A.14. EXPLOSIVE PROPERTIES

1. METHOD

1.1. INTRODUCTION

The method provides a scheme of testing to determine whether a solid or a pasty substance presents a danger of explosion when submitted to the effect of a flame (thermal sensitivity), or to shock or friction (sensitivity to mechanical stimuli), and whether a liquid substance presents a danger of explosion when submitted to the effect of a flame or shock.

The method comprises three parts:

(a) a test of thermal sensitivity (1);

(b) a test of mechanical sensitivity with respect to shock (1);

(c) a test of mechanical sensitivity with respect to friction (1).

The method yields data to assess the likelihood of initiating an explosion by means of certain common stimuli. The method is not intended to ascertain whether a substance is capable of exploding under any conditions.

The method is appropriate for determining whether a substance will present a danger of explosion (thermal and mechanical sensitivity) under the particular conditions specified in the directive. It is based on a number of types of apparatus which are widely used internationally (1) and which usually give meaningful results. It is recognised that the method is not definitive. Alternative apparatus to that specified may be used provided that it is internationally recognised and the results can be adequately correlated with those from the specified apparatus.

The tests need not be performed when available thermodynamic information (e.g. heat of formation, heat of decomposition) and/ or absence of certain reactive groups (2) in the srructural formula establishes beyond reasonable doubt that the substance is incapable of rapid decomposition with evolution of gases or release of heat (i.e. the material does not present any risk of explosion). A test of mechanical sensitivity with respect to friction is not required for liquids.

1.2. DEFINITIONS AND UNITS

Explosive:

Substances which may explode under the effect of flame or which are sensitive to shock or friction in the specified apparatus (or are more mechanically sensitive than 1,3-dinitrobenzene in alternative apparatus).

1.3. REFERENCE SUBSTANCES

1,3-dinitrobenzene, technical crystalline product sieved to pass 0,5 mm, for the friction and shock methods.

Perhydro-l,3,5-trinitro-l,3,5-triazine (RDX, hexogen, cyclonite -CAS 121-82-4), recrystallised from aqueous cyclohexanone, wet-sieved through a 250 µm and retained on a 150 µm sieve and dried at 103 ± 2 °C (for 4 hours) for the second series of friction and shock tests.

1.4. PRINCIPLE OF THE METHOD

Preliminary tests are necessary to establish safe conditions for the performance of the three tests of sensitivity.

1.4.1. Safety-in-handling tests (3)

For safety reasons, before performing the main tests, very small samples (circa 10 mg) of the substance are subjected to heating without confinement in a gas flame, to shock in any convenient form of apparatus and to friction by the use of a mallet against an anvil or any form of friction machine. The objective is to ascertain if the substance is so sensitive and explosive that the prescribed sensitivity tests, particularly that of thermal sensitivity , should be performed with special precautions so as to avoid injury to the operator.

1.4.2. Thermal sensitivity

The method involves heating the substance in a steel tube, closed by orifice plates with differing diameters of hole, to determine whether the substance is liable to explode under conditions of intense heat and defined confinement.

1.4.3. Mechanical sensitivity (shock)

The method involves subjecting the substance to the shock from a specified mass dropped from a specified height.

1.4.4. Mechanical sensitivity (friction)

The method involves subjecting solid or pasty substances to friction between standard surfaces under specified conditions of load and relative motion.

1.5. QUALITY CRITERIA

Not stated.

1.6. DESCRIPTION OF METHOD

1.6.1. Thermal sensitivity (effect of a flame)

1.6.1.1. Apparatus

The apparatus consists of a non-reusable steel tube with its re-usable closing device (figure 1), installed in a heating and protective device. Each tube is deep-drawn from sheet steel (see Appendix) and has an internal diameter of 24 mm, a length of 75 mm and wall thickness of 0,5 mm. The tubes are flanged at the open end to enable them to be closed by the orifice plate assembly. This consists of a pressure-resistant orifice plate, with a central hole, secured firmly to a tube using a two-part screw joint (nut and threaded collar). The nut and threaded collar are made from chromium-manganese steel (see Appendix) which is spark-free up to 800 °C. The orifice plates are 6 mm thick, made from heat-resistant steel (see Appendix), and are available with a range of diameters of opening.

