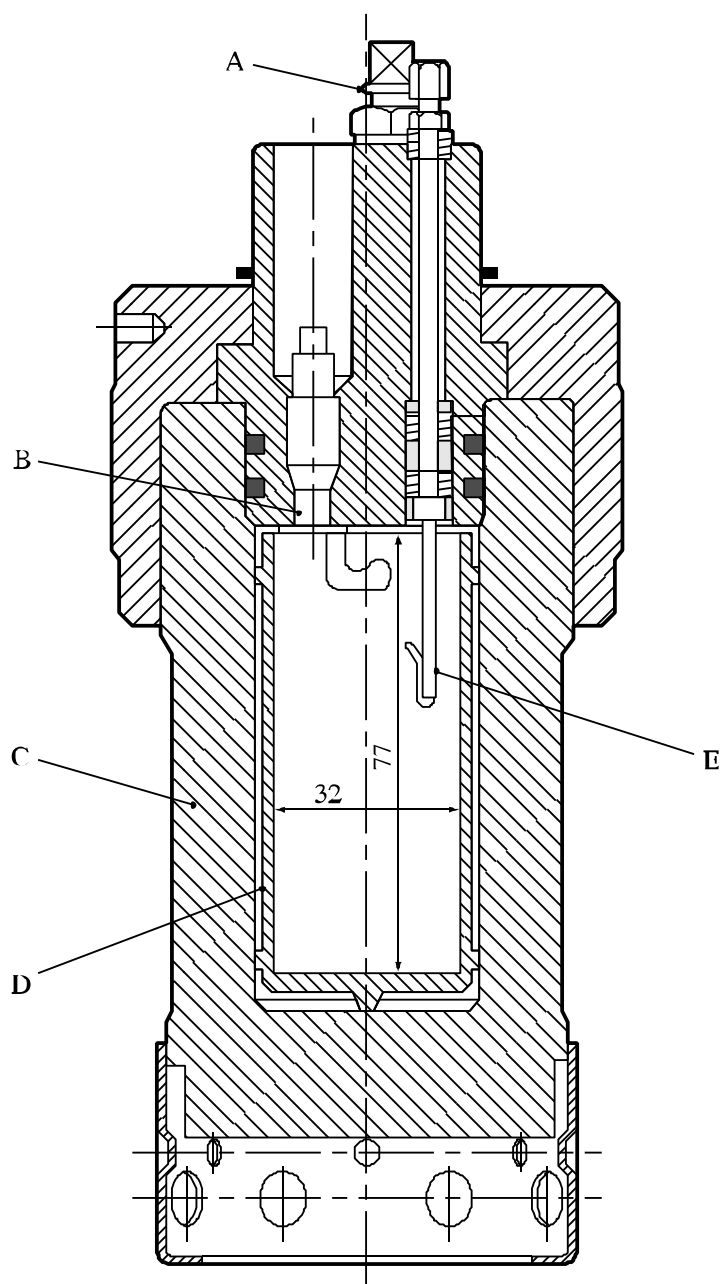
Where V = internal volume of pressure vessel - volume of steel of inner sample vessel;
 C = constant under the test conditions; and
 F = determination from the slope of the plot of V/M_o versus $1/P_m$.

The explosive power of a substance is based on the value of the specific energy F only.

26.4.5.4.2 The test criteria are as follows:

- "Not Low": - Specific energy greater than 100 J/g.
"Low": - Specific energy ≥ 5 J/g and ≤ 100 J/g.
"No": - Specific energy less than 5 J/g.

Substance	F-value (J/g)	Result
2,2'-Azodi(isobutyronitrile)	101	Not low
tert-Butyl peroxybenzoate	110	Not low
tert-Butyl peroxy-2-ethylhexanoate	56	Low
Cumyl hydroperoxide, 80% in cumene	60	Low
Dibenzoyl peroxide, 75% with water	41	Low
Di-tert-butyl peroxide	140	Not low
Dicetyl peroxydicarbonate	No reaction	No
Dicumyl peroxide, 40% with inert solid	No reaction	No
Dilauroyl peroxide	8	Low
Dilauroyl peroxide, 42%, stable dispersion, in water	1.3	No



- (A) Valve
- (B) Pressure transducer
- (C) Autoclave
- (D) Inner sample vessel
- (E) Electrodes

Figure 26.4.5.1: HIGH-PRESSURE AUTOCLAVE

SECTION 27

TEST SERIES G

27.1 Introduction

27.1.1 Test series G comprises tests and criteria concerning the determination of the effect of a thermal explosion of a substance as packaged ~~for transport~~, requested in box 10 of Figure 20.1. The test is only needed for substances which show a violent effect in tests involving heating under defined confinement (test series E).

27.2 Test methods

27.2.1 The question "Can it explode as packaged ~~for transport~~?" (box 10 of Figure 20.1) is answered on the basis of the results of one of the test methods in Table 27.1.

Table 27.1: TEST METHODS FOR TEST SERIES G

Test code	Name of test	Section
G.1	Thermal explosion test in package ^a	27.4.1
G.2	Accelerating decomposition test in package	27.4.2

^a *Recommended test.*

27.2.2 Both tests are considered equivalent for all substances excluding water-wetted solids. For water-wetted solids, in the event that the results of the two tests are not in agreement, the results of test G.1 have precedence over the results of test G.2.

27.3 Test conditions

27.3.1 The test of Series G should be applied to packages of substance (not more than 50 kg) in the condition and form in which they are offered for ~~transport~~classification.

27.3.2 *The preliminary procedure (see section 20.3) should be performed before carrying out these tests.*

27.4 Series G test prescriptions

27.4.1 Test G.1: Thermal explosion test in package

27.4.1.1 Introduction

This test is used to determine the potential for thermal explosion in a package. It may be used to answer the question in box 10 of Figure 20.1.

27.4.1.2 Apparatus and materials

27.4.1.2.1 Packaging (not larger than that needed for 50 kg of substance), substance, a suitable heating device (e.g. 2 kW for 25 kg of substance) and equipment for measuring temperatures.

27.4.1.3 Procedure

The test is applied to packed substances in the condition and form in which they are offered for **transport classification**. The method of obtaining the thermal explosion is by heating the substance as homogeneously as possible with an electric heating coil within the package. The surface temperature of the heating coil should not be so high that premature ignition of the substance can take place. It may be necessary to use more than one heating coil. The package should be mounted on a stand to keep it upright. The heating system is switched on and the temperature of the substance continuously recorded. The heating rate should be about 60 °C/hour. The difference in temperature between the substance at the top and bottom of the package should be as small as possible. **It is advisable to make provision in advance for the remote destruction of the package in the event of heater failure.** The test is performed in duplicate unless an explosion is observed.

27.4.1.4 Test criteria and method of assessing results

27.4.1.4.1 Observations are made on the evidence of an explosion of the package under investigation by fragmentation of the package. The results obtained are only valid for the package tested.

27.4.1.4.2 The test criteria are as follows:

- "Yes": - A fragmentation of inner and/or outer packaging(s) into more than three pieces (excluding bottom and top parts of the packaging(s) show(s) that the substance under investigation can give an explosion of that package.
- "No": - No fragmentation or a fragmentation into not more than three pieces shows that the substance under investigation does not explode in the package.

27.4.1.5 Examples of results

Substance	Packagings	Number of fragments ^a	Result
2,2'-Azodi-(isobutyronitrile)	4G, 30 kg	N.F.	No
tert-Butyl peroxybenzoate	1B1, 25 litres	> 30	Yes
tert-Butyl peroxybenzoate	6HG2, 30 litres	N.F.	No
tert-Butyl peroxy-2-ethylhexanoate	1B1, 25 litres	> 5	Yes
tert-Butyl peroxy-2-ethylhexanoate	6HG2, 30 litres	N.F.	No
tert-Butyl peroxy isopropyl carbonate	1B1, 25 litres	> 80	Yes
tert-Butyl peroxy isopropyl carbonate	6HG2, 30 litres	> 20	Yes
tert-Butyl peroxy pivalate, 75% in solution	6HG2, 30 litres	N.F.	No
Dibenzoyl peroxide, 75% with water	4G, 25 kg	N.F.	No
2,2-Di-(tert-butylperoxy)butane, 50% in solution	3H1, 25 litres	N.F.	No
2,2-Di-(tert-butylperoxy)butane, 50% in solution	6HG2, 30 litres	N.F.	No

^a N.F. means no fragmentation.

27.4.2 *Test **gG.2**: Accelerating decomposition in the package test*

27.4.2.1 *Introduction*

This test is used to determine the potential for thermal explosion in a package. It may be used to answer the question in box 10 of Figure 20.1.

27.4.2.2 *Apparatus and materials*

The equipment for this test is a typical SADT test cell as represented in Figure 27.4.2.1 and as described for test H.1 in section 28.

27.4.2.3 *Procedure*

The test is carried out in accordance with the procedure described for test H.1 in section 28. The temperature of the test cell may be set approximately 10 °C above the SADT, if known. The SADT test cell is designed to readily vent any significant pressure developed during the decomposition of a test sample. The cell covers are simply set in place and held by gravity alone.

