INTERNATIONAL STANDARD

**ISO 4625-1**

Second edition
2020-07

# Binders for paints and varnishes — Determination of softening point —

## Part 1: Ring-and-ball method

*Liants pour peintures et vernis — Détermination du point de ramollissement —*

*Partie 1: Méthode de l'anneau et de la bille*



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# Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 139, *Paints and varnishes,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 4625-1:2004), which has been technically revised. The main changes compared to the previous edition are as follows:

— the automated method has been classified to be the reference method;

— an introduction with information on all three methods described in the three parts of ISO 4625 series has been added;

— CAS-numbers have been added to the chemicals used;

— the text has been editorially revised;

— the normative references have been updated.

A list of all parts in the ISO 4625 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.



# Introduction

The ISO 4625 series specifies three widely used procedures for the measurement of the softening point of rosin-based resins. This document presents the ring-and-ball method, which has been the accepted standard for many years. ISO 4625-2 presents the Mettler cup-and-ball method. A new method, called the Mettler method without the ball, is to be presented in a future document.

This document is still the only standard test method accepted in regulatory documents such as Title 21 of the Code of Federal Regulations (CFR) – Food and Drugs.

Other parts of the ISO 4625 series concern Mettler cup-and-ball methods. Although the recommended testing conditions differ, the only difference between the equipment required in such methods is that Mettler method without the ball does not use a ball. Surveys have shown that the Mettler cup-and-ball method specified in ISO 4625-2 is the most widely used in the USA, while the Mettler method without the ball is the most widely used in Europe. These methods are less time consuming than the ring-and-ball manual method and the equipment is less expensive than the ring-and-ball automated method.

As a consequence of the thermoplastic nature of the test resins, the softening points obtained using the recommended test conditions for all three methods are not generally the same. Consequently, the test method and the testing conditions used should be noted in the final report.

# Binders for paints and varnishes — Determination of softening point —

## Part 1: Ring-and-ball method

## 1 Scope

This document specifies the test methods for determining the softening point of resins (including rosin) and similar materials by means of ring-and-ball apparatus.

Both manual and automated methods are specified, the automated method being the reference method.

## 2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 4618, *Paints and varnishes — Terms and definitions*

ISO 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling*

IEC 60751, *Industrial platinum resistance thermometer and platinum temperature sensors*

## 3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 4618 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

**3.1**
**softening point**
temperature at which a disc of sample held within a horizontal ring is forced downward a distance of 25 mm under the weight of a steel ball as the disc is heated at a prescribed rate in a water, glycerol, silicone oil, ethylene glycol/water or glycerol/water bath

## 4 Principle

In general, with materials of the types mentioned in Clause 1, softening does not take place at a definite temperature. As the temperature rises, these materials gradually change from brittle or exceedingly thick and slow-flowing materials to softer and less viscous liquids. For this reason, the determination of the softening point shall be made by a fixed, closely defined method if the results obtained are to be comparable.

For the purpose of these test methods, the definition of softening point given in Clause 3 applies.

# 5 Sampling and preparation of test pieces

## 5.1 Sampling

Take a representative sample of the product to be tested, as described in ISO 15528.

The sample shall consist of freshly broken lumps free of oxidized surfaces. For samples received as small lumps, scrape off the surface layer of the lumps immediately before use, avoiding inclusion of finely divided material or dust.

## 5.2 Preparation of test pieces by the pour method

### 5.2.1 Field of application

This preparation procedure is suitable for resins (including rosin) and other substances that can be heated and poured without adverse effects on the softening point.

### 5.2.2 Apparatus

**5.2.2.1 Container**, in which the sample can be melted.

**5.2.2.2 Knife or spatula**.

**5.2.2.3 Oven, hot-plate, sand bath or oil bath**.

### 5.2.3 Procedure

Take a quantity of the sample (see 5.1) which is at least twice that necessary to fill the desired number of rings (7.1.1), but in no case less than 40 g, and melt it immediately in a clean container (5.2.2.1) using an oven, hot-plate, sand bath or oil bath (5.2.2.3) to prevent local overheating. Take care to avoid incorporating air bubbles in the sample. Melt the sample completely, but do not heat it above the minimum temperature necessary to pour it easily. The time from the beginning of heating to the pouring of the sample shall not exceed 15 min.