1.6.1.2. Test conditions

Normally the substance is tested as received although in certain cases, e.g. if pressed, cast or otherwise condensed, it may be necessary to test the substance after crushing. For solids, the mass of material to be used in each test is determined using a two-stage dry run procedure. A tared tube is filled with 9 cm^3 of substance and the substance tamped with 80 N force applied to the total cross-section of the tube. For reasons of safety or in cases where the physical form of the sample can be changed by compression

other filling procedures may be used; e.g. if the substance is very friction sensitive then tamping is not appropriate. If the material is compressible then more is added and tamped until the tube is filled to 55 mm from the top. The total mass used to fill the tube to the 55 mm level is determined and two further increments, each tamped with 80 N force, are added. Material is then either added with tamping, or taken out, as required, to leave the tube filled to a level 15 mm from the top. A second dry run is performed, starting with a tamped quantity of a third of the total mass found in the first dry run. Two more of these increments are added with 80 N tamping and the level of the substance in the tube adjusted to 15 mm from the top by addition or subtraction of material as required. The amount of solid determined in the second dry run is used for each trial; filling being performed in three equal amounts, each compressed to 9 cm^3 by whatever force is necessary. (This may be facilitated by the use of spacing rings).

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. The threaded collar is slipped onto the tube from below, the appropriate orifice plate is inserted and the nut tightened 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.

Heating is provided by propane taken from an industrial cylinder, fitted with a pressure regulator (60 to 70 mbar), through a meter and evenly distributed (as indicated by visual observation of the flames from the burners) by a manifold to four burners. The burners are located around the test chamber as shown in figure 1. The four burners have a combined consumption of about 3.2 litres of propane per minute. Alternative fuel gases and burners may be used but the heating rate must be as specified in figure 3. For all apparatus, the heating rate must be checked periodically using tubes filled with dibutyl phthalate as indicated in figure 3.

1.6.1.3. Performance of the tests

Each test is performed until either the tube is fragmented or the tube has been heated for five minutes. A test resulting in the fragmentation of the tube into three or more pieces, which in some cases may be connected to each other by narrow strips of metal as illustrated in figure 2, is evaluated as giving an explosion. A test resulting in fewer fragments or no fragmentation is regarded as not giving an explosion.

A series of three tests with a 6,0 mm diameter orifice plate is first performed and, if no explosions are obtained, a second series of three tests is performed with a 2,0 mm diameter orifice plate. If an explosion occurs during either test series then no further tests are required.

1.6.1.4. Evaluation

The test result is considered positive if an explosion occurs in either of the above series of tests.

1.6.2. Mechanical sensitivity (shock)

1.6.2.1. Apparatus (figure 4)

The essential parts of a typical fall hammer apparatus are a cast steel block with base, anvil, column, guides, drop weights, release device and a sample holder. The steel anvil 100 mm (diameter) x 70 mm (height) is screwed to the top of a steel block 230 mm (length) x 250 mm (width) x 200 mm (height) with a cast base 450 mm (length) x 450 mm (width) x 60 mm (height). A column, made from seamless drawn steel tube, is secured in a holder screwed on to the back of the steel block. Four screws anchor the apparatus to a solid concrete block 60 x 60 x 60 cm such that the guide rails are absolutely vertical and the drop weight falls freely. 5 and 10 kg weights, made from solid steel, are available for use. The striking head of each weight is of hardened steel, HRC 60 to 63, and has a minimum diameter of 25 mm.

The sample under test is enclosed in a shock device consisting of two coaxial solid steel cylinders, one above the other, in a hollow cylindrical steel guide ring. The solid steel cylinders should be of 10 (-0,003, -0,005) mm diameter and 10 mm height and have polished surfaces, rounded edges (radius of curvature 0,5 mm) and a hardness of HRC 58 to 65. The hollow cylinder must have an external diameter of 16 mm, a polished bore of 10 (+ 0,005, + 0,010) mm and a height of 13 mm. The shock device is assembled on an intermediate anvil (26 mm diameter and 26 mm height) made of steel and centred by a ring with perforations to allow escape of fumes.

1.6.2.2. Test conditions .

The sample volume should be 40 mm^3, or a volume to suit any alternative apparatus. Solid substances should be tested in the dry state and prepared as follows:

(a) powdered substances are sieved (sieve size 0,5 mm); all that has passed through the sieve is used for testing;

(b) pressed, cast or otherwise condensed substances are broken into small pieces and sieved; the sieve fraction from 0,5 to 1 mm diameter is used for testing and should be representative of the original substance.

