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

12 October 2017

Sub-Committee of Experts on the Transport of Dangerous Goods

Fifty-second session

Geneva, 26 November-6December 2017

Item 2 (e) of the provisional agenda

Explosives and related matters: stability tests for industrial nitrocellulose

Stability tests for nitrocellulose

Transmitted by the European Chemical Industry Council (CEFIC) on behalf of the World Nitrocellulose Producers Association WONIPA

Introduction

1. The stabilization of nitrated cellulose (NC) mixture is a decisive and critical step in the production process of NC and must be done and controlled properly for each production lot in order to achieve stable NC products that can be transported and used safely without the danger of self-ignition over their entire shelf life. The wetting of NC mixtures with alcohol, water or plasticizer only reduces the burning speed of the NC; it has no effect on the stability of the NC mixtures. Additional measures are necessary to ensure the stability even if the NC mixture will get completely dry.

2. The Working Group on Explosives of the UN TDG Sub-Committee endorsed in the 51st meeting in July 2017 the statements of the German expert in the Working Paper ST/SG/AC.10/C.3/2017/3, that additional tests are necessary to ensure that NC in different mixtures are stable, even if these mixtures would get completely dry. The working group agreed that stabilization was required to ensure safe handling of NC but also determined that the 3(c) thermal stability test at 75 °C was not suited for evaluating NC stabilization. The working group unanimously concluded that the Bergmann Junk test and the Methyl Violet Paper tests were suitable tests for such assessment and recommended their performance in place of the 3(c) test when classifying NC.

3. The Working Group on Explosives concluded that CEFIC should lead an intersessional group to work out details of implementation, test procedures, placement of the Bergmann Junk test and the Methyl Violet Paper test in the Model Regulations and the MTC, and will consider some allowance for grandfathering currently existing NC approvals and prepare a new proposal for the next session.

4. The TDG Sub-Committee endorsed the conclusions of the Working Group on Explosives, (paragraph 25 and 26 report of the Sub-committee of Experts on the Transport of Dangerous Goods on its Fifty First session ST/SG/AC.10/C.3/102).

5. The Working Paper of Germany „Stability tests for Nitrocellulose“ (ST/SG/AC.10/C.3/2017/35) ensured that the issue “Stability Tests for Nitrocellulose will be discussed in the November/December 2017 UN TDG meeting. As the deadline of September 1, 2017 was too short for a detailed discussion of the detailed test descriptions in the intersessional correspondence group, these test description could not be included in the above mentioned Working Paper of Germany.

6. This INF-Paper provides the detailed descriptions of the tests, a proposal for the details of implementation and the placement of the Bergmann Junk test and the Methyl Violet Paper test in the Model Regulations and the MTC as the result of the discussion in the ICG for the discussion in the Working group on explosives in the Nov / Dec 2017 UN TDG meeting. A check of the existing stability test standards for Nitrocellulose showed that the 3(c) thermal stability test at 75 °C is not used in any of these standards. Therefore an allowance for grandfathering currently existing NC approvals is not needed.

Proposal

7. The expert from Germany is of the opinion that the stability of NC mixtures is crucial for it being transported, stored and handled safely. Provisions should be incorporated in the Model Regulations to ensure a sufficient level of stabilisation for worldwide and multimodal transport.

8. It is proposed to require a tested thermal stability for nitrocellulose mixtures of class 1 (UN 0340, UN 0341, UN 0342 und UN 0343) and class 4.1 (UN 2555, UN 2556, UN 2557 und UN 3380). A NC-mixture is classified as stable for transport,

- if the quantity of NO gas formed in the Bergmann Junk test within 2 hours at 132 °C is not higher than 2.5 ml NO gas per g of NC, or

- if a test time of min. 30 minutes is achieved with the Methyl Violet Paper Test, before the test paper has changed its color completely.

The Bergmann Junk Test and der Methyl Violet Paper Test should be included in the Manual of Tests and Criteria as applicable test methods. They could be included in a new appendix 8.