For materials that are heat-sensitive, continuously inert the atmosphere in the container holding the sample with nitrogen ($N_2$) during the melting procedure.

For materials that tend to crack or shrink in the rings on cooling, preheat the rings immediately before filling them to approximately the temperature at which the material is to be poured. The rings, while being filled, shall rest on a suitable metal surface. Pour a sufficient quantity of the sample into the ring so as to leave an excess on cooling. Allow to cool for at least 30 min and trim off the surplus material at the periphery of the ring. To remove excess material from the top, cut the excess material off cleanly with a slightly heated knife or spatula (5.2.2.2) or grasp the ring in a pair of tongs and draw the top surface of the test piece quickly and firmly over the surface of a heated metal plate. If the determination is repeated, use a clean container and a fresh quantity of the sample.

## 5.3 Preparation of test pieces from samples with a low softening point (up to 35 °C)

### 5.3.1 Apparatus

**5.3.1.1 Aluminium foil.**

**5.3.1.2 Dry ice [$CO_2$ (solid)] or freezer.**

**5.3.1.3 Knife or spatula.**

### 5.3.2 Procedure

Take a suitable quantity of the sample (see 5.1). Place one of the rings (7.1.1) on a piece of aluminium foil (5.3.1.1). Pour the material to be tested into the ring. Then place the foil and filled ring on dry ice or in a freezer (5.3.1.2) to cool. The material in the ring shall be free of bubbles.

After cooling, cut or scrape off any excess material using a slightly heated knife or spatula (5.3.1.3), then slide the ring gently from the foil. Place the ring in the ring holder (8.1.6) and immediately perform the softening point determination as described in 7.3.

## 6 Materials (heating-bath liquids)

**6.1 Distilled or deionized water**, freshly boiled, for softening points between 35 °C and 80 °C.

Use freshly boiled water that has been cooled to at least 27 °C below the anticipated softening point, but not lower than +5 °C. The use of freshly boiled water is essential, as otherwise air bubbles may form on the test piece and affect the result.

**6.2 Glycerol**, (CAS-No 56-81-5) for softening points between 80 °C and 150 °C, USP[1)] grade or equivalent.

Repeated use of glycerol increases the moisture content over time and may affect results. Use fresh glycerol if any change in appearance is noted.

Do not use glycerol for softening points greater than 150 °C due to the 160 °C flash point of glycerol.

**6.3 Silicone oil (polymethylsiloxane)**, 50 $mm^2/s$ viscosity, for softening points above 80 °C.

The silicone oil shall be stable up to a temperature of at least 200 °C, remain clear within this temperature range, have no apparent reactivity with the test piece, have high water repellence, and maintain a uniform viscosity and stirring rate within the temperature range.

Replace with fresh silicone oil if any change in appearance is noted. Do not use silicone oil that contains any gels as gels are an indicator that degradation has occurred.

**6.4 Ethylene glycol**, (CAS-No 107-21-1) for softening points below 35 °C.

Prepare a fresh 1 + 1 (by volume) mixture of distilled water and ethylene glycol prior to the determination. For softening points between 0 °C and 35 °C, a 1 + 1 (by volume) mixture of glycerol and water may be used as an alternative.

## 7 Automated ring-and-ball method (reference method)

### 7.1 Apparatus

**7.1.1 Shouldered rings**, of brass, conforming to the dimensions shown in Figure 1 a).

**7.1.2 Steel balls**, diameter (9,53 ± 0,1) mm and mass (3,50 ± 0,05) g.

**7.1.3 Beaker**, 600 ml. Ensure that the dimensions are such that the beaker will properly fit into the heating unit.

**7.1.4 Stir bar**, of dimensions such that the bar spins freely under the test insert.

1) U.S. Pharmacopeia.

### 7.2 Calibration

The calibration of any automated ring-and-ball softening point apparatus shall be performed on a regular basis since accurate temperature control is required. Follow the manufacturer's instructions for calibration of the instrument.

### 7.3 Procedure for materials with a softening point between 35 °C and 80 °C

Place the stir bar (7.1.4) in the 600 ml beaker (7.1.3) and fill the beaker with approximately 500 ml of freshly boiled distilled or deionized water (6.1) at a temperature at least 27 °C below the anticipated softening point. Ensure that the beaker is properly positioned on the heater in the test unit. Place the prepared rings, with their test pieces, in the test insert. Place a ball-centring guide, and ball on top of each test piece. Place the test insert in the beaker of water, suspending it from the support pins. Place the temperature-measuring device in the test insert.