Substances normally supplied as pastes should be tested in the dry state where possible or, in any case, following removal of the maximum possible amount of diluent. Liquid substances are tested with a 1 mm gap between the upper and lower steel cylinders.

1.6.2.3. Performance of the tests

A series of six tests are performed dropping the 10 kg mass from 0,40 m (40 J). If an explosion is obtained during the six tests at 40 J, a further series of 6 tests, dropping a 5 kg mass from 0,15 m (7,5 J), must be performed. In other apparatus, the sample is compared with the chosen reference substance using an established procedure (e.g. up-and-down technique etc.).

1.6.2.4. Evaluation

The test result is considered positive if an explosion (bursting into flame and/ or a report is equivalent to explosion) occurs at least once in any of the tests with the specified shock apparatus or the sample is more sensitive than 1,3-dinitrobenzene or RDX in an alternative shock test.

1.6.3. Mechanical sensitivity (friction)

1.6.3.1. Apparatus (figure 5)

The friction apparatus consists of a cast steel base plate on which is mounted the friction device. This consists of a fixed porcelain peg and moving porcelain plate. The porcelain plate is held in a carriage which runs in two guides. The carriage is connected to an electric motor via a connecting rod, an eccentric cam and suitable gearing such that the porcelain plate is moved, once only, back and forth beneath the porcelain peg for a distance of 10 mm. The porcelain peg may be loaded with, for example, 120 or 360 newtons.

The flat porcelain plates are made from white technical porcelain (roughness 9 to 32 μm) and have the dimensions 25 mm (length) x 25 mm (width) x 5 mm (height). The cylindrical porcelain peg is also made of white technical porcelain and is 15 mm long, has a diameter of 10 mm and roughened spherical end surfaces with a radius of curvature of 10 mm.

1.6.3.2. Test conditions

The sample volume should be 10 mm^3 or a volume to suit any alternative apparatus.

Solid substances are tested in the dry state and prepared as follows:

(a) powdered substances are sieved (sieve size 0,5 mm); all that has passed through the sieve is used for testing;

(b) pressed, cast or otherwise condensed substances are broken into small pieces and sieved; the sieve fraction < 0,5 mm diameter is used for testing.

Substances normally supplied as pastes should be tested in the dry state where possible. If the substance cannot be prepared in the dry state, the paste (following removal of the maximum possible amount of diluent) is tested as a 0,5 mm thick, 2 mm wide, 10 mm long film, prepared with a former.

1.6.3.3. Performance of the tests

The porcelain peg is brought onto the sample under test and the load applied. When carrying out the test, the sponge marks of the porcelain plate must lie transversely to the direction of the movement. Care must be taken that the peg rests on the sample, that sufficient test material lies under the peg and also that the plate moves correctly under the peg. For pasty substances, a 0,5 mm thick gauge with a 2 x 10 mm slot is used to apply the substance to the plate. The porcelain plate has to move 10 mm forwards and backwards under the porcelain peg in a time of 0,44 seconds. Each part of the surface of the plate and peg must only be used once; the two ends of each peg will serve for two trials and the two surfaces of a plate will each serve for three trials.

A series of six tests are performed with a 360 N loading. If a positive event is obtained during these six tests, a further series of six tests must be performed with a 120 N loading. In other apparatus, the sample is compared with the chosen reference substance using an established procedure (e.g. up-and-down technique, etc.).

1.6.3.4. Evaluation

The test result is considered positive if an explosion (crepitation and/or a report or bursting into flame are equivalent to explosion) occurs at least once in any of the tests with the specified friction apparatus or satisfies the equivalent criteria in an alternative friction test.

2. **DATA**

In principle, a substance is considered to present a danger of explosion in the sense of the directive if a positive result is obtained in the thermal, shock or friction sensitivity test.

3. **REPORTING**

3.1. TEST REPORT

The test report shall, if possible, include the following information:

-identity, composition, purity, moisture content etc. of the substance tested,

-the physical form of the sample and whether or not it has been crushed, broken and/ or sieved,

-observations during the thermal sensitivity tests (e.g. sample mass, number of fragments etc.),

-observations during the mechanical sensitivity tests (e.g. formation of considerable amounts of smoke or complete decomposition without a report, flames, sparks, report, crepitation etc.),

-results of each type of test,

-if alternative apparatus has been used, scientific justification as well as evidence of correlation between results obtained with specified apparatus and those obtained with equivalent apparatus must be given,

-any useful comments such as reference to tests with similar products which might be relevant to a proper interpretation of the results,

-all additional remarks relevant for the interpretation of the results.