Annex 1

Proposed amendments to the Model Regulations

Insert a new number 2.1.3.4.4

2.1.3.4.4 The chemical stability of nitrocellulose mixtures of Class 1 (UN 0340, UN 0341, UN 0342 and UN 0343) shall be tested in accordance with the test methods given in the Manual of Tests and Criteria, appendix 8. A NC-mixture is classified as stable for transport,

- if the quantity of NO gas formed in the Bergmann Junk test within 2 hours at 132 °C is not higher than 2.5 ml NO gas per g of NC, or

- if a test time of min. 30 minutes is achieved with the Methyl Violet Paper Test, before the test paper has changed its color completely.

Insert a new number 2.4.2.4.3

2.4.2.4.3 The chemical stability of nitrocellulose mixtures of Class 4.1 (UN 2555, UN 2556, UN 2557 and UN 3380), shall be tested in accordance with the test methods given in the Manual of Tests and Criteria, appendix 8. A NC-mixture is classified as stable for transport,

- if the quantity of NO gas formed in the Bergmann Junk test within 2 hours at 132 °C is not higher than 2.5 ml NO gas per g of NC, or

- if a test time of min. 30 minutes is achieved with the Methyl Violet Paper Test, before the test paper has changed its color completely.

Amendments to the UN Manual of Tests and Criteria

Insert a new appendix 8

Appendix 8

Stability tests for nitrocellulose

1 Bergman-junk stability test

1.1 Introduction

The Bergman-Junk test is a quantitative stability test applicable to all types of nitrocellulose (NC). The test measures the quantity of nitrous vapors given off by 1 (one) or 2 (two) gram(s) of nitrocellulose heated for two hours at 132 °C ± 1 °C *(Plasticised NC: 3 (three) grams are heated for 1 hour)* is determined by titration with alkali. The Bergmann Junk test method is more time-consuming than the Methyl Violet Paper but allows a reliable and reproducible quantitative assessment of chemical stability. Thus this test is the preferred method.

1.2 Apparatus and materials

1.2.1 Analytical Balance, precision 1 mg or better.

1.2.2 Bergman-Junk tube made of clear glass, approximately 17.5mm inner diameter, 19.5 mm, outer diameter, and 270 mm to 350 mm long fitted with a condensing chamber. Several different types of suitable condensing chambers are commercially available. (for examples see Figure 23.4.4.1 and Figure 23.4.4.2).

1.2.3 Stability bath: Oil or suitable fluid bath or metal block capable of maintaining the temperature of the stability tubes at 132 °C ± 1 °C. The temperature of the bath should be monitored with a calibrated thermometer or thermocouple (precision 0.1 ^{o}C) which is located in one of the test wells.

1.2.4 Polycarbonate protective screen or safety cabinet to prevent horizontal, and limit vertical projection of material should the tubes break.

1.2.5 The following apparatus is required

10 cm^3 semi-automatic pipette or equivalent.

250 cm^3 conical flash with wide neck.

50 cm^3 test tube.

Titration burette 10 ml to 25 ml

Sodium hydroxide (NaOH) solution N/100.

1.2.6 Suitable pH indicator e.g. methyl orange, methyl red, methyl red/methylene blue or R8 B3 coloured indicating fluid (Tacchiro). Solution composed of 1 % alcohol mixed with 8 g of methyl red and 3 g of purple methyl.

1.2.7 Fully deionized or distilled water with a conductivity < 1 µS.

1.3 Procedure

1.3.1 Weigh 1 (one) or 2 (two) gram(s) of dry NC to an accuracy of 0,001 g. *(Weigh 3 (three) grams of plasticised NC to an accuracy of 0,001 g)*. The moisture content of the sample must be below 1 % after the drying process and at the time, when it is introduced in the tube. With the help of a funnel introduce this into the tube which must be dry and clean. Wipe the ground section thoroughly and adjust the condensing chamber making sure that the above is well greased with silicone grease; it may also not be greased.

1.3.2 Measure out 15 ml to 50 ml of distilled water, depending on the condenser type, in a test tube and pour into the bulbs of the condenser. Ensure that no water enters the stability tube.

1.3.3 Make sure that the stability bath has reached a temperature of 132 °C ± 1 °C and then insert each tube into one of the apertures in the bath. The depth of immersion of the tube will vary depending on the type of stability bath used but must be between 110 mm and 220 mm. Make a note of the time at which the experiment begins.