27.4.2.4 *Test criteria and method of assessing results*

27.4.2.4.1 The condition of the sample, the package, the test cell, and the immediate surroundings provide a measure of the violence of the decomposition reaction of the product/package configuration tested.

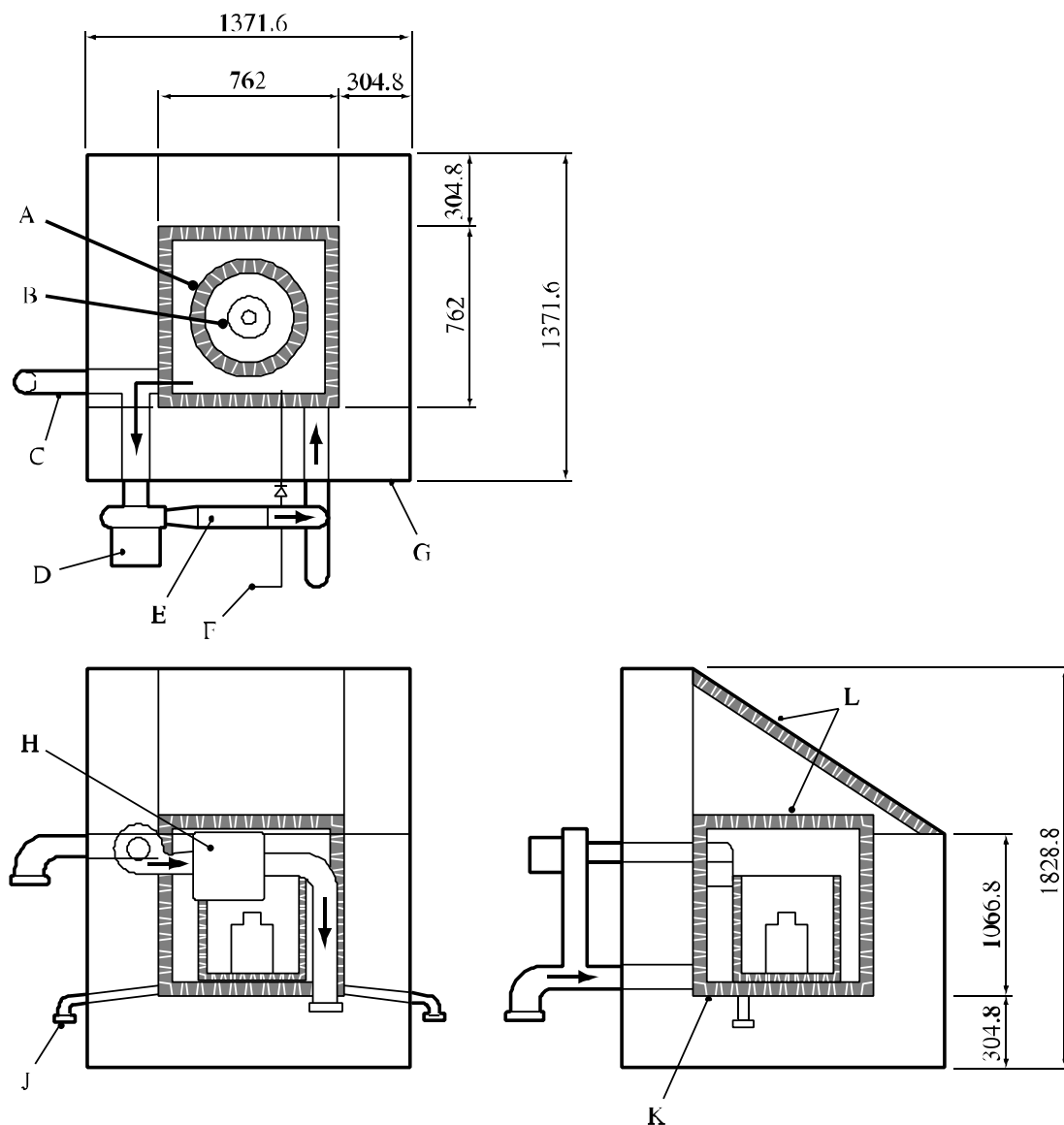
27.4.2.4.2 The test criteria are defined in terms of the condition of the test cell, the package and the occurrence of an explosion and are as follows:

"Yes": - Significant disruption of the inside of the test cell would be noted. The outer cover may be lifted off and carried at least two metres indicating significant internal cell pressure. The test package would be severely damaged, breaking into at least three fragments.

"No": - Slight to no disruption of the test cell. The outer cover may be lifted off but not carried further than two meters from the cell. The test package may be disrupted and damaged e.g. split inner packaging, torn carton.

27.4.2.5 *Examples of results*

Substance	Package	Result
tert-Butyl peroxyacetate, 75% in solution	6HG2, 20 litres	Yes
tert-Butyl peroxybenzoate	6HG2, 20 litres	No
tert-Butyl peroxy-2-ethylhexanoate	6HG2, 20 litres	No
tert-Butyl peroxy isopropyl carbonate, 75% in solution	6HG2, 20 litres	No
tert-Butyl peroxy pivalate, 75% in solution	6HG2, 20 litres	No
Dibenzoyl peroxide	4G, 0.454 kg	Yes
2,5-Dimethyl-2,5-di-(tert-butylperoxy)-hexyne-3	6HG2, 20 litres	Yes



- | | |
|---------------------------|--------------------|
| (A) Test container | (B) Test package |
| (C) Air duct | (D) Fan |
| (E) Heater | (F) Carbon dioxide |
| (G) Frame | (H) Recirculator |
| (J) Pipe drains with caps | (K) Insulation |
| (L) Insulated covers | |

Figure 27.4.2.1: ACCELERATING DECOMPOSITION TEST IN THE PACKAGE

SECTION 28

TEST SERIES H

28.1 Introduction

This test series contains test methods for the determination of the self-accelerating decomposition temperature (SADT). The SADT is defined as the lowest temperature at which self-accelerating decomposition may occur with a substance in the packaging ~~as used in transport~~. The SADT is a measure of the combined effect of the ambient temperature, decomposition kinetics, package size and the heat transfer properties of the substance and its packaging. To assist in interpreting the results, models can be used in which the main resistance to heat flow is:

- (a) At the boundary i.e. packaging (Semenov model);
- (b) Within the substance (Frank-Kamenetskii model); or
- (c) A combination of these (Thomas model).

The text should be used in conjunction with the temperature control requirements given in sub-section 2.5.3.4 of the Model Regulations.

References: *N.N. Semenov, Z. Physik, 48, 1928, 571.*
D.A. Frank-Kamenetskii, Zhur. Fiz. Khim., 13, 1939, 738.
P.H. Thomas, Trans. Faraday Soc., 54, 1958, 60.

28.2 Test methods

28.2.1 Test series H comprises tests and criteria concerning the thermal stability of substances ~~at transport temperatures~~ or concerning the determination of whether a substance meets the definition of a self-reactive substance.

28.2.2 Each test involves either storage at a fixed external temperature and observation of any reaction initiated or storage under near adiabatic conditions and measurement of the rate of heat generation versus temperature. The test methods included in test series H are given in Table 28.1. Each of the methods listed is applicable to solids, liquids, pastes and dispersions.

Table 28.1: TEST METHODS FOR TEST SERIES H

Test code	Name of test	Section
H.1	United States SADT test ^a	28.4.1
H.2	Adiabatic storage test (AST) ^b	28.4.2
H.3	Isothermal storage test (IST)	28.4.3
H.4	Heat accumulation storage test ^c	28.4.4

^a Recommended test for substances ~~transported~~ contained in packagings.

^b Recommended test for substances ~~transported~~ contained in packagings, IBCs or tanks.

^c Recommended test for substances ~~transported~~ contained in packagings, IBCs or small tanks.

The list of tests is not exhaustive; other tests may be used provided that they give the correct SADT of the substance as packaged for ~~transport~~ classification.

28.2.3 When necessary (SADT \leq 50 °C for organic peroxides, SADT \leq 55 °C for self-reactive substances), control and emergency temperatures may be derived from the SADT using Table 28.2.

Table 28.2: DERIVATION OF CONTROL AND EMERGENCY TEMPERATURES

Type of receptacle	SADT ^a	Control temperature	Emergency temperature
Single packagings and IBCs	\leq 20 °C	20 °C below SADT	10 °C below SADT
	over 20 °C to 35 °C	15 °C below SADT	10 °C below SADT
	over 35 °C	10 °C below SADT	5 °C below SADT
Portable tanks	$<$ 50 °C	10 °C below SADT	5 °C below SADT

^a *i.e. the SADT of the substance as packaged ~~for transport~~.*

28.2.4 If a substance is being tested to determine whether it is a self-reactive substance ~~of Division 4.1~~, a test of series H, or a suitable alternative test, should be performed to determine if its SADT would be less than or equal to 75 °C when ~~transported~~ contained in a 50 kg package.