3.2. INTERPRETATION AND EVALUATION OF RESULTS

The test report should mention any results which are considered false, anomalous or unrepresentative. If any of the results should be discounted, an explanation and the results of any alternative or supplementary testing should be given. Unless an anomalous result can be explained, it must be accepted at face value and used to classify the substance accordingly.

4. REFERENCES

(1) Recommendations on the Transport of Dangerous Goods: Tests and criteria, 1990, United Nations, New York.

(2) Bretherick, L., Handbook of Reactive Chemical Hazards, 4th edition, Butterworths, London, ISBN 0-750-60103-5, 1990.

(3) Koenen, H., Ide, K.H. and Swart, K.H., Explosivstoffe, 1961, vol.3, 6-13 and 30-42.

(4) NF T 20-038 (Sept. 85). Chemical products for industrial use -Determination of explosion risk.

Appendix

Example of Material specification for thermal sensitivity test (see DIN 1623)

(1) Tube: Material specification No 1.0336.505 g

(2) Orifice plate: Material specification No 1.4873

(3) Threaded collar and nut: Material specification No 1.3817

Figure 1

Thermal sensitivity test apparatus (all dimensions in millimetres)

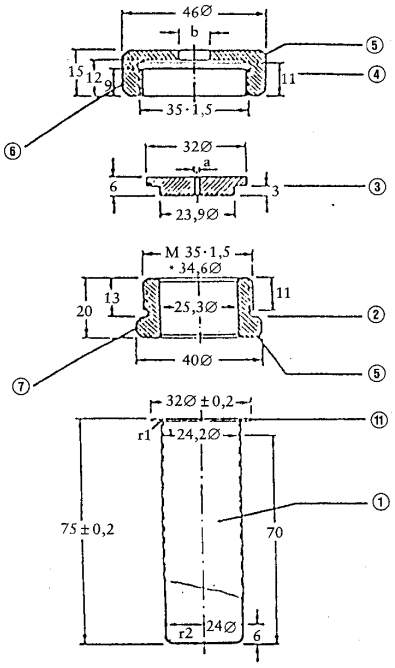


Fig. 1a Steel tube and accessories

(1) tube
(1a) outer flange
(2) threaded collar; low-friction thread
(3) orifice plate a = 2,0 or 6,0 mm diameter
(4) nut b = 10 mm diameter
(5) chamfered surface
(6) 2 flat for spanner size 41

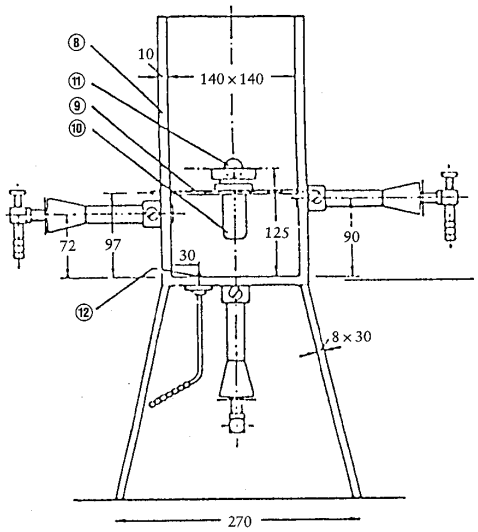


Fig. 1b Heating and protective device

(7) 2 flat for spanner size 36
(8) splinter-proof box
(9) 2 supporting rods for tube
(10) assembled tube
(11) position for rear burner; the other burners are visible
(12) pilot jet

Figure 2

Thermal sensitivity test (example of fragmentation)