1.3.4 If using a protective screen, the operator must take care to turn the open side of the protective screen towards the wall or an unoccupied part of the room both when loading and removing the test tubes from the bath. If there is no protective screen the face should be protected with a visor.

1.3.5 Maintain the tubes at a temperature of 132 °C ± 1 °C for two hours unless pronounced fuming is observed. If fuming occurs, the test shall be stopped immediately and the duration of the heating period noted.

1.3.6 After two hours at 132 °C *(1 hour for plasticised NC)* remove the tube from the bath, place it in its stand and allow to cool behind a safety screen. During this time some water may be drawn into the lower tube. After thirty minutes cooling transfer the contents of the condensing chamber into the lower tube and rinse the condensing chamber with distilled water.

1.3.7 Transfer the contents of the lower tube into the conical flask and rinse with distilled water. The total amount of liquid should not be more than 175 ml.

1.3.8 Titrate with N/100 sodium hydroxide solution.

1.3.9 Calculations

$$\mathbf{2\ NaOH + 2\ NO + ½\ O_2 \rightarrow 2\ NaNO_2 + H_20}$$

$$V_{NO}\ \frac{c_{NaOH} \times C_{NaOH} \times V_{NO,m}}{m_{NC}} = CNaOH \times 0.22$$

V_{NO} = volume of the evolved nitrogen oxide in cm^3/g

c_{NaOH} = concentration of caustic soda = 0.01 mol/l

C_{NaOH} = consumption of caustic soda in ml.

$V_{NO,m}$ = molar volume of NO = 22.38 l/mol

m_{NC} = mass nitrocellulose in g

1.3.10 The total absence of acidity in the water is verified by a mock test; otherwise the value determined by the mock test is subtracted.

1.3.11 Also aliquot portions of the water containing the NO_x may be used, resulting in different factors in the formula.

1.4 Test criteria and method of assessing results

1.4.1 The tested substance is classified as stable, if the quantity of nitrous vapours given off is not more than 2.5 ml NO per g of NC.

