International Standard

ISO 19403-6

Second edition
2024-10

Paints and varnishes — Wettability —

Part 6: Measurement of dynamic advancing and receding angle by changing the volume of a drop

Peintures et vernis — Mouillabilité —

Partie 6: Mesurage des angles d'avancée et de recul dynamiques en changeant le volume d'une goutte

Reference number
ISO 19403-6:2024(en)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

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 document 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).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of 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 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*, 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 19403-6:2017), which has been technically revised.

The main changes are as follows:

— the part title has been changed to: Measurement of dynamic advancing and receding angle by changing the volume of a drop;

— the term 3.2 “advancing angle” has been replaced by “dynamic advancing contact angle” and the definition has been reworded;

— the term 3.3 “receding angle” has been replaced by “dynamic receding contact angle” and the definition has been reworded;

— normative references have been updated.

A list of all parts in the ISO 19403 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

Dynamic contact angles describe the processes on the interface liquid or solid during volume increase (dynamic advancing contact angle) or volume decrease (dynamic receding contact angle) of a drop. As an alternative to the static method (see ISO 19403-2), the dynamic advancing or dynamic receding methods measure the contact angle while the three-phase contact line is moving. The contact angle for the dynamic advancing contact angle is measured while wetting a previously unwetted surface. For the dynamic receding contact angle, the contact angle is observed during dewetting. By determining the difference between the dynamic advancing contact angle and the receding contact angle, information on chemical homogeneity and roughness can be concluded. The dynamic receding contact angle is not recommended for the determination of the surface energy.

Paints and varnishes — Wettability —

Part 6: Measurement of dynamic advancing and receding angle by changing the volume of a drop

1 Scope

This document specifies a method to measure the dynamic contact angle with an optical method. The dynamic advancing and the dynamic receding contact angles are determined.

By using the measurement specified in this document, the wetting and dewetting properties can be characterized. The morphological and chemical homogeneity of interfaces can also be determined.

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 — Vocabulary*

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

ISO 19403-1:2022, *Paints and varnishes — Wettability — Part 1: Vocabulary and general principles*

ISO 19403-2:2024, *Paints and varnishes — Wettability — Part 2: Determination of the surface free energy of solid surfaces by measuring the contact angle*

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 terminology databases for use in standardization at the following addresses:

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

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

3.1
dynamic contact angle
contact angle, which is measured during advancing or receding of the three-phase point

Note 1 to entry: For the definition of “contact angle”, see ISO 19403-1:2022, 3.1.9.

Note 2 to entry: The advancing or receding of the three-phase point can be achieved by changing the volume of the liquid drop to be measured, by relative movement (immersing and pulling out) of a solid body to an interface, or by moving the drop over the interface (e.g. rolling off). This document only describes the determination of the dynamic contact angle by changing the volume of a drop.

3.2
dynamic advancing contact angle
dynamic advancing angle
θ_a
contact angle measured at the three-phase line during advancing the liquid phase

Note 1 to entry: The values depend on the method.

3.3
dynamic receding contact angle
dynamic receding angle
θ_r
contact angle measured at the three-phase line during receding the liquid phase

Note 1 to entry: The values depend on the method.

3.4
contact angle hysteresis
θ_{ar}
difference between the *dynamic advancing contact angle* (3.2) and the *dynamic receding contact angle* (3.3)