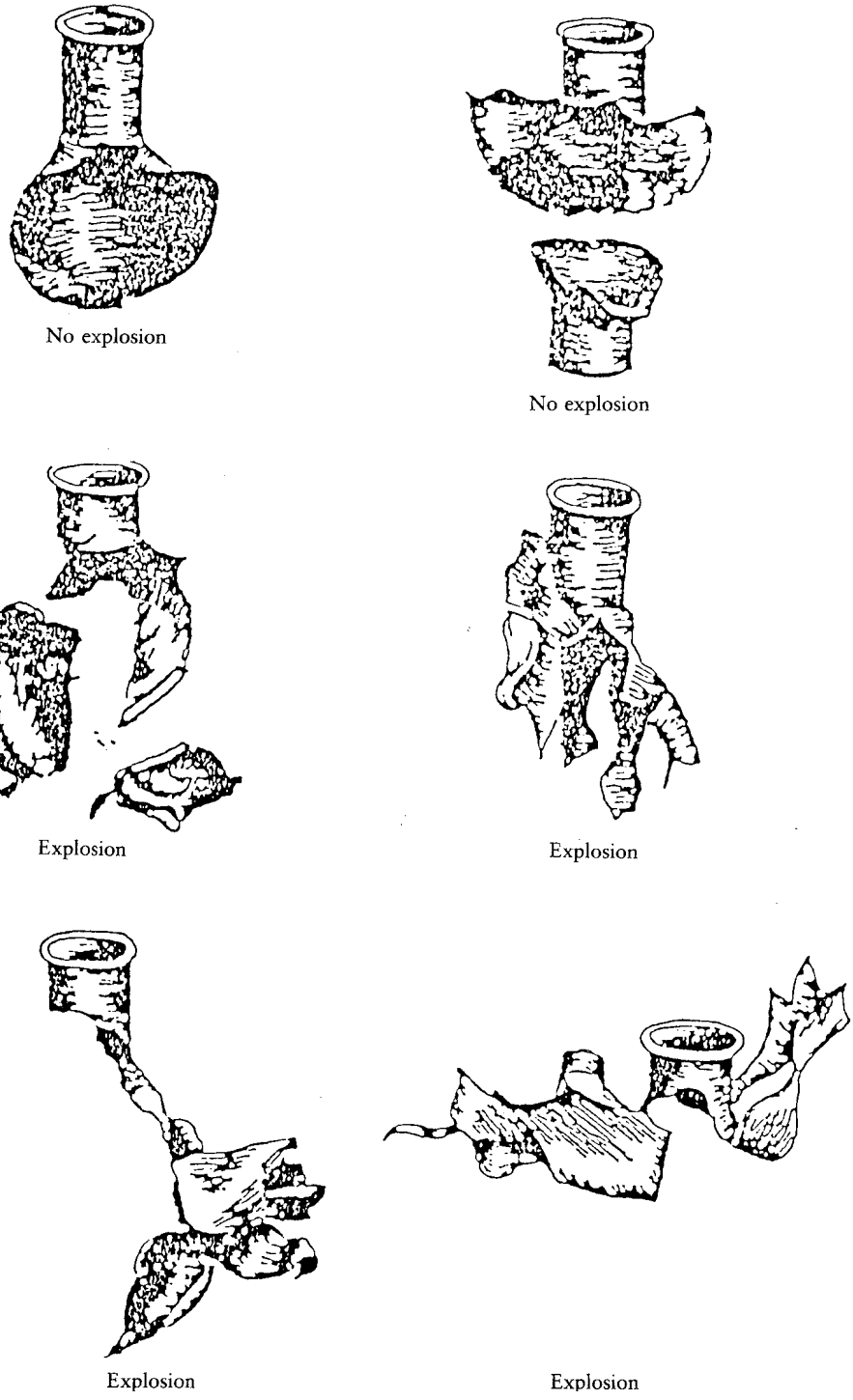
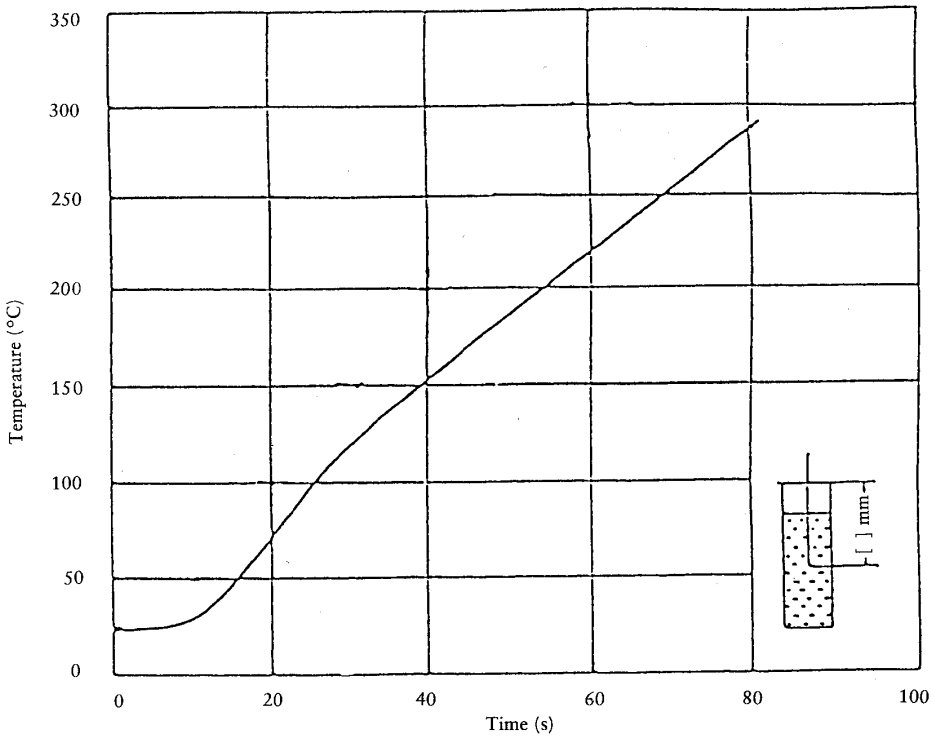