28.2.5 The results obtained for the largest commercial package are applicable to smaller packages of similar construction and material provided that the heat transfer per unit mass is no smaller than from the larger package.

28.3 Test conditions

28.3.1 The preliminary procedure (see section 20.3) should be performed and the effect of heating under confinement (test series E) determined before performing SADT tests. ***Safety precautions should be taken which allow for the possibility of catastrophic failure of the test vessel and for the hazards arising from the ignition of secondary fuel-air mixtures and the evolution of toxic decomposition products. Substances liable to detonate should only be tested with special precautions.***

28.3.2 The test selected should be conducted in a manner which is representative, both in size and material, of the package ~~to be transported~~. For ~~transport in~~ metal packagings, IBCs or tanks, it may be necessary to include a representative amount of the metal in the sample tested i.e. representative of both the metal(s) and the area of contact.

28.3.3 ***Extra care should be taken when handling samples which have been tested since changes may have occurred rendering the substance more unstable and more sensitive. Tested samples should be destroyed as soon as possible after the test.***

28.3.4 Samples which have been tested at a particular temperature and are apparently unreacted may be used again, for screening purposes only, provided extra care is taken. Fresh samples should be used for the actual determination of the SADT.

28.3.5 If the complete package is not tested, the heat loss data used for the determination of the SADT should be representative of the package, IBC or tank ~~offered for transport~~. The heat loss per unit of mass of the package, IBC or tank may be determined by calculation (taking account of the quantity of substance, dimensions of the package, heat transfer in the substance and the heat transfer through the packaging to the environment) or by measuring the half-time of cooling of the package filled with the substance or another substance having similar physical properties. The heat loss per unit mass, L (W/kg.K), can be calculated from the half-time of cooling, $t_{1/2}$ (s), and the specific heat, C_p (J/kg.K), of the substance using the formula:

$$L = \ln 2 \times \left(\frac{C_p}{t_{1/2}} \right)$$

28.3.6 The half-time of cooling can be determined by measuring the period of time in which the temperature difference between the sample and surroundings is decreased by a factor of 2. For example, for liquids, the packaging may be filled with dibutyl phthalate or dimethyl phthalate and this heated to about 80 °C. Water should not be used as erratic results may be obtained through evaporation / condensation. The temperature drop is measured at the centre of the package over the temperature range which includes the expected SADT. For scaling, it may be necessary continuously to monitor the temperature of the substance and surroundings and then use linear regression to obtain the coefficients of the equation:

$$\ln(T - T_a) = c_o + c \times t$$

where: T = substance temperature (°C)
T_a = ambient temperature (°C)
c_o = ln (Initial substance temperature - initial ambient temperature); and
c = L/C_p
t = time (s)

28.3.7 Examples of the heat loss characteristics of some typical packages are given in Table 28.3. The actual value obtained will depend on the shape, wall thickness, surface coating etc. of the packaging.

Table 28.3: HEAT LOSS PER UNIT MASS FROM PACKAGES, IBCs AND TANKS

Type of receptacle	Normal capacity (litres)	Filling	Heat loss per unit mass (L) (mW/K.kg)
<i>For liquids:</i>			
1A1	50	47.5 kg DMP ^a	63
1H1	50	47.5 kg DMP ^a	94
1H1	200	200 kg water	56
3H1 (black)	60	47.5 kg DMP ^a	105
6HG2	30	35.0 kg DMP ^a	69
IBC 31 HA1	500	500 kg water	51
Tank	3 400	3 400 kg water	18 ^b
Tank container (insulated)	20 000	14 150 kg isododecane	1.7
<i>For solids:</i>			
1G	38	28.0 kg DCHP ^c	35
1G	50	37.0 kg DCHP ^c	29
1G	110	85.0 kg DCHP ^c	22
4G	50	32.0 kg DCHP ^c	27

^a DMP = dimethyl phthalate

^b Calculated using a heat transfer coefficient of 5 W/m².K

^c Dicyclohexyl phthalate (solid)

28.4 Series H test prescriptions

28.4.1 *Test H.1: United States SADT test*

28.4.1.1 *Introduction*

This method determines the minimum constant temperature air environment at which auto-accelerative decomposition occurs for a substance in a specific package. Packages of up to 220 litres may be tested by this method. An indication of the explosion hazard from the decomposition reaction can also be obtained.

28.4.1.2 *Apparatus and materials*

28.4.1.2.1 The test substance and packaging should be representative of that intended for commercial use. The packaging forms an essential part of the test.

28.4.1.2.2 The apparatus consists of a test chamber in which the air surrounding the package under test can be maintained at a constant temperature for a period of at least ten days.

28.4.1.2.3 The test chamber should be constructed such that:

- (a) It is well insulated;
- (b) Thermostatically controlled air circulation is provided so as to maintain a uniform air temperature within ± 2 °C of the desired temperature; and
- (c) The minimum separation distance from the package to the wall is 100 mm.

Any type of oven may be used provided that it is capable of meeting the temperature control requirements and will not ignite any decomposition products. Examples of a suitable small-package and large-package oven are given in 28.4.1.2.4 and 28.4.1.2.5 respectively.

28.4.1.2.4 A small-package oven may be constructed from an open head 220 litre steel drum. This will readily accommodate packages of up to 25 litres capacity. Construction details are shown in Figure 28.4.1.1. Larger packages may be tested as long as a 100 mm clearance between the package and the oven wall is maintained.

28.4.1.2.5 An expendable large-package oven may be made from 50 mm \times 100 mm lumber formed into a cubic frame 1.2 m on each side, which is lined inside and out with 6 mm thick waterproof plywood and insulated all around with 100 mm fibreglass insulation. Construction details are shown in Figure 28.4.1.2. The frame should be hinged on one side to permit loading and unloading of test drums. The floor should be provided with 50 mm \times 100 mm lumber on edge, spaced 200 mm on centres to keep the test container off the floor and allow free air circulation around the package. Cleats should run normal to the door to permit a fork-lift to move the drums. A circulating fan should be located on the side opposite the door. The air flow should be from the upper corner of oven to the fan discharge at the diagonally opposite lower corner. An electric heater of 2.5 kW is suitable for heating the air. Thermocouples should be placed in the air intake and outflow ducts as well as the top, middle and bottom of the oven. For substances with an SADT below ambient temperature, the test should be performed in a cooling chamber or solid carbon dioxide should be used for cooling the oven.

28.4.1.2.6 The package should be equipped with a thermowell which positions the thermocouple at the package mid-point. The thermowell may be constructed of glass, stainless steel or other suitable material but should be introduced in a manner which does not reduce package strength or venting capability.

28.4.1.2.7 Continuous temperature-measuring and recording equipment, which is protected from fire and explosion hazards, is required.

28.4.1.2.8 ***The tests should be performed in an area which provides adequate protection from fire and explosion hazards, and from toxic fumes. A safety distance, e.g. 90 m, from public roads and occupied buildings is recommended. If there may be toxic fumes, longer safety distances may be required.***

28.4.1.3 *Procedure*

28.4.1.3.1 The package is weighed. A thermocouple is inserted in the package to be tested such that the temperature in the centre of the sample can be monitored. If the required oven temperature is below ambient, the oven is switched on and the inside of the oven cooled to the desired temperature before placing the package in the oven. If the required oven temperature is at or above ambient temperature, the package is inserted in the oven at ambient temperature and the oven then switched on. There should be a minimum clearance of 100 mm between the package and the sides of the oven.

28.4.1.3.2 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 the 2 °C below the test chamber temperature to its maximum temperature.

28.4.1.3.3 When the test is completed, cool the sample and remove it from the test chamber. Note the variation of temperature with time. If the package remains intact, note the percentage mass loss and determine any changes in composition. Dispose of the sample as soon as possible.

