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Paints and varnishes — Wettability —

Part 7: Measurement of the contact angle on a tilt stage (roll-off angle)

Peintures et vernis — Mouillabilité —

Partie 7: Mesurage de l'angle de contact sur un plan incliné (angle d'écroulement)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 9, *General test methods for paints and varnishes*.

A list of all parts in the ISO 19403 series can be found on the ISO website.

Introduction

Dynamic contact angles describe the processes on the interface liquid/solid during volume increase (advancing angle) or volume decrease (receding angle) of a drop in horizontal position. As an alternative to the static method (see ISO 19403-2), for the advancing angle always a surface area is wetted, which was previously unwetted. For the receding angle, the contact angle during dewetting is observed. From the difference between advancing angle and receding angle, information on chemical homogeneity and roughness can be concluded. The receding angle is not suitable for the determination of the surface energy.

Paints and varnishes — Wettability —

Part 7: Measurement of the contact angle on a tilt stage (roll-off angle)

1 Scope

This document specifies a method for the dynamic measurement of the roll-off angle of a liquid drop on a solid surface. From the dynamic measurement, the advancing and receding angles of the drop rolling off can also be determined. The roll-off angle plays a role when evaluating, for example, easy-to-clean or anti-adherent surfaces.

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 19403-1, *Paints and varnishes — Wettability — Part 1: Terminology and general principles*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 4618, ISO 19403-1 and the following apply.

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

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

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

3.1
roll-off angle
α_s
tipping of the surface of the solid body, due to which a liquid drop put down onto this surface rolls off

3.2
advancing angle
θ_a
contact angle, which is measured during advancing of the three-phase point

Note 1 to entry: Generally, the advancing angle is used for the determination of the interface energy, in which case the measurement should be carried out close to the thermodynamic equilibrium. This is approximately reached if there is no influence of, for example, the dosing speed on the contact angle.

[SOURCE: ISO 19403-6:2017, 3.2]

3.3
receding angle
θ_r
contact angle, which is measured during receding of the three-phase point

[SOURCE: ISO 19403-6:2017, 3.3]

4 Principle

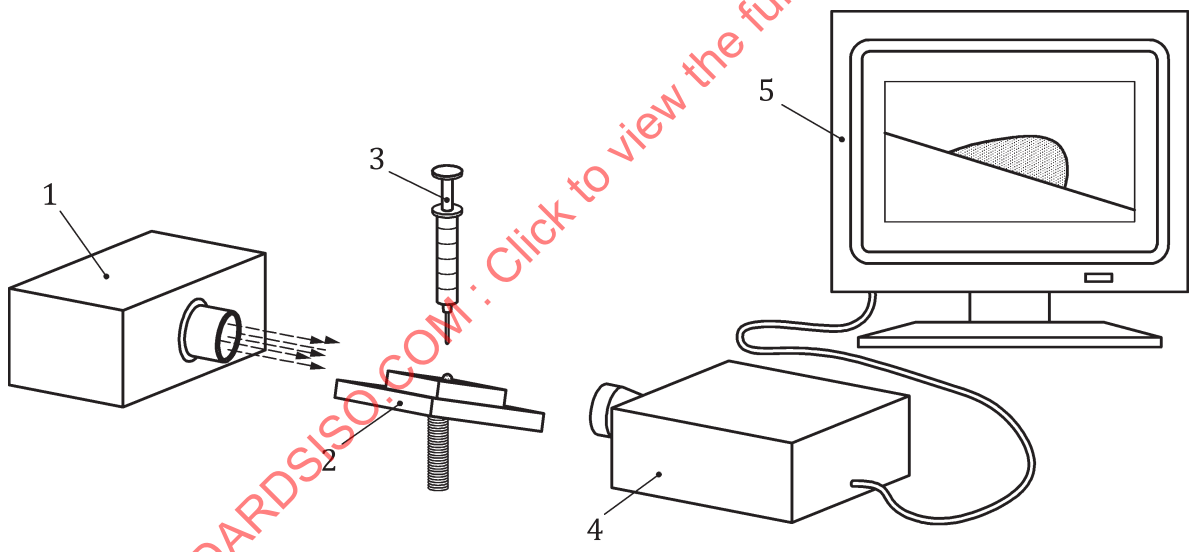
A drop is put down onto the surface to be tested. The surface is tipped with constant inclination speed until the drop rolls off. The advancing and receding angles are determined from the time curve of the left and right three-phase point.