Verify that the control unit is set for the correct bath liquid and start the determination. The test is complete when the light beam has been interrupted by the falling ball and material.

Record as the softening point the temperature displayed on the unit after the light beam has been interrupted by the falling ball and material.

Start the cooling process in the instrument. Immediately remove the temperature-measuring device from the test insert, then remove the test insert from the beaker. Thoroughly clean the test insert, balls and rings in a suitable solvent.

### 7.4 Procedure for materials with a softening point between 80 °C and 150 °C

Use the same procedure as described in 7.3, except fill the bath with glycerol (6.2) or silicone oil (6.3).

For materials softening around 80 °C, report the bath liquid since a glycerol or silicone oil bath will yield a slightly higher result than a water bath.

### 7.5 Procedure for materials with a softening point above 150 °C

Use the same procedure as described in 7.3, except fill the bath with silicone oil (6.3).

Replace the silicone oil with fresh oil if any change in appearance is noted. Do not use silicone oil that contains any gels as gels are an indicator that degradation has occurred.

## 8 Manual ring-and-ball method (alternate method)

### 8.1 Apparatus

**8.1.1 Shouldered rings,** of brass or steel, conforming to the dimensions shown in Figure 1 a).

**8.1.2 Steel balls,** diameter (9,53 ± 0,1) mm and mass (3,50 ± 0,05) g.

**8.1.3 Ball-centring guide** (optional), constructed of brass and with the shape and dimensions illustrated in Figure 1 b).

**8.1.4 Heat-resistant glass beaker**, not less than 85 mm in diameter and not less than 125 mm in depth from the bottom to the flare (an 800 ml low-form beaker of heat-resistant glass meets this requirement).

**8.1.5 Thermometers.**

**8.1.5.1 Thermometer for low softening points**, with a range from −2 °C to +80 °C.



**8.1.5.2 Thermometer for medium softening points**, with a range from 30 °C to 200 °C.

**8.1.5.3 Thermometer for high softening points**, with a range from −2 °C to +300 °C.

Or, as an alternative to any of the above three thermometers:

**8.1.5.4 Resistance thermometer**, e.g. Pt100 in accordance with IEC 60751.

### 8.1.6 Holder for ring and thermometer.

Any convenient apparatus may be used to hold the ring and thermometer in place, provided that it meets the following requirements.

— The rings (8.1.1) shall be held in a horizontal position.