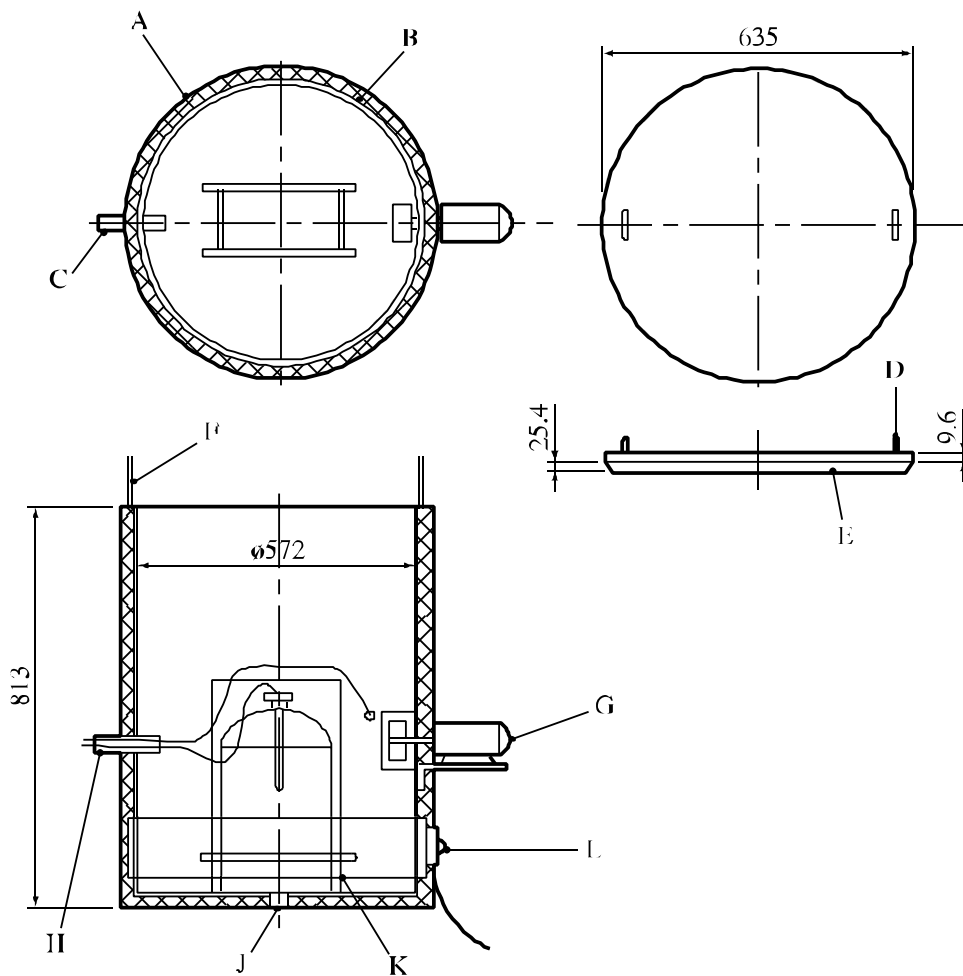
28.4.1.3.4 If the temperature of the sample does not exceed the oven temperature by 6 °C or more then repeat the test with a new sample in an oven at a 5 °C higher temperature. The self-accelerating decomposition temperature (SADT) is defined as the lowest oven temperature at which the sample temperature exceeds the oven temperature by 6 °C or more. If the substance is being tested to determine if temperature control is necessary, perform sufficient tests to determine the SADT to the nearest 5 °C or to determine if the SADT is greater than or equal to 60 °C. If the substance is being tested to determine if it meets the SADT criterion for a self-reactive substance, perform sufficient tests to determine if the SADT for a 50 kg package is 75 °C or less.

28.4.1.4 *Test criteria and method of assessing results*

28.4.1.4.1 The SADT is reported as the lowest temperature at which the sample exceeds the oven temperature by 6 °C or more. If the sample temperature does not exceed the oven temperature by 6 °C or more in any test, the SADT is recorded as being greater than the highest oven temperature used.

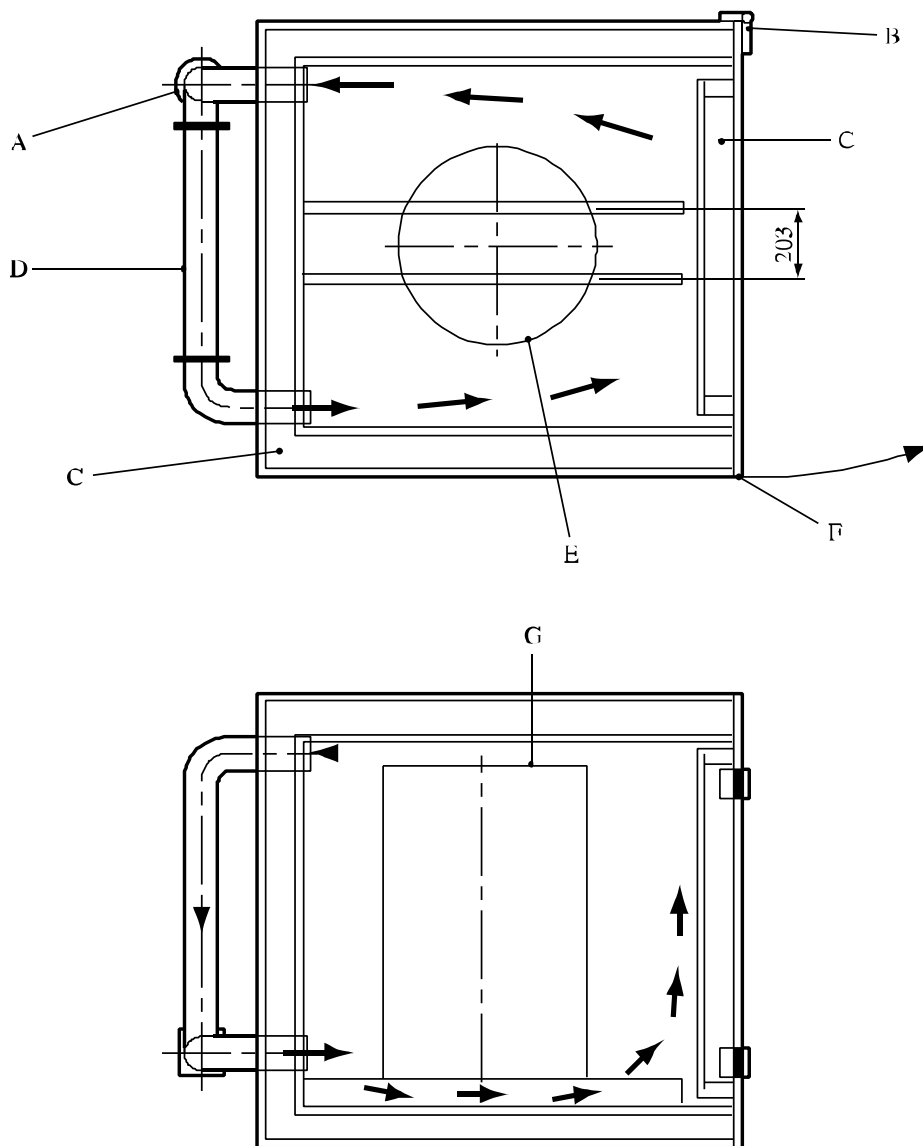
28.4.1.5 *Examples of results*

Substance	Sample mass (kg)	Packaging	SADT (°C)
tert-Amyl peroxybenzoate	18.2	6HG2, 22.8 litres	65
tert-Butyl peroxyacetate (60%)	7.2	6HG2, 22.8 litres	75
Dibenzoyl peroxide	0.45	1G	70
Di-(4-tert-butylcyclohexyl) peroxydicarbonate	43	1G	40
2,5-Diethoxy-4-morpholinobenzene-diazonium zinc chloride (66%)	30	1G, 50 litres	50
2-(N-ethoxycarbonyl-N-phenylamino)-3-methoxy-4-(N-methyl-N-cyclohexyl-amino)benzenediazonium zinc chloride (62 %)	10	6HG1, 25 litres	50



- | | | | |
|-----|---------------------------|-----|--------------------------------|
| (A) | Insulation 25 mm thick | (B) | 220 litres open top drum |
| (C) | 19 mm pipe | (D) | 9.6 mm eye bolt in steel cover |
| (E) | Insulation on steel cover | (F) | 3 mm control cable |
| (G) | Fan | (H) | Thermocouples and controls |
| (J) | Drain | (K) | 25 mm angle stand |
| (L) | 2 kW drum heater | | |

Figure 28.4.1.1: SMALL PACKAGE OVEN



-
- | | |
|---------------------------------|----------------|
| (A) Fan | (B) Hinges (2) |
| (C) Insulation | (D) Heater |
| (E) Drum | (F) Latch |
| (G) Drum (e.g. 0.58 m x 0.89 m) | |
-

Figure 28.4.1.2: LARGE PACKAGE OVEN (top view and side view)

28.4.2 *Test H.2: Adiabatic storage test*28.4.2.1 *Introduction*

28.4.2.1.1 This test method determines the rate of heat generation produced by a reacting substance as a function of temperature. The heat generation parameters obtained are used with the heat loss data relating to the package to determine the SADT of a substance in its packaging. The method is appropriate for every type of packaging, including IBCs and tanks.

28.4.2.1.2 Measurements can be performed in the temperature range from -20 °C to 220 °C. The smallest temperature rise that can be detected corresponds to a rate of heat generation of 15 mW/kg. The upper limit is determined by the capacity of the cooling system to safely cool the substance (up to 500 W/kg if water is used as the coolant). Although the test is not perfectly adiabatic, the heat losses are less than 10 mW. The maximum error is 30% at 15 mW/kg and 10% from 100 mW/kg to 10 W/kg.