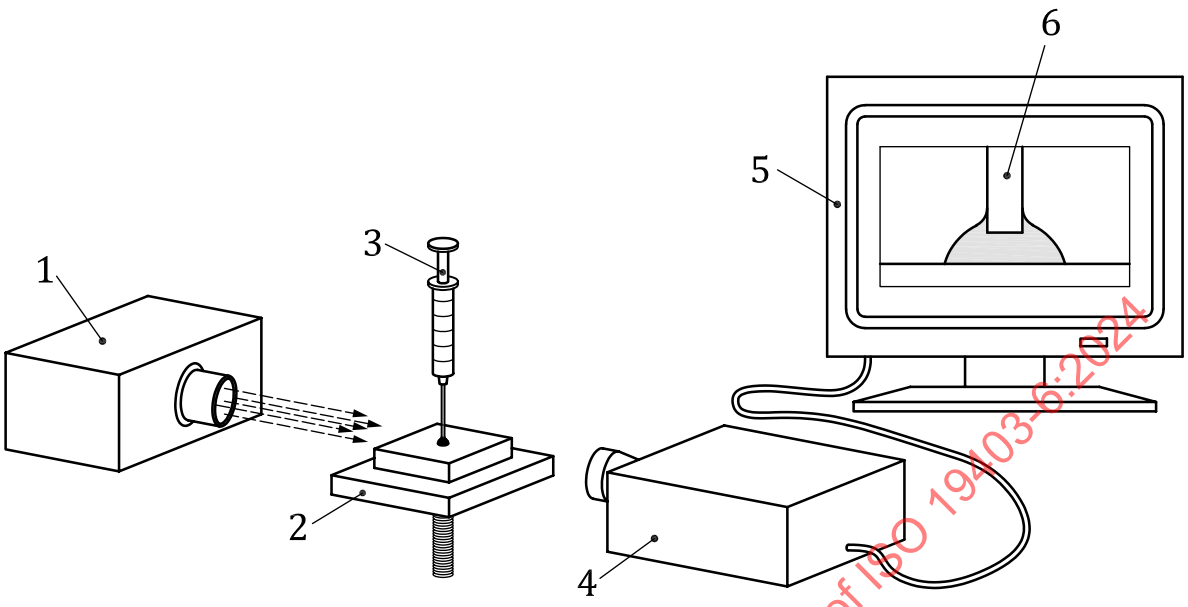
4 Principle

A drop of the respective test liquids is dosed onto the flat surface of a test specimen. The volume of the respective drop is continuously increased (dynamic advancing contact angle) or decreased (dynamic receding contact angle). The procedure is repeated with at least two drops. The contact angle is preferably determined by means of the polynomial method, synchronously with the dosing. If the polar and dispersive fraction of the surface free energy is determined according to ISO 19403-2, the dynamic advancing contact angle shall be used.

5 Apparatus and materials

Ordinary laboratory apparatus, together with the following shall be used.

5.1 Contact angle measuring system, i.e. any state-of-the-art contact angle measuring device. It is preferred to use systems with digital image capture and analysis for measuring the contact angle. Figure 1 shows a schematic example of a contact angle measuring system.



Key

1 light source
2 specimen holder
3 system with microlitre syringe for continuous dosing
4 optical system
5 screen
6 needle positioned in the drop

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

Figure 1 — Schematic diagram of a contact angle measuring system

The image capturing system should be oriented in a way that the optimal image resolution ratio (ratio of width and height) can be used.

5.2 Dosing unit, which makes it possible to continuously change the drop volume on the surface in the range of microlitres.

NOTE Typical dosing rates for test liquids for the determination of the surface energy are in the range of 10 µl/min.

5.3 Test liquids, which shall not physically or chemically affect the surface. They shall not have a yield point. The test liquids shall not crosslink during measuring, not form skins and not volatilize distinctly. Liquids having a vapour pressure higher than 42,470 hPa (vapour pressure of water at 30 °C) shall be measured in the saturated vapour phase.

6 Sampling

Take a representative specimen of the solid substrate to be tested as specified in ISO 15528. The specimens shall not be contaminated before measuring.

Preferably, the sample should have a minimum size of 4 cm × 4 cm and be as flat as possible.

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

7 Procedure

7.1 General for measuring on the horizontal drop

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.

Tilt the camera back to front (maximum 4°) to be able to see the reflection and detect the three-phase line, accurately.

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

If not otherwise agreed, 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.

NOTE Other conditioning parameters can be necessary if the surface of the test sample changes its chemical state at 50 % relative humidity.