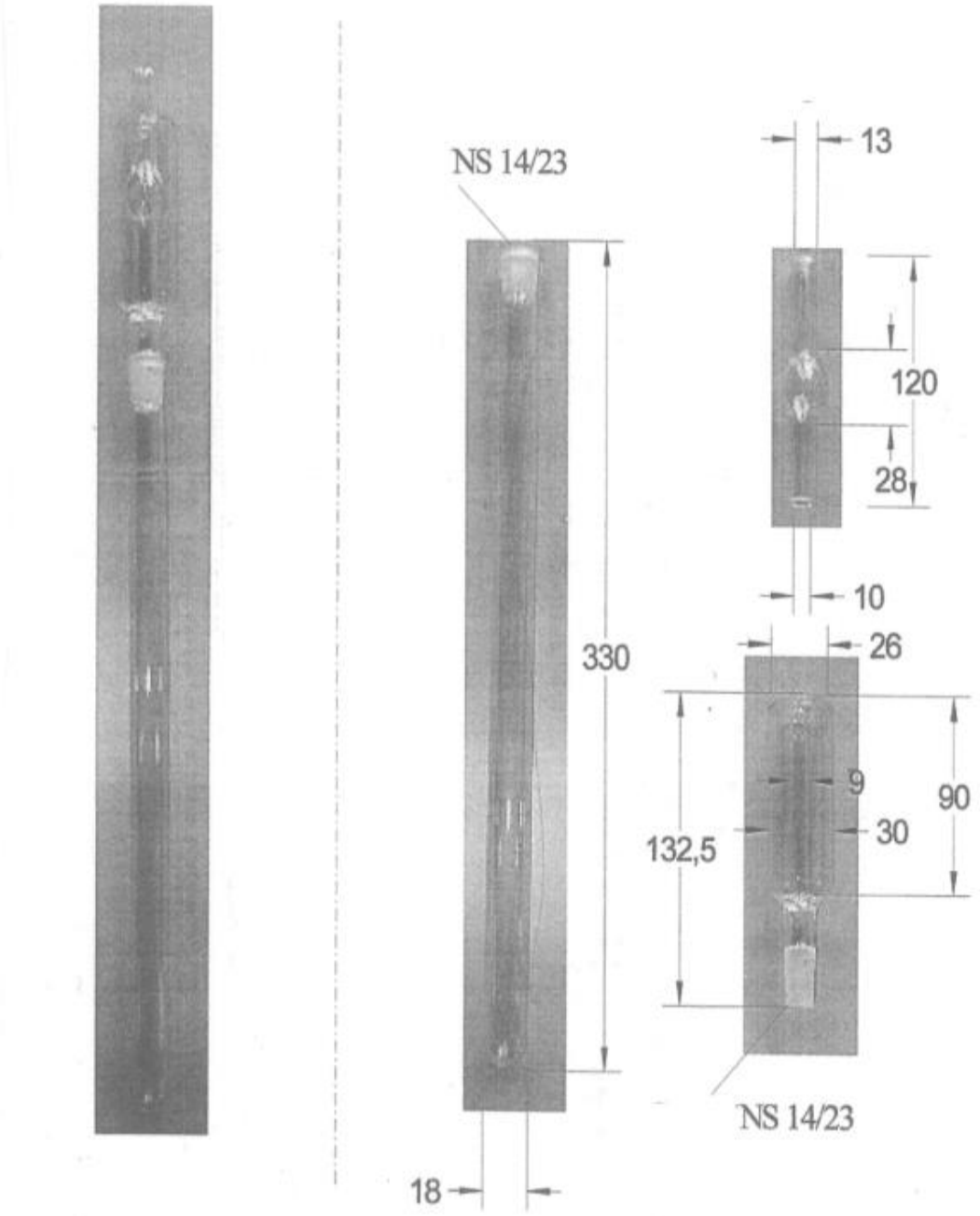

Figure 23.4.4.1: Condensing chamber for Bergmann Junk test example 1

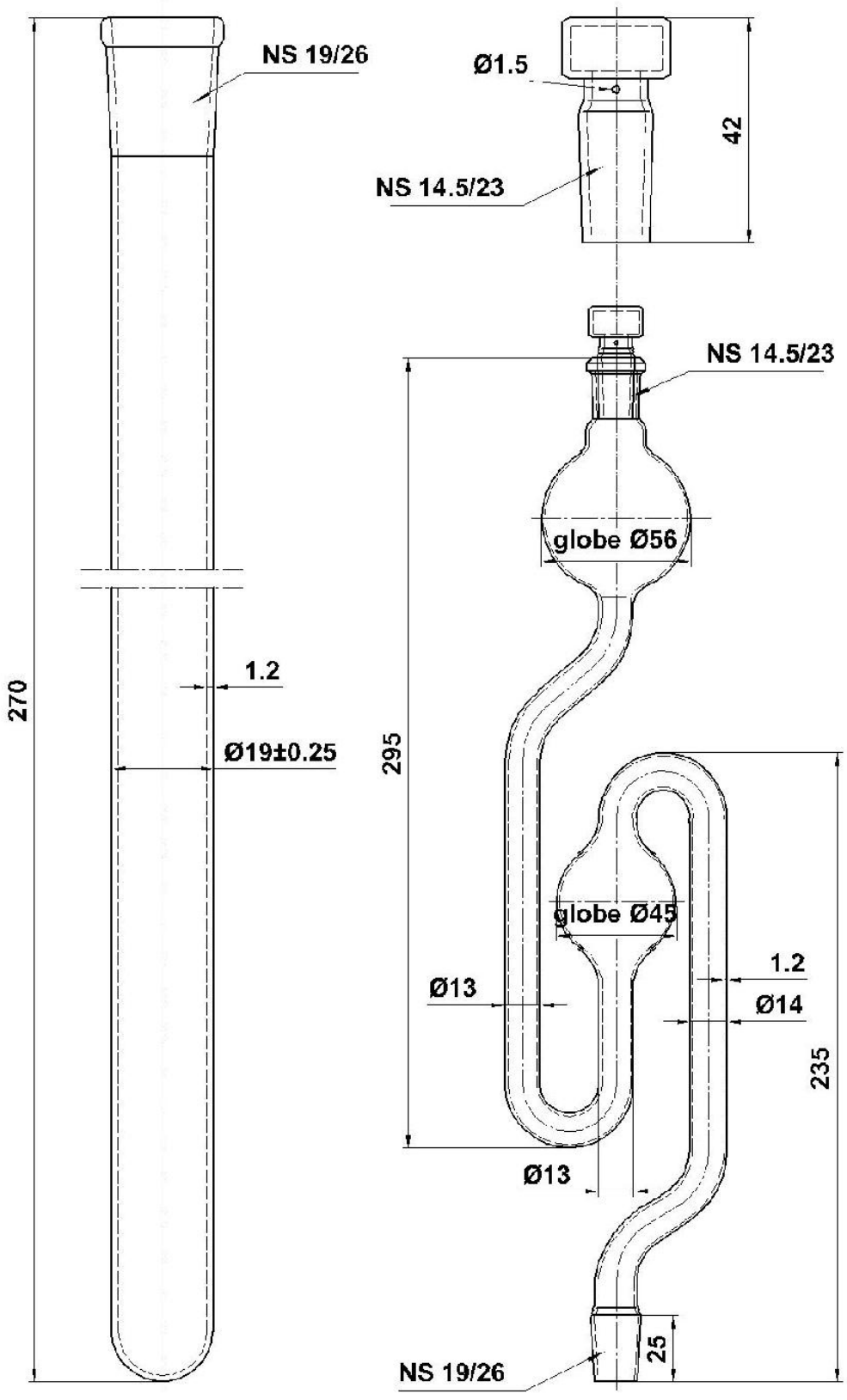

Figure 23.4.4.2: Condensing chamber for Bergmann Junk test example 2

2 Methyl Violet Paper Test (134.5° C Heat Test)

2.1 Introduction

In the Methyl Violet Paper Test (134.5°C Heat Test), the sample is heated in a test tube which has a piece of methyl violet test paper just above it. The nitrogen oxides released from the heated sample react with the dyes in the paper. The time until the paper has completely changed color gives an indication of the stability of the nitrocellulose. The Test paper should be obtained from a reputable source that has calibrated it against a known standard.

2.2 Apparatus and materials

2.2.1 Analytical Balance, precision 10 mg or better.

2.2.2 Stability bath: Water-ethylene glycol bath, oil bath, or metal block oven capable of maintaining the temperature of the stability tubes at 134.5 ± 0.5 °C. Temperature of bath has to be monitored with a calibrated thermometer or thermocouple (precision 0.1 °C) which is located in a test tube filled with inert material (e.g., sand); the test tube is placed in one of the thermowells. The inner diameter of each thermowell in the apparatus shall be 19 ± 0.5 mm. Depth of immersion of the stability test tubes shall be such that no more than 6 to 7 mm of the tubes project above the bath.

2.2.3 Stability test tubes made of clear glass, approximately 15 mm inner diameter; 18 mm outer diameter; and 290 mm length.

2.2.4 Powder funnel; metal or conductive plastic funnel with a long tube (to prevent electrostatic charging).

2.2.5 Corks, each containing one breather hole 4 mm in diameter (or notch of equivalent area).

2.2.6 Standardized methyl violet test papers approximately 70 ± 1.0 mm long and 20 ± 0.6 mm wide or methyl violet test papers prepared and tested using the following method:

2.2.6.1 Preparation of the indicator solution. To prepare 100 mL of indicator solution (note: if different amount of solution is required, it can be prepared while maintaining these proportions): 0.250 g of basic rosaniline (equivalent to CAS number 632- 99-5) is weighed into a porcelain dish, and about 10 mL of reagent grade acetic acid is added. The dish is heated on a water bath until all excess of acid is removed. In a 100 mL graduate cylinder, 0.168 g of crystal violet (equivalent to CAS number 548-62-9) is dissolved in 30 mL of high purity water and 5.0 g (4 mL) of reagent grade glycerine is added. The content of the porcelain dish is added to the cylinder using ethanol (minimum 95% v/v) and adjusted to produce 100 mL of solution. The solution is mixed thoroughly.