28.4.2.1.3 If the cooling system is activated at a stage where the rate of heat generation exceeds the cooling capacity, an explosion may occur. ***The test site should therefore be carefully selected to reduce to a minimum the possible hazards from an explosion and of a possible subsequent gas explosion of the decomposition products (secondary explosion).***

28.4.2.2 *Apparatus and materials*

28.4.2.2.1 The apparatus consists of a glass Dewar vessel (1.0 or 1.5 litre) to contain the sample, an insulated oven with a differential control system to keep the temperature in the oven to within 0.1 °C of the sample temperature and an inert lid for the Dewar vessel. In special cases, sample holders of other construction materials may have to be used. An inert heating coil and cooling tube pass through the lid into the sample. Pressure build-up in the Dewar vessel is prevented by a 2 m long PTFE capillary tube which passes through the insulated lid. A constant power heating unit is used for internal heating of the substance to a pre-set temperature or for calibration. Internal heating and cooling may be stopped or started automatically at pre-set temperatures. In addition to the cooling system, a secondary safety device is fitted which disconnects the power supply to the oven at a pre-set temperature. A schematic drawing of the AST is given in Figure 28.4.2.1.

28.4.2.2.2 The temperature of the substance is measured at its centre by means of thermocouples or platinum resistance sensors placed in a steel or glass tube. The temperature of the surrounding air is measured at the same height as the sample temperature, also with thermocouples or platinum resistance sensors. Continuous temperature measuring and recording equipment is required to monitor the temperature of substance and the air in the oven. This equipment should be protected from fire and explosion. For substances with an SADT below ambient temperature, the test should be performed in a cooling chamber or solid carbon dioxide should be used for cooling the oven.

28.4.2.3 *Procedure*

28.4.2.3.1 Calibration procedure

The calibration procedure is as follows:

- (a) Fill the Dewar vessel with sodium chloride, dibutyl phthalate or with a suitable oil and place it in the vessel holder of the AST oven;
- (b) Heat the sample in 20 °C steps using the internal heating system at a known power rating, e.g. 0.333 or 1.000 W, and determine the heat losses at 40 °C, 60 °C, 80 °C and 100 °C;
- (c) Use the data to determine the heat capacity of the Dewar vessel using the method given in 28.4.2.4.

28.4.2.3.2 Test procedure

The test procedure is as follows:

- (a) Fill the Dewar vessel with the weighed sample, including a representative amount of packaging material (if metal), and place it in the vessel holder of the AST oven;
- (b) Start the temperature monitoring and then increase the sample temperature using the internal heater to a pre-set temperature at which detectable self-heating may occur. The specific heat of the substance can be calculated from the temperature rise, heating time and heating power;
- (c) Stop the internal heating and monitor the temperature. If no temperature rise due to self-heating is observed within 24 hours, increase the temperature by 5 °C. Repeat this procedure until self-heating is detected;
- (d) When self-heating is detected, the sample is allowed to heat up under adiabatic conditions to a pre-set temperature where the rate of heat generation is less than the cooling capacity, upon which the cooling system is activated;
- (e) On cooling, determine the loss in mass, if any, and determine the change in composition (if desired).

28.4.2.4 *Test criteria and method of assessing results*

28.4.2.4.1 Calculate the rate of temperature drop, A (°C/h), of the Dewar vessel at the different temperatures used in the calibration procedure. Plot a graph through these values in order to allow determination of the rate of temperature drop at any temperature.

28.4.2.4.2 Calculate the heat capacity, H (J/°C), of the Dewar vessel using the formula:

$$H = \frac{3600 \times E_1}{A + B} - (M_1 \times Cp_1)$$

where:

E_1	=	power applied to the internal heater (W)
A	=	rate of temperature drop at the temperature of calculation (°C/h)
B	=	slope of the curve on internal heating (calibration substance) at the temperature of calculation (°C/h)
M_1	=	mass of calibration substance (kg)
Cp_1	=	specific heat of calibration substance (J/kg.°C)

28.4.2.4.3 Determine the heat loss, K (W), using:

$$K = \frac{A \times (H + M_1 \times Cp_1)}{3600}$$

at each desired temperature and draw a graph through these values.

28.4.2.4.4 Calculate the specific heat, Cp_2 (J/kg.°C) of the substance using:

$$Cp_2 = \frac{3600 \times (E_2 + K)}{C \times M_2} - \frac{H}{M_2}$$

where:

E_2	=	power applied to the internal heater (W)
C	=	slope of the curve on internal heating (sample) at the temperature of calculation (°C/h)
M_2	=	mass of sample (kg)

28.4.2.4.5 Calculate the heat generation, Q_T (W/kg), of the substance at intervals of 5 °C using the following formula for each temperature:

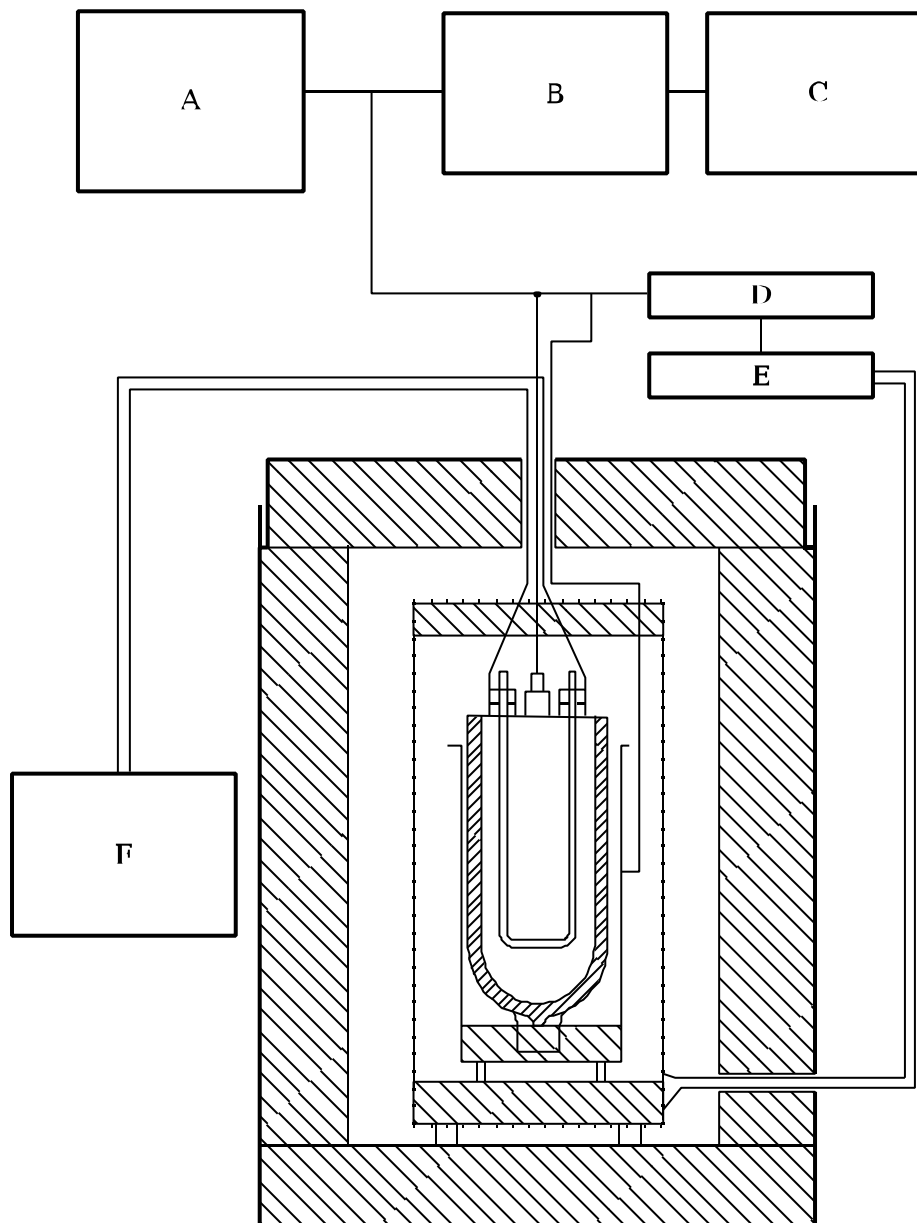
$$Q_T = \frac{(M_2 \times C_{p_2} + H) \times \frac{D}{3600} - K}{M_2}$$

where: D = slope of the curve during the self-heating at the temperature of calculation (°C/h)

28.4.2.4.6 Plot the calculated rates of heat generation per unit of mass as a function of the temperature in a graph with linear scales and draw the best-fit curve through the plotted points. Determine the heat losses per unit of mass, L (W/kg.°C) of the specific package, IBC or tank (see 28.3.5). Draw a straight line of gradient L tangential to the heat generation curve. The intersection of the straight line and the abscissa is the critical ambient temperature i.e. the highest temperature at which the substance as packaged does not show self-accelerating decomposition. The SADT is the critical ambient temperature (°C) rounded to the next higher multiple of 5 °C. An example is given in Figure 28.4.2.2.