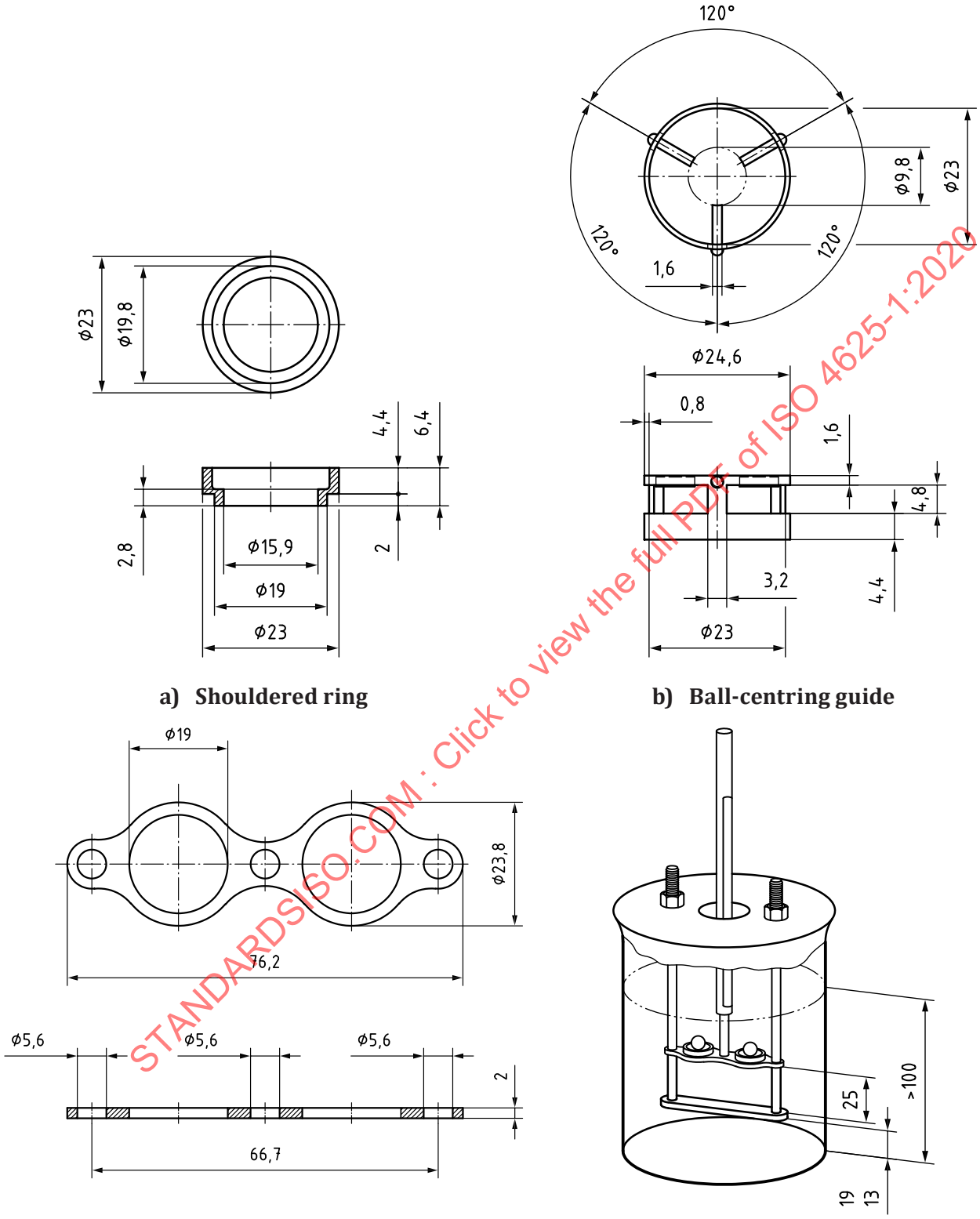
— When using the apparatus as shown in Figure 1 d), the bottom of each ring shall be 25 mm above the horizontal plate below it, the bottom surface of the horizontal plate shall be 13 mm to 19 mm above the bottom of the beaker (8.1.4), and the depth of liquid in the beaker shall be not less than 100 mm.

— The thermometer shall be suspended so that the bottom of the bulb is level with the bottoms of the rings and within 13 mm of each ring, but not touching either ring. For referee work, no more than two rings shall be used.

### 8.1.7 Stirrer.

The liquid in the heating bath (beaker) shall be stirred at a speed sufficient to ensure uniform heat distribution without causing sideways displacement of the resin as it softens in the ring. A stirring rate of 500 $min^{-1}$ to 700 $min^{-1}$ is typical. A mechanical motor-driven stirrer, mounted so that any vibrations created by its rotation are not conveyed directly to the ring holder shown in Figure 1 c), or a magnetic stirrer placed under the bath, can be used.

Dimensions in millimetres
All tolerances ±0,2 mm




a) Shouldered ring

b) Ball-centring guide

c) Ring holder

d) Assembled apparatus

**Figure 1 — Apparatus used for manual determination of softening point**

**8.1.8 Device for heating the heating-bath liquid,** capable of maintaining the required heating rate.

Apparatus may be used which increases the temperature and registers the softening point automatically.

## 8.2 Calibration

A calibration check of any temperature controllers used in the manual ring-and-ball softening point apparatus shall be performed on a regular basis since accurate temperature control is required.

## 8.3 Procedure

### 8.3.1 Procedure for materials with a softening point between 35 °C and 80 °C

#### 8.3.1.1 Assembly of apparatus

Fill the beaker (8.1.4) to a depth of (105 ± 3) mm with freshly boiled distilled or deionized water (6.1). Use freshly boiled water that has been cooled to at least 27 °C below the anticipated softening point, but not lower than +5 °C.