5 Apparatus and materials

Ordinary laboratory apparatus, together with the following.

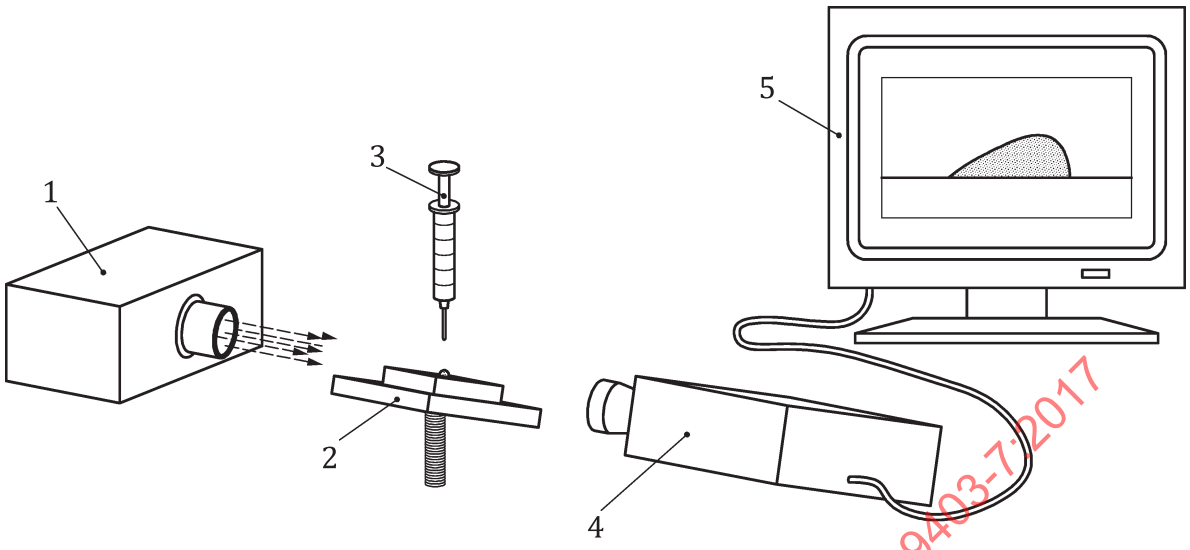
5.1 Contact angle measuring system.

Any state-of-the-art contact angle measuring device fitted with a tilting device, preferably systems with digital image capture and analysis for measuring the contact angle. Figure 1 shows a schematic example of a contact angle measuring system for which only the sample table is inclined. Figure 2 shows a system for which the camera as well as the sample table are inclined.



Key
1 light source
2 specimen holder
3 graduated microsyringe
4 optical system
5 screen

Figure 1 — Schematic diagram of a contact angle measuring system for which only the sample table is inclined



Key

1 light source
2 specimen holder
3 graduated microsyringe
4 optical system
5 screen

Figure 2 — Schematic diagram of a contact angle measuring system for which the camera as well as the sample table are inclined

The image capturing system should be oriented in a way that the drop is within the left third of the image (when the table is inclined to the right).

NOTE The device used can differ from the schematic diagram in regard to light path and the arrangement of the components.

5.2 Dosing unit.

Dosing unit, which makes it possible to precisely apply drops in the range of microlitres to the surface.

5.3 Test liquids.

If not otherwise agreed, use at least one of the test liquids suggested in Table 1. The test liquids shall have at least "purity grade" for analysis. Water shall have a surface tension of at least 71,5 mN/m.