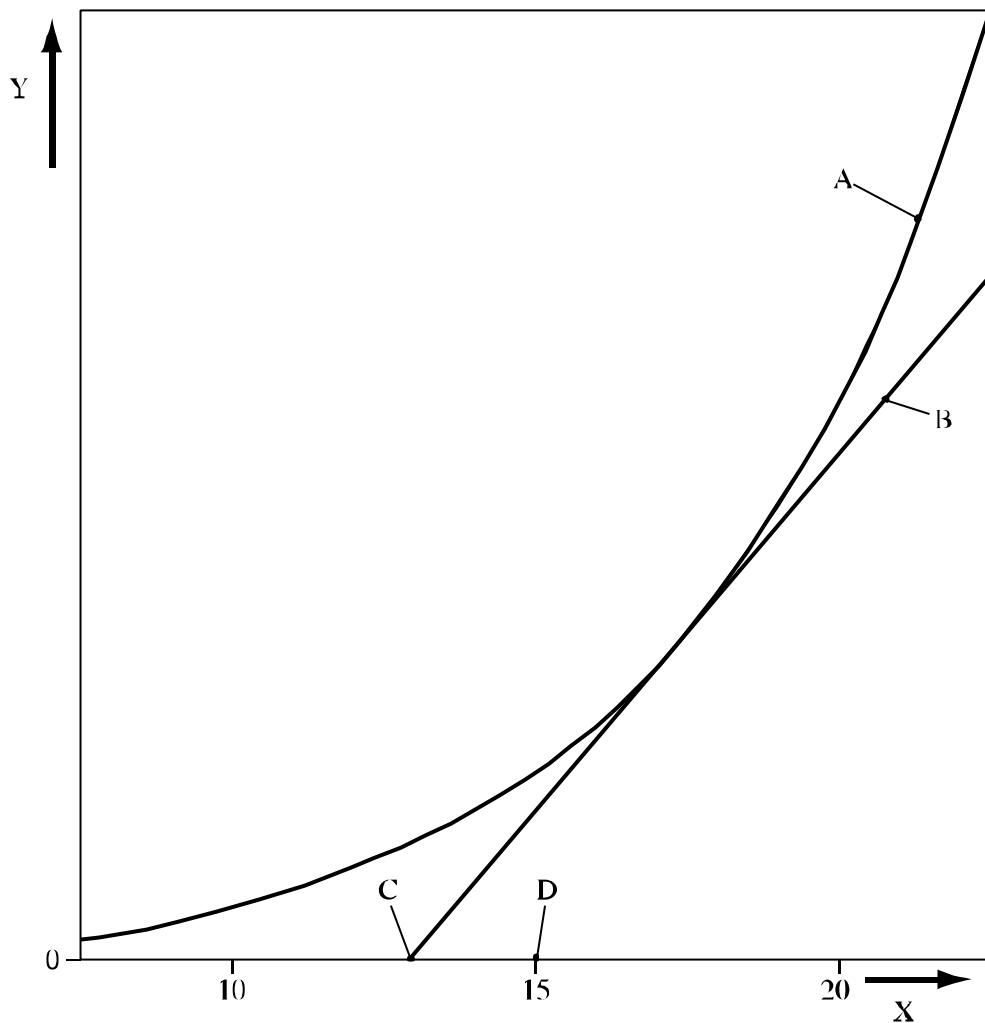
28.4.2.5 *Examples of results*

Substance	Mass (kg)	Packaging	Heat loss per unit mass (mW/kg.K)	SADT (°C)
Azodicarbonamide	30	1G	100	> 75
tert-Butyl peroxybenzoate	25	6HG2	70	55
tert-Butyl peroxy-2-ethylhexanoate	25	6HG2	70	40
tert-Butyl peroxy-pivalate	25	6HG2	70	25



-
- (A) Multi-point recorder and temperature controller (10 mV)
 - (B) External zero set
 - (C) Recorder set for greatest accuracy
 - (D) Control
 - (E) Relay
 - (F) Internal pre-heater
-

Figure 28.4.2.1: ADIABATIC STORAGE TEST



- (A) Heat generation curve
- (B) Line with gradient equal to the rate of heat loss and tangential to the heat generation curve
- (C) Critical ambient temperature (intercept of heat loss line with the abscissa)
- (D) Self-accelerating decomposition temperature (SADT) - critical ambient temperature rounded up to next higher multiple of 5 °C
- (X) Temperature
- (Y) Heat flow (generation or loss) per unit mass

Figure 28.4.2.2: EXAMPLE OF DETERMINATION OF SADT

28.4.3 *Test H.3: Isothermal storage test (IST)*

28.4.3.1 *Introduction*

28.4.3.1.1 This method determines the rate of heat generation produced by reacting or decomposing substances as a function of time at constant temperature. The heat generation parameters obtained are used with the heat loss data relating to the package to determine the SADT of a substance in its packaging. The method is appropriate for every type of packaging including IBCs and tanks. Some substances may show an increase in the rate of heat generation with increasing decomposition (e.g. due to autocatalysis or induced decomposition). This property is also taken into account by this test method.

28.4.3.1.2 Measurements can be performed in the temperature range of -20 °C to 200 °C. Heat generation values can be measured from 5 mW/kg to 5 W/kg. The thermal resistance between the sample holder and aluminium block via the heat flow meters is about 0.1 W/°C. The apparatus is able to measure rates of heat generation from 15 mW/kg to 1 500 mW/kg with a maximum error of 30% at 15 mW/kg and 5% from 100 to 1 500 mW/kg.

28.4.3.1.3 The robust construction of the apparatus, the relatively small sample size and the well-defined operating conditions enable the test to be performed in an ordinary laboratory. The effects of a thermal explosion, e.g. fragmentation of the sample holder and generation of pressure, should be contained within the apparatus.

28.4.3.2 *Apparatus and materials*

28.4.3.2.1 The apparatus consists of an air-insulated heat sink (an aluminium block) which is kept at a constant temperature by means of controlled heating. A cryostat is used to maintain temperatures below 40 °C. The heat controller is capable of maintaining the temperature to within 0.2 °C of the set temperature. The temperature of the heat sink is measured with a platinum-resistance sensor. The two holes drilled in the block contain heat flow meters (e.g. Peltier elements). A schematic drawing of the IST is given in Figure 28.4.3.1. For substances with an SADT below ambient temperature, the test should be performed in a cooling chamber or solid carbon dioxide should be used for cooling the oven.

28.4.3.2.2 Holders are placed on both heat flow meters: one with the sample and one with an inert substance. Both holders are identical and have a volume of 70 cm³. The amount of substance in each holder is about 20 g. The holders are made of glass or stainless steel. The steel must be compatible with the test substance. When using a glass holder, it is provided with a long capillary tube which prevents pressure build-up in the holder and evaporation of the sample.

28.4.3.2.3 The voltage difference resulting from the difference in heat flow from sample holder to the heat sink and inert substance holder to the heat sink is continuously recorded as a function of time (differential measurement) by a recorder or computer.

28.4.3.3 *Procedure*

28.4.3.3.1 Calibration procedure

Before a measurement can be performed, the blank signal and the sensitivity of the heat flow meter need to be determined by the following calibration procedure.

- (a) Set the IST at the selected test temperature;
- (b) Insert a heating coil in the sample holder. Fill the sample and reference holders with inert material (e.g. sodium chloride or milled glass beads) ensuring that the heating coil is completely covered with material. Place both holders in the IST;
- (c) Determine the blank signal (the output of the recorder when no electric power is applied to the heating coil);
- (d) Determine the sensitivity of the heat flow meter using two or three different electrical heating powers which lie within the expected range of heat generation of the sample to be tested.

28.4.3.3.2 Test procedure

The test procedure is as follows:

- (a) Set the IST for the desired test temperature;
- (b) Fill the sample holder with the weighed sample and with a representative quantity of packaging material (if metal) and insert the holder into the apparatus. The amount of sample should be sufficient to give a rate of heat generation between 5 mW to 1 500 mW per kg of substance;
- (c) Start monitoring the rate of heat production. The results from the first 12 hours of the test should not be used because this period is required for temperature equilibration. The duration of each test depends on the test temperature and on the rate of heat production. The test should last for at least 24 hours after the 12 hour equilibration period but can then be stopped if the rate of heat generation is falling from the maximum or if the rate of heat generation is greater than 1.5 W/kg;
- (d) At the end of the test the change in sample mass should be determined;
- (e) The test is repeated with new samples at temperature intervals of 5 °C so that there are seven results with a maximum heat generation rate between 15 and 1 500 mW/kg.