2.2.6.2 Preparation of the methyl violet paper. Sheets of paper are prepared by cutting filter papers (equivalent to Whatman 597, typically 580 mm x 580 mm with approximately 8.5 mg/cm2) into square parts that will fit into a low edge dish large enough to fit the cut sheet (typically cut in 4 square parts about 290 mm by 290 mm). In a fume-hood, the methyl violet solution is poured into the low edge dish. Separately, each cut sheet of paper is dipped completely into the solution for about 30 seconds. The strip is removed from the solution and the wet sheet of paper rotated vertically until the solution stops dripping (excess alcohol will evaporate in about 1 minute). The strip is hung up overnight to dry in a room free from deleterious fumes. When dry, the strips are cut in the size of 70 ± 1.0 mm long and 20 ± 0.6 mm wide. Once certified, they are kept in tightly closed amber glass bottles or opaque plastic bottles with a maximum of 200 papers per bottle. The bottle shall be kept closed, stored at room temperature, and out of direct light at all times except to briefly extract indicator papers.

2.2.6.3 Certification of the methyl violet paper. A minimum of one paper from each 200 max bottle is tested for the content in water and shall be 7.5 to 15% water content by oven drying.If required, the paper may be rehydrated by keeping the paper in a controlled humidity chamber controlled at 60 to 80% RH until the correct water content is obtained.

To confirm that the reactivity of the methyl violet paper is acceptable, a minimum of 1 paper from each 200 max bottle shall be tested using nitrogen dioxide gas of known concentration in air between 1500 and 2500 ppm (v/v). The gas may be obtained already diluted and certified or obtained by dilution using pure nitrogen dioxide. The gas concentration shall be known with an accuracy of ± 2.5%. Based on the concentration of the nitrogen dioxide gas, the required flowrate for an end-point centered at 55 minutes is given by: Flowrate (ml/min) = 83636 / Gas concentration in ppm (v/v) of nitrogen dioxide gas. The flowrate shall be maintained within ± 1.5 ml/min of the calculated value during the certification of the paper. The paper is tested using the standard gas and a cylindrical flow cell of about 30 ml containing one paper (the flow cell diameter is similar to the MV paper width). The end-point is obtained when the paper is completely salmon pink after 55 ± 7 minutes. Only the batches that meet those 2 criteria (water content and reaction time) will be considered certified methyl violet paper. The paper shall be stored at room temperature and in the shade. The maximum shelf-life of the indicator papers in a sealed bottle is 5 years. Once the bottle is open, the shelf-life of the bottle's contents is reduced to 1 year. After 1 year, the water content of the paper shall be verified and adjusted, if necessary. The bottle containing the verified indicator papers shall be given another 1 year of shelf-life. Under no circumstances shall the indicator paper shelf-life be extended beyond 5 years after manufacture.

2.3 Procedure

2.3.1 Sample and interior of test tubes shall not be touched by bare hands. The test is to be performed in duplicate; with further repetition of test if the two results of the duplicate measurement differ by more than 5 minutes.

Two portions of 2.5 ± 0.01 g each of dry nitrocellulose sample are transferred into the stability test tubes, preferably by a powder funnel. Each tube is tapped gently in order to settle the material, and any material adhering to the sides of the tubes is brushed down. If the nitrocellulose occupies a greater length than 5 cm, it has to be compressed to that length by means of a flat headed rod. Into each tube a piece of the test paper is placed vertically so that the lower end of the paper is 25 mm above the specimen. Then a cork is placed in each tube. The two tubes are placed in the bath and maintained at a temperature of 134.5 ± 0.5 °C. In order to determine the test time, the test papers are examined after the first 20 minutes in the bath, and thereafter at 5 minute intervals. For each examination of test papers, the tubes are lifted half way out of the bath to monitor test paper color change, and quickly replaced. When the test paper in any tube has changed color completely to salmon pink, the test is considered complete. The test time is then recorded (for example, if the violet paper is not completely changed in 25 minutes, but is completely changed in 30 minutes, the time of the test is recorded as 30 minutes). The test is discontinued when the salmon pink end point is attained in any of the papers.

2.3.2 Calculation

The test time in minutes of stability of the nitrocellulose.

2.4 Test criteria and method of assessing results

2.4.1 When the test paper in any tube has changed color completely to salmon pink, the test is considered complete. The test time is then recorded (for example, if the violet paper is not completely changed in 25 minutes, but is completely changed in 30 minutes, the time of the test is recorded as 30 minutes). The test is discontinued when the salmon pink end point is attained in any of the papers.

The tested substance is classified as stable, if the time for the complete change of the colour of the test paper is minimum 30 minutes.