Figure 3

Heating rate calibration for thermal sensitivity test



Temperature/time curve obtained on heating dibutyl phtalate (27 cm^3) in a closed (1,5 mm orifice plate) tube using a propane flow rate of 3,2 litre/minute. The temperature is measured with a 1mm diameter stainless steel sheathed chromel/alumel thermocouple, placed centrally 43 mm below the rim of the tube. The heating rate between 135 °C and 285 °C should be between 185 and 215 K/minute.

Figure 4

Shock test apparatus

(all dimensions in millimetres)

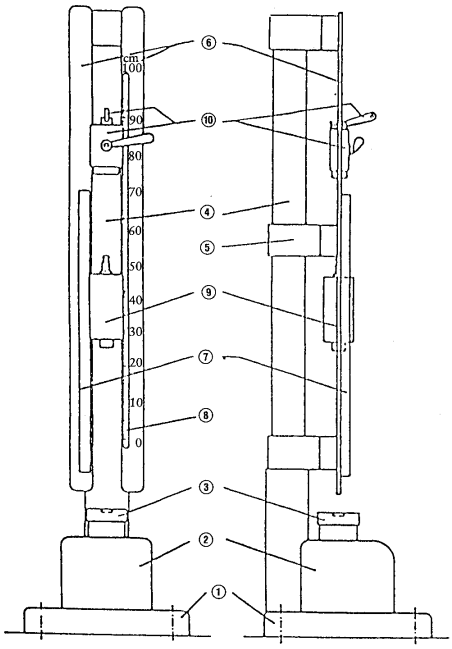


Fig. 4a Fall-hammer, front and side, general view

(1) base, 450 × 450 × 60
(2) steel block, 230 × 250 × 200
(3) anvil, 100 diameter × 70
(4) colum
(5) median cross-member
(6) 2 guides
(7) toothed rack

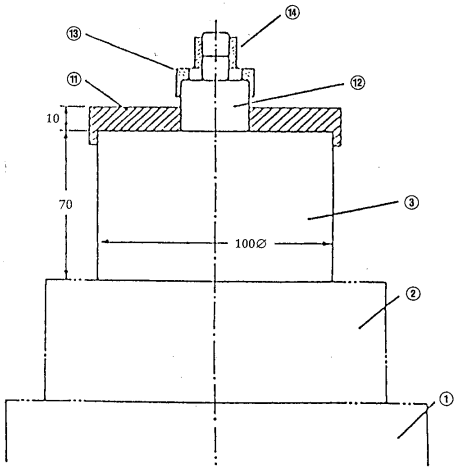


Fig. 4b Fall-hammer, lower part

(8) graduated scale
(9) fall-hammer(drop mass)
(10) holding and releasing device
(11) locating plate
(12) intermediate anvil (interchangeable), 26 diameter × 26
(13) locating ring with orifices
(14) impact device

