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Paints and varnishes — Wettability —

Part 1:
Vocabulary and general principles

Peintures et vernis — Mouillabilité —

Partie 1: Vocabulaire et principes généraux

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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

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Contents

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*, 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 19403-1:2017), which has been technically revised.

The main changes are as follows:

- in the title, "Terminology" has been changed to "Vocabulary";
- text from the Scope has been moved to the Introduction;
- 3.1.5, 3.1.7, 3.1.8 and 3.1.9 have been slightly modified;
- the following terms and definitions have been added: hydrophobic, superhydrophobic, hydrophilic, superhydrophilic and superhydrophobic coating;
- Clause 4 has been moved to Annex A;
- Figure 1 and Figure A.1 have been updated;
- the designation of the X-axis in Figure A.2 has been corrected;
- the derivation of Formula (A.4) has been improved;
- Formula (A.6) has been corrected;
- bibliographic entries [1] and [12] have been added and cross-references 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

The ISO 19403 series specifies optical test methods:

- for the measurement of the contact angle;
- for the determination of the surface free energy of a solid surface, including the polar and dispersive fractions;
- for the determination of the surface tension of liquids, including the polar and dispersive fractions;
- for the checking of the measurement arrangement with reference materials.

The ISO 19403 series can be applied for the characterization of substrates, coatings and coating materials.

The applicability can be restricted for liquids with non-Newtonian flow behaviour (see DIN 1342-1[4]).

Paints and varnishes — Wettability —

Part 1:
Vocabulary and general principles

1 Scope

This document specifies general terms and definitions for wettability. Some general principles are described in Annex A. This document is intended to be used in conjunction with ISO 4618.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

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 Terms relating to determination of the surface free energy

3.1.1
chemical homogeneity
chemically homogeneous composition of a surface to be examined

Note 1 to entry: The definition regards a purely qualitative assessment of the surface. Regarding the measurement of the contact angle, a surface is considered chemically and topologically sufficiently homogeneous if no significant differences of the contact angles can be determined when measuring on several locations on the surface. The significance limits can be specified by the user in accordance with standard laboratory methods.

3.1.2
topological homogeneity
uniformity of the macroscopic surface, including evenness and smoothness

Note 1 to entry: The definition regards a purely qualitative assessment of the surface. Regarding the measurement of the contact angle, a surface is considered chemically and topologically sufficiently homogeneous if no significant differences of the contact angles can be determined when measuring on several locations on the surface. The significance limits can be specified by the user in accordance with standard laboratory methods.

3.1.3
interfacial free energy
interfacial tension
σ
energy or tension resulting from intermolecular forces on interfaces

Note 1 to entry: The term interfacial energy pertains to the interaction with solid surfaces and is indicated as free energy in relation to the surface unit (mJ/m^2). The term interfacial tension pertains to the interaction with liquids and is indicated as force per length unit (mN/m). The respective indices “l” for “liquid” and “s” for “solid” indicate the phases involved.

3.1.4
surface free energy
free energy of the surface
σ_s
interfacial free energy (3.1.3) of a solid surface

Note 1 to entry: For detailed explanations of the principles for the determination of the surface free energy, see A.1.

3.1.5
surface tension
σ_l
interfacial tension of a liquid surface

Note 1 to entry: The surface tension is indicated as force per unit length (mN/m). Its numerical value corresponds to the free energy of the interface or surface.

Note 2 to entry: The surface tension corresponds to the work which shall be done in order to enlarge a given surface by a specific value.

Note 3 to entry: If the liquid of a droplet is in equilibrium with its vapour phase, then the surface tension is thermodynamically defined. It is experimentally very challenging to ensure thermodynamical equilibrium during measurements. This would include constant temperature, constant pressure and saturated vapour phase. This does not mean that any violation of this condition does not allow to measure dynamic contact angles which shall be "near the thermodynamic equilibrium" (see ISO 19403-6:2017, 3.2, note 1) which is obviously not in equilibrium, yielding in dynamic surface tensions.

Note 4 to entry: For detailed explanations of the principles for the measurement of the surface tension at the pendant drop, see A.2.

3.1.6
interfacial energy
σ_{sl}
energy on the phase interface between a solid and a liquid phase

3.1.7
three-phase point
contact point
point at which solid phase, liquid phase and vapour phase are in contact with each other

Note 1 to entry: See Figure A.1.

3.1.8
base line
straight or curved line at the interface between a solid and liquid phase which connects two *three-phase points* (3.1.7)

Note 1 to entry: See Figure A.1.

3.1.9
contact angle
θ
angle to the *base line* (3.1.8) within the drop, formed by means of a tangent on the drop contour through one of the *three-phase points* (3.1.7)

Note 1 to entry: See Figure A.1.

Note 2 to entry: The contact angle is preferably indicated in degrees (°). 1° = (π/180) rad. If the system is in thermodynamic equilibrium, this contact angle is also referred to as thermodynamic equilibrium contact angle.