28.4.3.4 Test criteria and method of assessing results

28.4.3.4.1 Calculate the sensitivity, S (mW/mV), of the instrument at the various electrical powers used in the calibration procedure using the following formula:

$$S = \frac{P}{U_d - U_b}$$

where: P = electric power (mW)
 U_d = dummy signal (mV)
 U_b = blank signal (mV)

28.4.3.4.2 Use these values and the test data to calculate the maximum rate of heat generation, Q (mW/kg), at the different test temperatures using the formula:

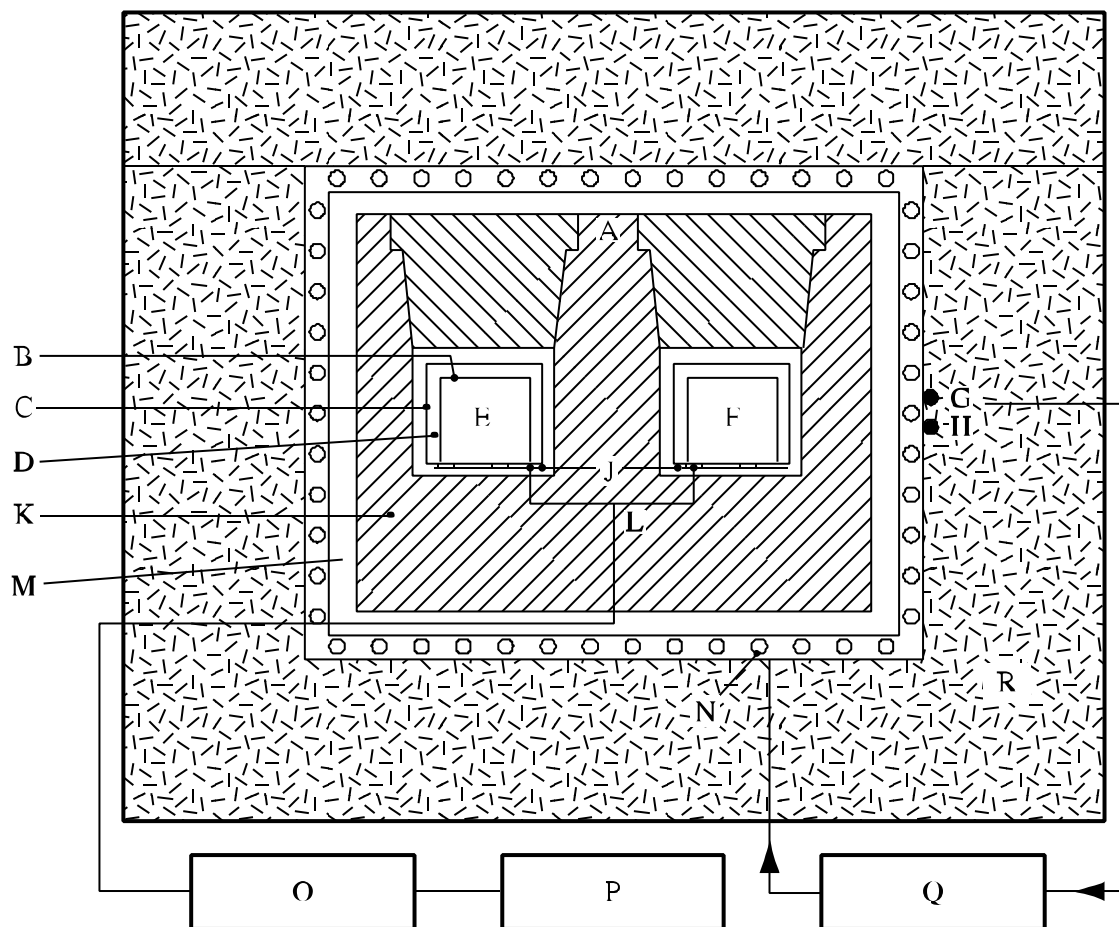
$$Q = \frac{(U_s - U_b) \times S}{M}$$

where: U_s = sample signal (mV)
 M = mass (kg)

28.4.3.4.3 Plot the calculated maximum rate of heat generation per unit of mass as a function of the test temperature on a graph with linear scales and draw the best-fit curve through the plotted points. Determine the heat losses per unit of mass, L (W/kg.°C) of the specific package, IBC or tank (see 28.3.5). Draw a straight line of gradient L tangential to the heat generation curve. The intersection of the straight line and the abscissa is the critical ambient temperature i.e. the highest temperature at which the substance as packaged does not show self-accelerating decomposition. The SADT is the critical ambient temperature (°C) rounded to the next higher multiple of 5 °C. An example is given in Figure 28.4.3.2.

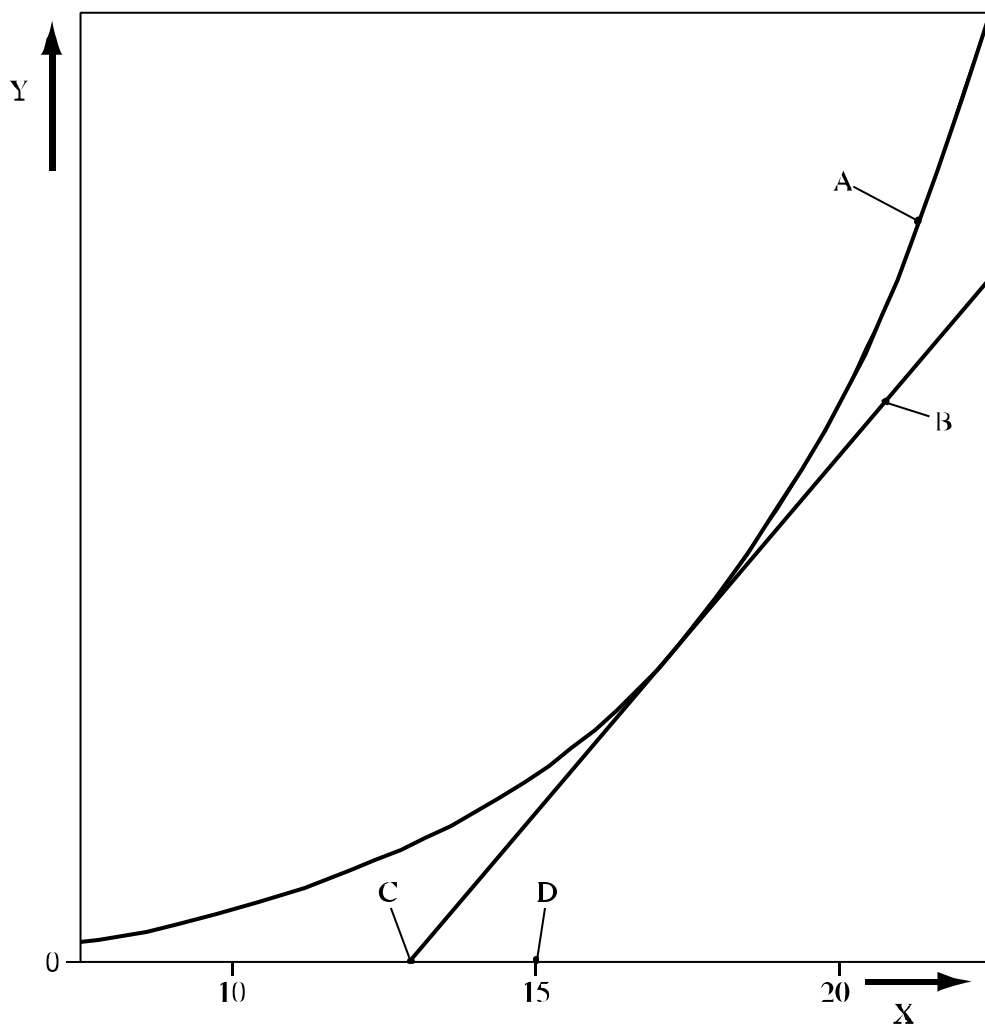
28.4.3.5 *Examples of results*

Substance	Mass (kg)	Packaging	Heat loss per unit mass (mW/kg.K)	SADT (°C)
Azodicarbonamide	30	1G	100	> 75
tert-Butyl peroxybenzoate	25	6HG2	70	55
tert-Butyl peroxy-2-ethylhexanoate	25	6HG2	70	40
tert-Butyl peroxy-pivalate	25	6HG2	70	25
2,5-Diethoxy-4-morpholinobenzenediazonium zinc chloride (90%)	25	1G	150	45
2,5-Diethoxy-4-morpholinobenzenediazonium tetrafluoroborate (97%)	25	1G	15	55
2,5-Diethoxy-4-(phenylsulphonyl)-benzenediazonium zinc chloride (67%)	25	1G	15	50
2-(N-ethoxycarbonyl-N-phenylamino)-3-methoxy-4-(N-methyl-N-cyclohexylamino)-benzenediazonium zinc chloride (62%)	25	1G	15	45
3-Methyl-4-(pyrrolidin-1-yl) benzenediazonium tetrafluoroborate (95%)	25	1G	15	55



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|--|---|
| (A) Platinum resistance thermometer | (B) Sample vessel |
| (C) Cylindrical holder | (D) Air spaces |
| (E) Sample | (F) Inert material |
| (G) Platinum resistance sensor for temperature control | (H) Platinum resistance sensor for safety control |
| (J) Peltier elements | (K) Aluminium block |
| (L) Electric circuit | (M) Air space |
| (N) Heating wires | (O) Amplifier |
| (P) Recorder | (Q) Temperature controller |
| (R) Glass wool | |

Figure 28.4.3.1: ISOTHERMAL STORAGE TEST



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- (A) Heat generation curve
 - (B) Line with gradient equal to the rate of heat loss and tangential to the heat generation curve
 - (C) Critical ambient temperature (intercept of heat loss line with the abscissa)
 - (D) Self-accelerating decomposition temperature (SADT) - critical ambient temperature rounded up to next higher multiple of 5 °C
 - (X) Temperature
 - (Y) Heat flow (generation or loss) per unit mass
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Figure 28.4.3.2: EXAMPLE OF DETERMINATION OF SADT

28.4.4 *Test H.4: Heat accumulation storage test*28.4.4.1 *Introduction*

28.4.4.1.1 This method determines the minimum constant air environment temperature at which thermally unstable substances undergo exothermic decomposition at conditions representative of the substance when packaged ~~as for transport~~. The method is based on the Semenov theory of thermal explosion i.e. the main resistance to heat flow is considered to be at the vessel walls. The method can be used for the determination of the SADT of a substance in its packaging, including IBCs and small tanks (up to 2 m³).