7.1.4 Conditioning of the test liquids

Condition the liquids in a closed container at a temperature of (23 ± 2) °C 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 regarding brightness and contrast (taking into account the specifications given by the manufacturer).

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

Bring the needle into focus. Adjust the zoom of the contact angle measuring device so that the maximum width of the contour of the drop is imaged entirely at maximum expansion.

7.2.2 Measuring method

Choose the distance between the dosing needle and the surface so that the influence on the expected contour of the drop is as slight as possible.

NOTE 1 As initial guidance for the distance between the needle and the surface of the test specimen, the one-and-a-half-times diameter of the needle can be used.

Especially for low contact angles, minimize the pull-up of liquid on the needle, if necessary, by using a needle of poorly wettable material.

For very low-energy surfaces and superhydrophobic surfaces, pull-up of liquid can be challenging, even when the needle is of poorly wettable material. For such cases, it is common practice to make a hole in the surface and inject the drop from underneath.

Choose a dosing speed which is as slow as possible so that the contact angle of the drop is as close to the thermodynamic equilibrium contact angle as possible.

Typical dosing speeds for the determination of the surface energy are in the range of 10 µl/min. For test liquids with higher viscosity than the test liquids given in ISO 19403-2:2024, Table 1, the dosing speeds shall be reduced. This especially applies for glycerol.

NOTE 2 It is common practice to start measuring only after a dosing of 3 µl minimal volume.

NOTE 3 Due to the limited image section and the limited precision, it can be difficult to measure dynamic advancing contact angles below 10° by means of the dynamic method.

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

NOTE 4 A top-view angle of the camera to the horizontal can be adjusted to help find the three-phase points. The top-view angle causes an image error of the drop projection. This can have an influence on the measuring result of the contact angle and can be corrected.

Start measuring the contact angle immediately after dosing the minimal volume. Record the measuring values as function of time.

7.2.3 Determination of the contact angle

Preferably, determine the dynamic advancing and dynamic receding contact angle. Select the fitting method according to the device manufacturer's instructions in order to exclude the influence of the cannula on the fit.

Measure on a minimum of three different measuring points on the test specimen to obtain sufficient information in regard to the homogeneity of a test specimen. Previously wetted positions shall not be used. Arguable readings which can be caused by dust, contaminations, etc. shall not be included in the calculation of the mean value. Discarded, possibly contaminated test liquid shall not be reused.

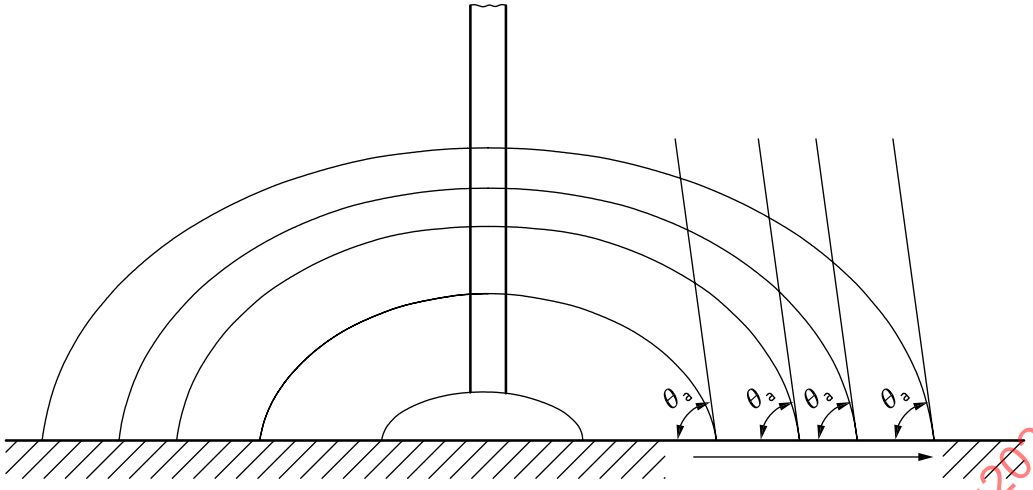
Repeat the measuring with at least one more liquid, which was selected in accordance with the criteria given in 5.3.