It is recommended to test the suitability of the liquids used in accordance with ISO 19403-3 or EN 14370 prior to measuring their surface tensions. For guidance, the values from the literature for the surface tension, σ_l, are indicated in Table 1. It is also possible to use an individually measured value of the surface tension as reference value. According to experience, the measured value should not deviate more than ±2 % from the value from the literature or the individually determined value.

The test liquids shall not physically or chemically affect the surface. They may not show a notable yield value.

NOTE 1 A notable yield value is shown when a lamella of the liquid teared with a needle does not level within a given time limit (e.g. 30 s).

The test liquids shall not cross-link, show any skinning or evaporate during the measurement.

Liquids having a vapour pressure higher than water at 30 °C shall be measured in the saturated vapour phase.

The test liquids used should have a maximum of different polar and dispersive fractions of surface tension.

NOTE 2 The values given in Table 1 refer to 25 °C measuring temperature. For measuring under standard atmosphere (see 7.1.2), no significant deviations can be assumed.

Table 1 — Suggested test liquids

Test liquid	Surface tension σ_l mN/m	Dispersive fraction σ_l^d mN/m	Polar fraction σ_l^p mN/m	Source
Water	72,8	21,8	51,0	Reference [6]
Di-iodomethane	50,8	50,8	0,0	Reference [6]
1,2-ethanediol (ethylene glycol)	47,7	30,9	16,8	Reference [6]
1,2,3-propanetriol (glycerol)	63,4	37,0	26,4	Reference [6]
Hexadecane	27,6	27,6	0,0	Reference [6]
1-bromo-naphthalene	44,6	44,6	0,0	Reference [6]
Benzyl alcohol	38,9	29,0	9,9	Reference [7]
Decalin (isomer mixture)	30,6	30,6	0,0	Reference [6]
cis-Decalin	32,2	32,2	0,0	Reference [8]
trans-Decalin	29,9	29,9	0,0	Reference [8]

6 Sampling

Take a representative specimen of the substrate to be tested. The specimens shall not be contaminated before measuring.

Preferably, the specimen should have the minimum size of 10 cm × 10 cm.

For advice on sampling and sample preparation, see Annex A.

7 Procedure

7.1 General for measuring the roll-off angle

7.1.1 Setting up the contact angle measuring system

Choose the location of the contact angle measuring system so that it is not exposed to

— vibrations,

— intense air flows (e.g. caused by air conditioning), and

— intense exposure to light from outside (e.g. windows, bright lighting).

Align the contact angle measuring system horizontally.

7.1.2 Test conditions

Carry out the test at (23 ± 2) °C and a relative humidity of (50 ± 5) % (see ISO 3270) and make sure that all test media have this temperature.

7.1.3 Conditioning of the test panels

Condition the test panels at a temperature of (23 ± 2) °C and a relative humidity of (50 ± 5) % for a minimum of 16 h prior to testing. Carry out the test immediately after conditioning.

7.2 Measurement

7.2.1 General

Place a preferably flat test specimen of the surface to be measured on the specimen holder. Adjust the specimen holder so that the surface of the test specimen is located in the lower half of the image and that it is horizontally aligned.

Fill the dosing system with the chosen liquid. Pay attention to fill without contamination or bubbles.

Adjust an image representation that is sufficient in regard to brightness and contrast (mind the specifications given by the manufacturer).

If possible, adjust the light source of the contact angle measuring device so that the grey values within the drop close to the phase interface do not exceed the value 40 (referring to 256 grey value grades) and amount to a minimum of 170 on the outside of the drop.

NOTE It can be reasonable to test the modes of operation of the optical components by means of two-dimensional images of drops. Such reference images are commercially available.