28.4.4.1.2 The effectiveness of the method depends on selecting a Dewar vessel with heat loss per unit mass characteristics similar to the package ~~offered for transport~~.

28.4.4.2 *Apparatus and materials*

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

28.4.4.2.2 ***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.

28.4.4.2.3 For tests at temperatures up to 75 °C, a double walled metal chamber (ca. 250 mm inner diameter, 320 mm outer diameter and 480 mm high made from 1.5 to 2.0 mm thick stainless steel sheet) is used with fluid from a temperature-controlled circulating bath passed between the walls at the desired temperature. The test chamber is loosely closed by an insulated lid (e.g. made from 10 mm thick polyvinyl chloride). The temperature control should allow the desired temperature for a liquid inert sample in the Dewar vessel to be maintained with a deviation of not more than ± 1 °C for up to 10 days.

28.4.4.2.4 Alternatively, and particularly for tests at temperatures above 75 °C, 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.

28.4.4.2.5 For tests at sub-ambient temperatures, a double walled chamber (e.g. a freezer) of suitable size provided with a loose door or lid (e.g. with a magnetic closure) may be used. The temperature of the air in the chamber should be controlled to ± 1 °C of the set temperature.

28.4.4.2.6 Dewar vessels, with their closure system, are used with heat loss characteristics which are representative of the maximum size of package ~~offered for transport~~. The closure of the Dewar vessel should be inert. Particularly for solids, cork or rubber bungs may be used. A closure system for use with liquids with low or medium volatility is illustrated in Figure 28.4.4.1. Samples which are highly volatile at the test temperature should be tested in a pressure-tight metal vessel fitted with a pressure relief valve. The pressure vessel is placed in the Dewar vessel and the effect of the heat capacity of the metal vessel taken into account by calculation.

28.4.4.2.7 The heat loss characteristics of the system used, i.e. Dewar vessel and closure, should be established (see 28.3.6) 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. In order to achieve the required level of sensitivity, Dewar vessels with sample capacities below 0.5 litres should not be used.

28.4.4.2.8 Dewar vessels, filled with 400 ml of substance, with a heat loss of 80 to 100 mW/kg.K are normally suitable for representing a 50 kg package. For larger packages, IBCs or small tanks larger Dewar vessels with lower heat losses per unit mass should be used. For example, spherical 1 litre Dewar vessels having heat loss characteristics in the range 16 to 34 mW/kg.K may be suitable for IBCs and small tanks.

28.4.4.3 *Procedure*

28.4.4.3.1 Set the test chamber at the selected storage temperature. Fill the Dewar vessel, to 80% of its capacity, with the substance under test and note the mass of the sample. Solids should be moderately compressed. 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.

28.4.4.3.2 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.

28.4.4.3.3 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.

28.4.4.3.4 Repeat the test with fresh samples, varying the storage temperature in 5 °C steps. If the substance is being tested to determine if temperature control is necessary, perform sufficient tests to determine the SADT to the nearest 5 °C or to determine if the SADT is greater than or equal to 60 °C. If the substance is being tested to determine if it meets the SADT criterion for a self-reactive substance, perform sufficient tests to determine if the SADT for a 50 kg package is 75 °C or less.

28.4.4.4 *Test criteria and method of assessing results*

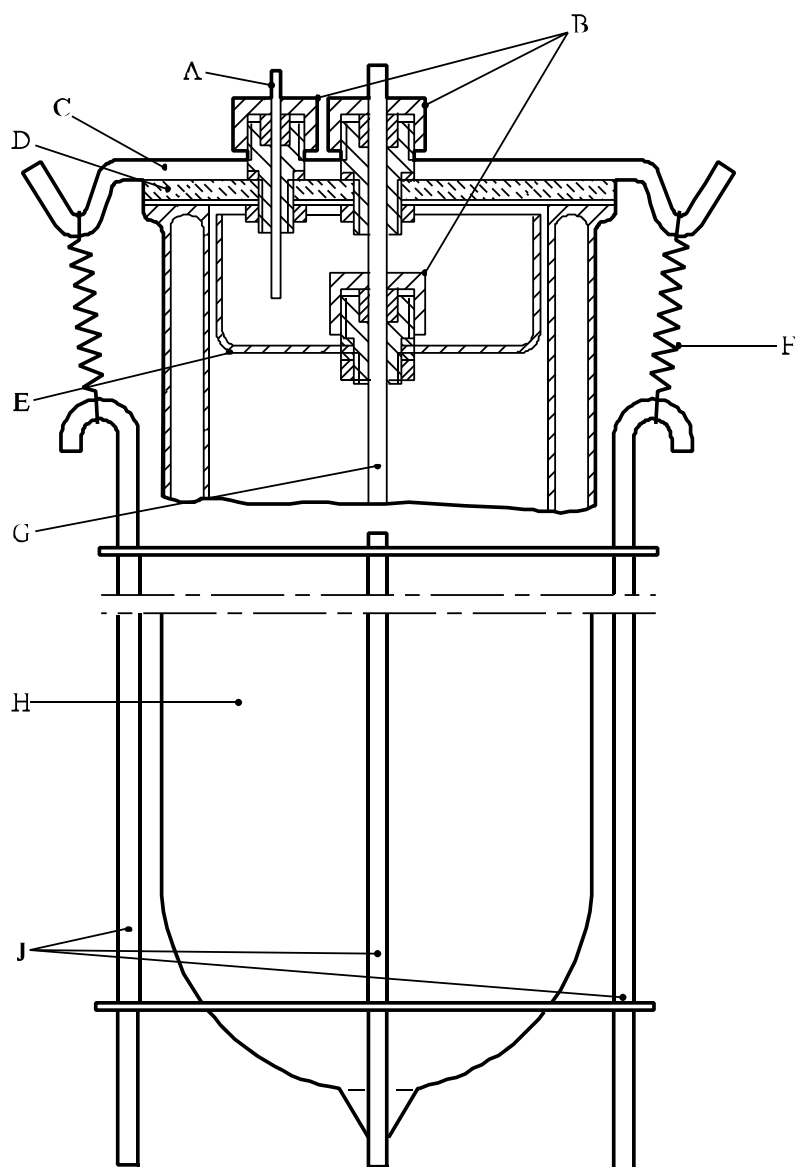
28.4.4.4.1 The SADT is reported as the lowest temperature at which the sample undergoes exceeds the test chamber temperature by 6 °C or more. If the sample temperature does not exceed the test chamber temperature by 6 °C or more in any test, the SADT is recorded as being greater than the highest storage temperature used.

28.4.4.5 *Examples of results*

Substance	Sample mass (kg)	Dewar heat loss (mW/kg.K)	SADT (°C)
Azodicarbonamide	0.28	74	> 75
Azodicarbonamide, 90% with 10% activator	0.21	70	55
2,2'-Azodi(isobutyronitrile)	0.18	62	50
Benzene-1,3-disulphohydrazide, 50%	0.52	81	70
tert-Butyl hydroperoxide, 80% with 12% di-tert-butyl peroxide	0.30	72	100 ^a
tert-Butyl peroxyneodecanoate, 40%	0.42	65	25
tert-Butyl peroxy-3,5,5-trimethylhexanoate	0.38	79	60
Dibenzoyl peroxide, 50%	0.25	91	60
Di-(4-tert-butylcyclohexyl) peroxydicarbonate	0.19	79	45
2,2-Di-(tert-butylperoxy)butane, 50%	0.31	88	80
Di-(2-ethylhexyl) peroxydicarbonate	0.39	64	0
2,5-Diethoxy-4-morpholinobenzenediazonium zinc chloride (66%)	0.25	58	45
Diisotridecyl peroxydicarbonate	0.38	80	10
Peroxyacetic acid, 15%, with 14% hydrogen peroxide (type F)	1.00	33	> 50 ^b

^a *In a pressure vessel contained with a 2 litres Dewar vessel.*

^b *In a spherical, 1 litre Dewar vessel.*



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|-----|------------------------|-----|--|
| (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 | | |
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Figure 28.4.4.1: DEWAR VESSEL WITH CLOSURE FOR TESTING LIQUIDS AND WETTED SOLID