If a motor-driven stirrer (8.1.7) is used, locate the axis of the shaft of the stirrer near the back wall of the beaker, with the blades clearing the wall and with the bottom of the blades approximately 19 mm above the tops of the rings (8.1.1). Unless a ball-centring guide (8.1.3) is used, make a slight indentation in the centre of each test piece by pressing a ball (8.1.2) or a rounded rod, slightly heated for hard materials, into the material at this point. Centre a ball on the surface of each test piece. Suspend the rings containing the test pieces in the water in the manner described in 8.1.6. when using the apparatus shown in Figure 1 d).

Suspend a thermometer for low softening points (8.1.5.1) so that the bottom of the bulb is level with the bottoms of the rings and within 13 mm of, but not touching, the rings. Maintain the initial temperature of the water for 15 min.

Start stirring with the stirrer (8.1.7). Continue stirring until completion of the determination.

#### 8.3.1.2 Heating

Heat in such a manner that the temperature of the water is raised at a rate of 5 °C/min. Protect the beaker from draughts by using a shield if necessary. The rate of increase of the temperature shall be uniform, i.e. not averaged over the period of the determination. After the first 3 min, the maximum permissible variation over any period of 1 min shall be ±0,5 °C/min. Reject the results of any determinations in which the rate of increase is not within these limits.

Rigid adherence to the prescribed rate of heating is absolutely essential for reproducibility of results.

#### 8.3.1.3 Determination of softening point

Record as the softening point the temperature of the thermometer at the instant the test piece touches the lower horizontal plate. Make no correction for the emergent stem of the thermometer. The softening point can be recorded automatically, using a suitable light-beam device, for example.

When a ball drops through the ring, it shall be completely surrounded by softening resin and shall drop straight down to the lower horizontal plate.

Thoroughly clean the ring holder, balls and rings in a suitable solvent after each determination.

#### 8.3.2 Procedure for materials with a softening point between 80 °C and 150 °C

Use the same procedure as described in 8.3.1 but fill the bath with glycerol or silicone oil and use a thermometer for medium softening points (8.1.5.2). The maximum allowable starting temperature of the oil bath is 27 °C below the anticipated softening point.

NOTE For materials softening around 80 °C, a glycerol or silicone oil bath yields a slightly higher result than a water bath.

Repeated use of glycerol will increase the moisture content over time and can affect results. Replace with fresh glycerol if any change in appearance is noted.

#### 8.3.3 Procedure for materials with a softening point above 150 °C

Use the same procedure as described in 8.3.1 but fill the bath with silicone oil and use a thermometer for high softening points (8.1.5.3).

Replace the silicone oil with fresh oil if any change in appearance is noted. Do not use silicone oil that contains any gels as gels are an indicator that degradation has occurred.

#### 8.3.4 Procedure for materials with a softening point below 35 °C

Cool an ethylene glycol bath, prepared as described in 6.4, to −25 °C in an isopropanol/ethanol/dry-ice bath. Use the same procedure as described in 8.3.1, except for the bath liquid. Begin heating immediately once the test pieces in the rings, with the balls on them, have been placed in the bath.

## 9 Expression of results

Calculate the mean of two determinations and round it to the nearest 1,0 °C.

## 10 Precision and bias

### 10.1 Precision of the automated method

#### 10.1.1 General

An interlaboratory study of the automated ring-and-ball method, using rosin and three resins, was run in 1998 by 21 laboratories. The design of the experiment, similar to that specified by ASTM E 691, and an analysis of the data are given in ASTM Research Report No. D01-1113[2)].

#### 10.1.2 Precision data

The precision data given below for the ring-and-ball softening point of rosin at the 70 °C level in a water bath and of resins at the 100 °C to 135 °C level in a glycerol bath or oil bath, respectively, are for the comparison of two test results.

For a material with a 70 °C ring-and-ball softening point run in a water bath:

— repeatability limit, 95 % (within laboratory): 0,9 °C;

— reproducibility limit, 95 % (between laboratories): 2,4 °C.

For a material with a 100 °C to 135 °C ring-and-ball softening point run in a glycerol or silicone oil bath:

— repeatability limit, 95 % (within laboratory): 1,3 °C;

— reproducibility limit, 95 % (between laboratories): 3,9 °C.

2) Available from ASTM Headquarters, 100 Barr Harbor Drive, West Conshohocken, PA 19428, USA.