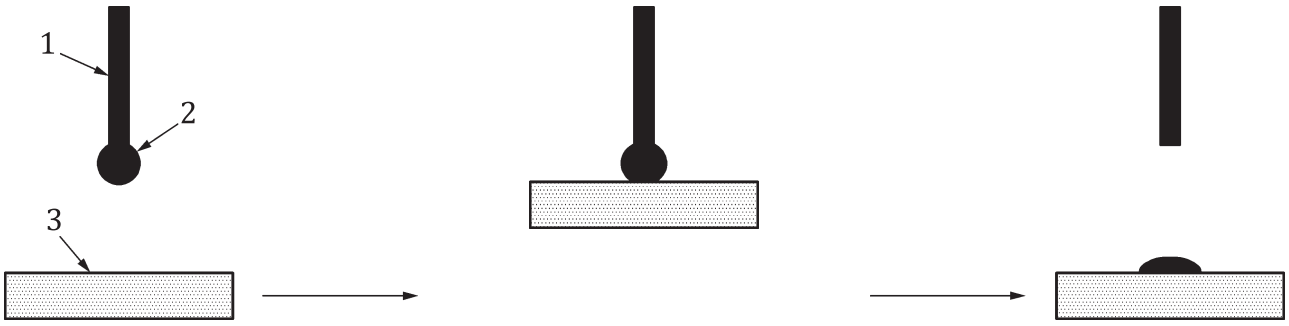
Move the needle to the upper margin of the image and bring into focus.

7.2.2 Application of the drop

Position the dosing needle approximately 3 mm to 6 mm above the surface of the test specimen. The volume of the drop depends on the used liquid, the test specimen, the inclination speed and shall be included in the test report.

Apply a drop of the test liquid on the surface (see Figure 3).

NOTE 1 The contact between the drop and the solid surface can be achieved by putting down by means of the needle or by picking up by means of the sample table.



a) Drop on the needle **b) Transfer of the drop** **c) Drop on the surface**

Key

1 needle
2 test liquid
3 surface of test specimen

Figure 3 — Putting down or picking up the drop

Align the baseline so that it runs through the three-phase points of the drop.

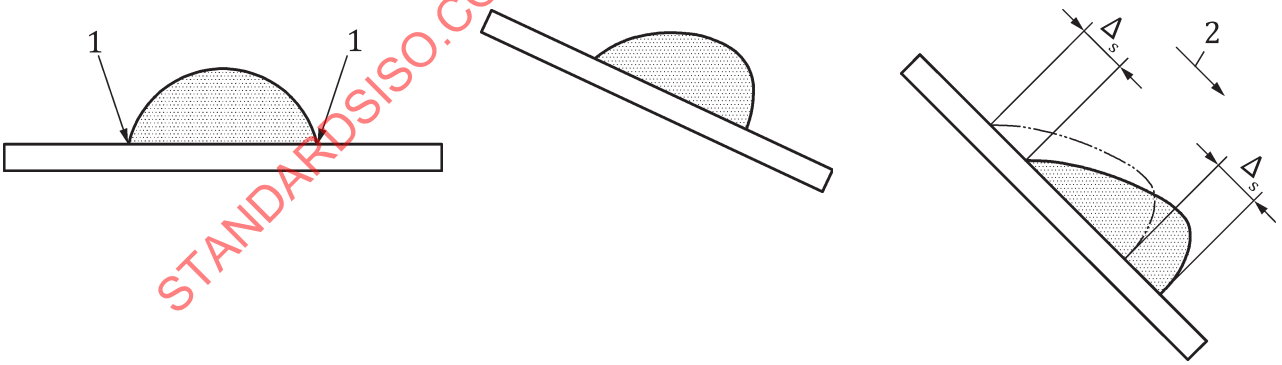
NOTE 2 A top-view angle can be adjusted to help find the three-phase points.

Start measuring the contact angle immediately after finishing dosing.