8 Evaluation

Present the measured contact angles as a function of time. Determine the dynamic advancing and dynamic receding contact angle from these data (see Figure 2 and Figure 3). A dynamic advancing and dynamic receding contact angle can only be described if a respective plateau forms in the contact angle vs. time plot (see Figure 4). This requires that the measured dynamic advancing or dynamic receding contact angle remains constant over a certain time period or at least varies around a mean value.

The wettability behaviour is characterized by the dynamic advancing contact angle. The dewettability behaviour is characterized by the dynamic receding contact angle.

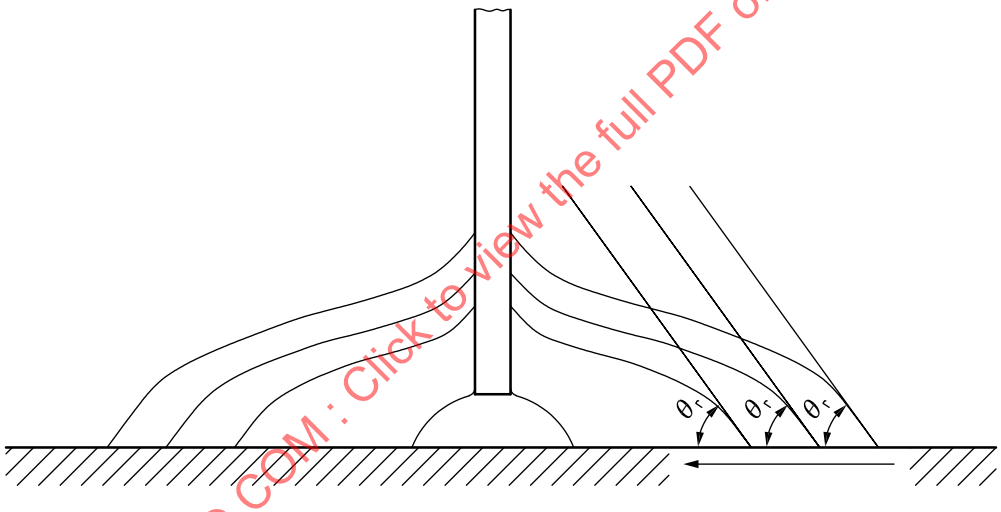
The method for determining the surface free energy is specified in ISO 19403-2.



Key

θ_a dynamic advancing contact angle

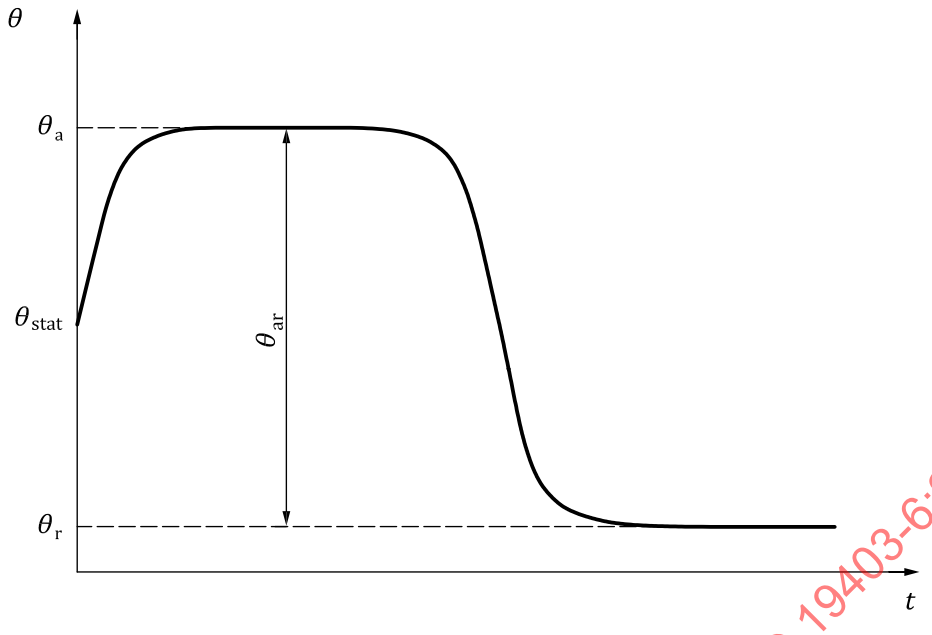
Figure 2 — Applying a drop through a needle for the dynamic measurement of the dynamic advancing contact angle