Figure 4

Continued

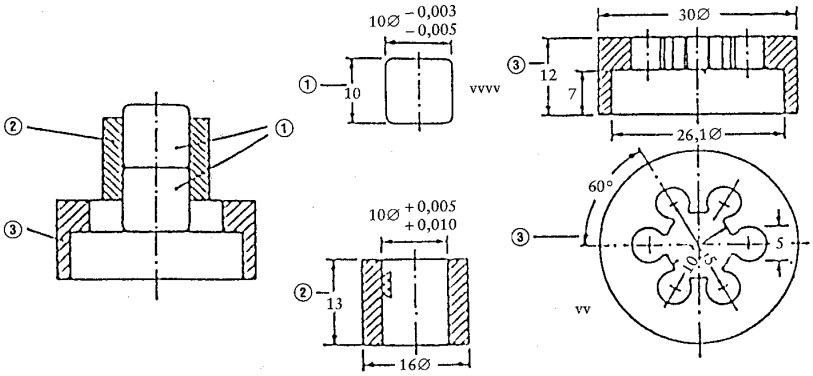
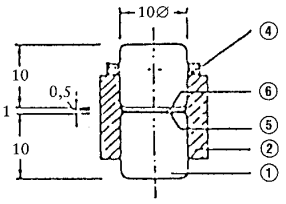


Fig. 4c Shock device for substances in powdered or paste-like form

(1) steel cylinders
(2) guide ring for steel cylinders
(3) locating ring with orifices
  (a) vertical section
  (b) plan
(4) rubber ring
(5) liquid substance (40 mm^3)
(6) space free from liquid

Fig. 4d Shock device for liquid substances



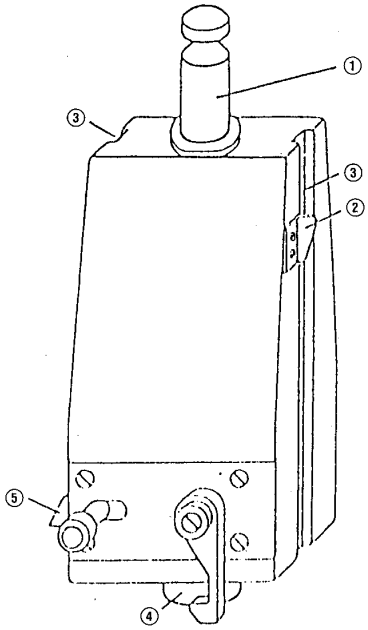


Fig. 4e Hammer (drop mass of 5 kg)

(1) suspension spigot
(2) height marker
(3) positioning groove
(4) cylindrical striking head
(5) rebound catch

Figure 5

Friction sensitivity apparatus

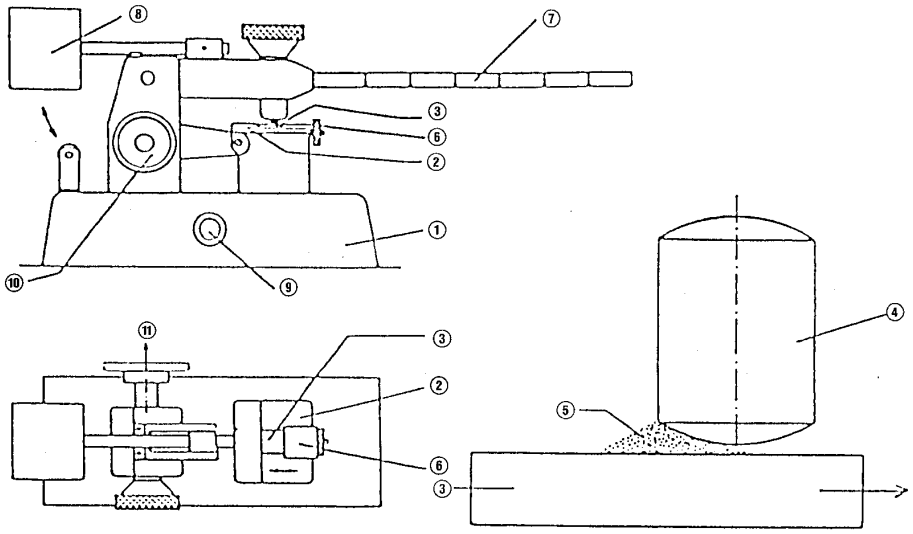


Fig. 5a Friction apparatus; elevation and plan view

(1) steel base
(2) movable carriage
(3) porcelain plate, 25 × 25 × 5 mm,
hel on carriage
(4) fixed porcelain peg, 10 diameter × 15 mm
(5) sample under test, approximately 10 mm^3

Fig. 5b Starting position of peg on sample

(6) peg-holder
(7) loading arm
(8) counterweight
(9) switch
(10) wheel for setting carriage at starting position
(11) direction to electric drive motor