7.2.3 Determination of the roll-off angle

Tip the test specimen with a constant inclination speed without vibration. During tipping, observe the left and right three-phase point. The roll-off angle has been reached, as soon as both of the three-phase points have moved over a specified distance, Δ_s, (see Figure 4). To a large extent, the roll-off angle depends on the drop volume and the inclination speed (see also Annex B).

At least Δ_s = 1 mm is required.

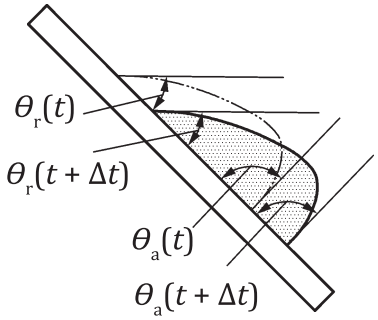


Key

1 left and right three-phase point
2 movement
Δ_s specified distance

Figure 4 — Tipping of the test specimen

Upon reaching the roll-off angle, the advancing and receding angles can also be read (see Figure 5).

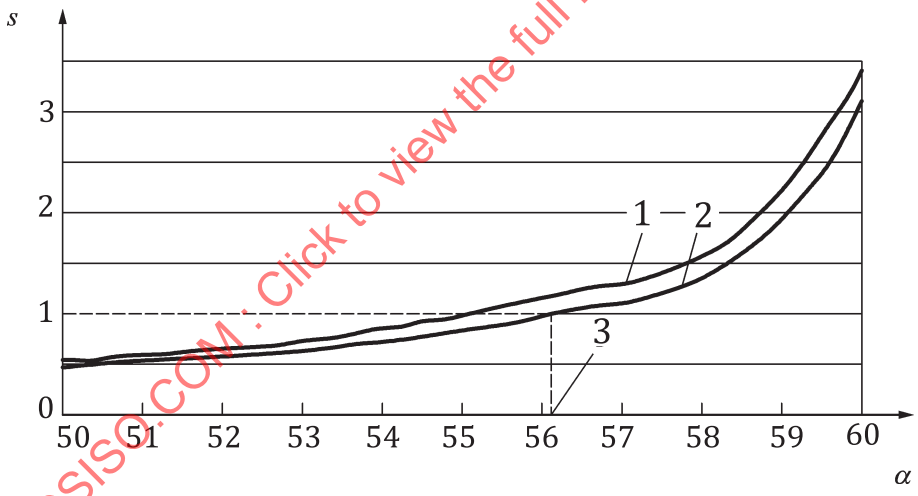


Key

$\theta_r(t)$	receding angle at time t
$\theta_r(t + \Delta t)$	receding angle at time $t + \Delta t$
$\theta_a(t)$	advancing angle at time t
$\theta_a(t + \Delta t)$	advancing angle at time $t + \Delta t$

Figure 5 — Roll-off angle: inclination angle, for which both of the three-phase points have moved by at least 40 pixels (about 1 mm)

Generally, the receding angle is lower than the advancing angle and the right three-phase point moves before the left one does (see Figure 6).