Key

θ_r dynamic receding contact angle

Figure 3 — Extracting a drop through a needle for the dynamic measurement of the dynamic receding contact angle

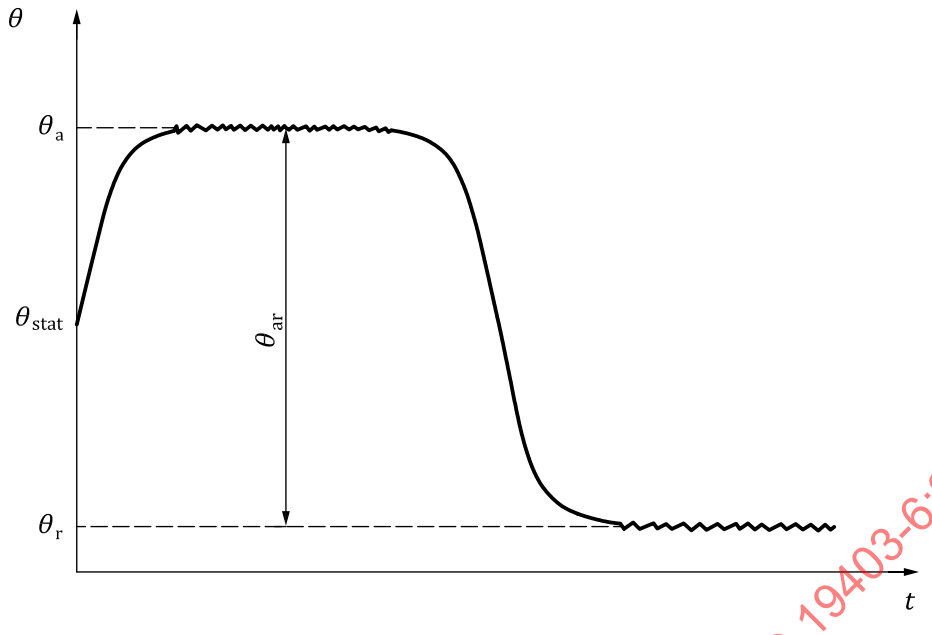


Key

θ dynamic contact angle
θ_a dynamic advancing contact angle
θ_{stat} static contact angle
θ_r dynamic receding contact angle
θ_{ar} contact angle hysteresis
t time

Figure 4 — Time curve of the dynamic contact angle during advancing and receding measuring

In the case of rough and chemically inhomogeneous surfaces, severe time variations of the dynamic advancing contact angle can occur. These occur when the base diameter of the drop does not change even though the volume of the drop is continuously increased. This results in an increase of the contact angle until this contact angle is decreased instantly by the abrupt expansion of the drop. This phenomenon is called slipstick (see Figure 5).



Key

θ dynamic contact angle
θ_a dynamic advancing contact angle
θ_{stat} static contact angle
θ_r dynamic receding contact angle
θ_{ar} contact angle hysteresis
t time

Figure 5 — Slipstick behaviour of the time curve of the contact angle during dynamic advancing and dynamic receding measuring

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 19403-6:2024;

c) the used test liquids;

d) the used drop volumes at the beginning and upon completion of measurement;

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

f) the 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 dynamic advancing and dynamic receding contact angle, if necessary, including mean value and standard deviation;

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

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