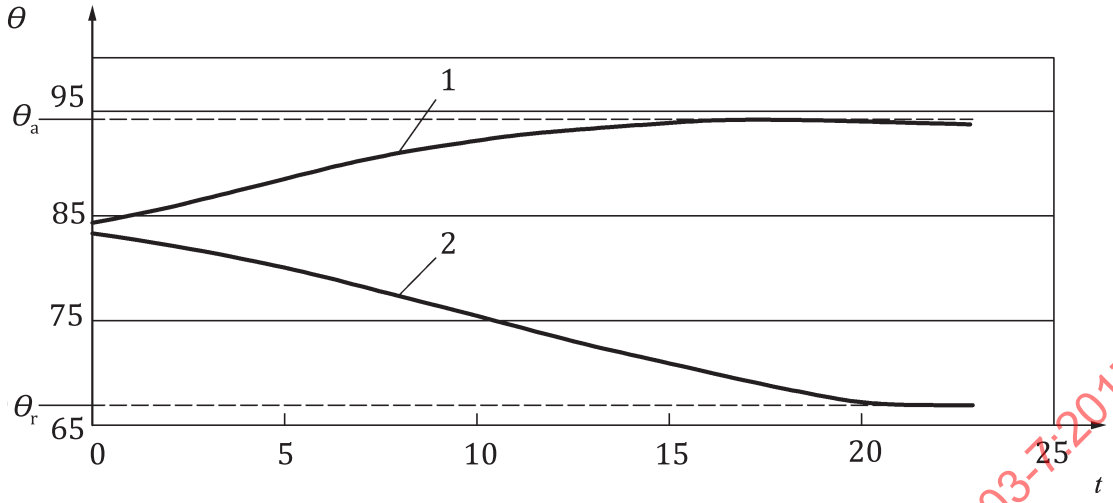


Key

s	distance, in millimetres
α	inclination angle, in degrees
1	three-phase point (right)
2	three-phase point (left)
3	roll-off angle

Figure 6 — Change of position of the three-phase points depending on the roll-off angle

Figure 7 shows the change of the advancing and receding angle over time after reaching the roll-off angle. After a phase of acceleration, the drop reaches constant speed and advancing and receding angle reach a stable plateau.



Key

θ contact angle
θ_a advancing angle
θ_r receding angle
t time, in seconds
1 time curve of the advancing angle
2 time curve of the receding angle

Figure 7 — Time curve of the advancing and receding angles after reaching the roll-off angle

Measure on a minimum of three different measuring points on the test specimen. Previously wetted positions shall not be used. Arguable readings, which may be caused by dust, contaminations, etc., shall not be included in the calculation of the mean value.

8 Precision

At the time of publication, information on precision is not available.

9 Test report

The test report shall contain at least the following information:

a) all details necessary to identify the test specimen (manufacturer, product identification, batch number, etc.);

b) a reference to this document, i.e. ISO 19403-7;

c) the used test liquids;

d) the used drop volumes at the beginning of measurement;

e) the dosing speed and waiting times, if necessary;

f) method with which the contact angle of the drop was obtained, if deviating from the polynomial method;

g) the top-view angle and, if necessary, the used correction;

h) the contact angle/time diagram;

i) the amount of measuring points per test liquid;

j) the advancing and receding angle, if necessary, including mean value and standard deviation;

k) all deviations from the specified method and their possible influences on the results;

l) any unusual observation (deviation) during the test;

m) the type of device;

n) the name of the test person;

o) the date of the test.

Annex A
(informative)

Notes on sampling and treatment of test specimens

A.1 Ambient conditions

For materials which are to be tested under general conditions, the notes on sample conditioning indicated in 7.1.3 apply. For materials, which are to be tested under process conditions, these conditions should be simulated in regard to pressure, temperature and humidity.

A.2 Sources of contamination and cleaning

During sampling, the contact of the test specimen with air containing smoke or aerosol with liquids or other solid surfaces should be avoided in order not to transfer surface-active substances. The test specimen shall only be touched in locations which are not intended for measuring. For transport, an air-tight container is recommended.

Contaminated surfaces of test specimens can also be measured. These contaminations can influence the wettability behaviour and dewettability behaviour.

In case a contaminated surface is to be cleaned, this can be done by using a rapidly and residue-free evaporating solvent, which does not chemically alter the material.

Surface-active cleaning agents shall only be used if they can be removed residue-free.

Solvents used for cleaning may possibly not evaporate without residue.

An ultrasonic bath is recommended for cleaning. After cleaning, the test specimen should dry in clean room air for 1 h.

Drying with pressurized air increases the danger of contamination and is not recommended.

For comparative measurements, the same cleaning procedure should be conducted in each case even if no contamination occurred.

A.3 Electrostatic charging

Electrostatic charging of the test specimen alters the wettability behaviour and should be avoided. In case test specimens are inclined to electrostatic charging due to process or material, this can be dissipated by means of commercially available ionizers.