3.1.10
top-view angle
angle to the plane of the sample surface under which the drop is being observed

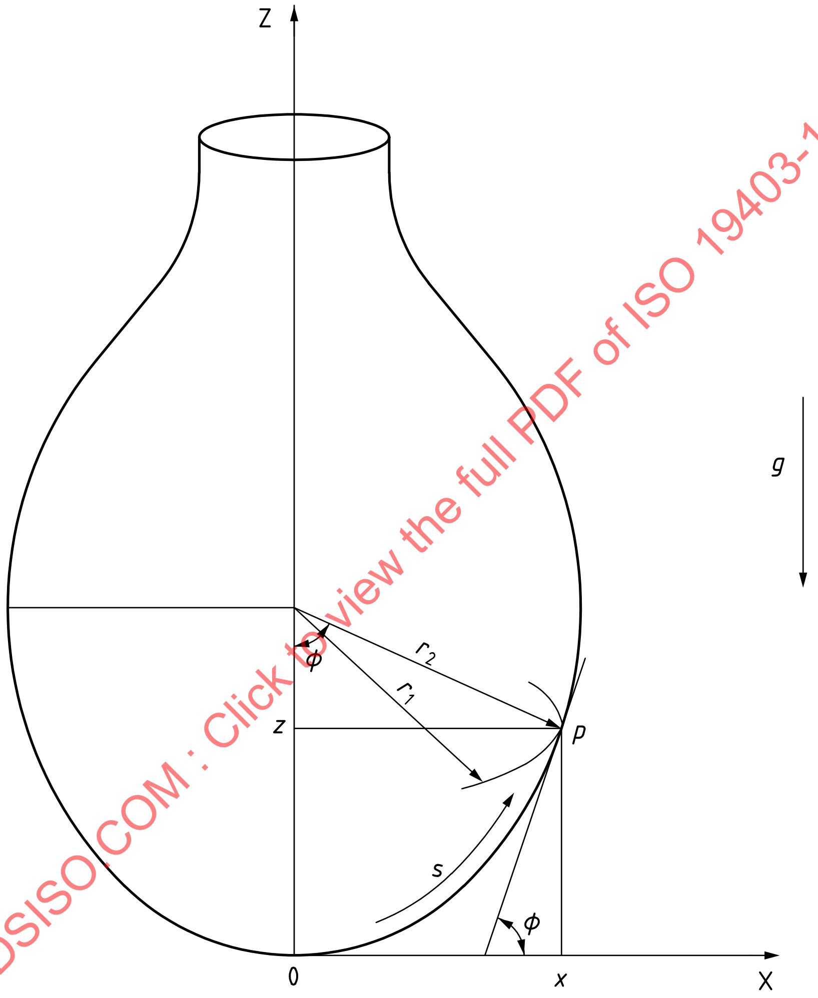
3.2 Terms relating to determination of the surface tension of liquids

3.2.1

pendant drop

drop hanging on a hollow needle

Note 1 to entry: The curvature of the contour of a pendant drop is generally determined by its own mass and its surface tension. The surface tension can be calculated from the shape and size of a pendant drop by means of drop contour analysis, provided that the drop is large enough (see ISO 19403-3) so that its shape significantly differs from a spherical shape due to its own mass. See Figure 1.



Key

X, Z	axes of coordinates
p	point on the drop contour
x, *z*	cartesian coordinates of a drop contour point
s	arc length from the origin in the drop apex to the drop contour point *p*
r_1, r_2	main curvature radiuses of the drop surface in drop contour point *p*
Φ	tangent angle in drop contour point *p* to the X-axis
g	gravity attraction

Figure 1 — Pendant drop

3.2.2
Young-Laplace equation

equation which describes the pressure difference, Δp, between the inside and the outside of a curved surface in dependence on the *surface tension* (3.1.5) or *interfacial tension* (3.1.3), σ, and the main curvature radiuses of the surface (r_1 and r_2)

$$\Delta p = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$

3.2.3
shape parameter

B

non-dimensional and numerically obtained parameter, describing the shape of the drop contour when analysing the drop

$$B = \frac{1}{a \cdot k_{\text{apex}}}$$

where

k_{apex} is the main curvature radius in the apex of the drop;

a is the capillary constant.

$$a = \sqrt{\frac{\sigma}{\Delta\rho \cdot g}}$$

where

σ is the surface tension of the liquid to be tested;

$\Delta\rho$ is the density difference of the liquid to be tested compared to the ambient phase;

g is the local acceleration of gravity.

Note 1 to entry: In the literature, the shape parameter, *B*, is also referred to as “shape factor” or “Bond number”.

3.2.4
fit error

average distance of the measured contour points to the mathematically obtained model prediction

Note 1 to entry: Indicated in micrometre per measuring point[6].

3.3 Terms relating to wetting

3.3.1
wetting

adhesive contact between solid and liquid

3.3.2
wettability

degree of *wetting* (3.3.1)

Note 1 to entry: Contact angle $\theta = 0°$ indicates a fully wetted surface and $\theta = 180°$ indicates not wetted surface.

3.3.3
hydrophobic

surface with a *contact angle* (3.1.9) of a water droplet which exceeds 90°

3.3.4
superhydrophobic

surface with a *contact angle* (3.1.9) of a water droplet which exceeds 150° and contact angle hysteresis is less than 10°

3.3.5
hydrophilic

surface with a *contact angle* (3.1.9) of a water droplet less than 90°

3.3.6
superhydrophilic

surface with a *contact angle* (3.1.9) of a water droplet of about 0°

3.3.7
superhydrophobic coating

coated surface with *superhydrophobic* (3.3.4) characteristics

Annex A
(informative)

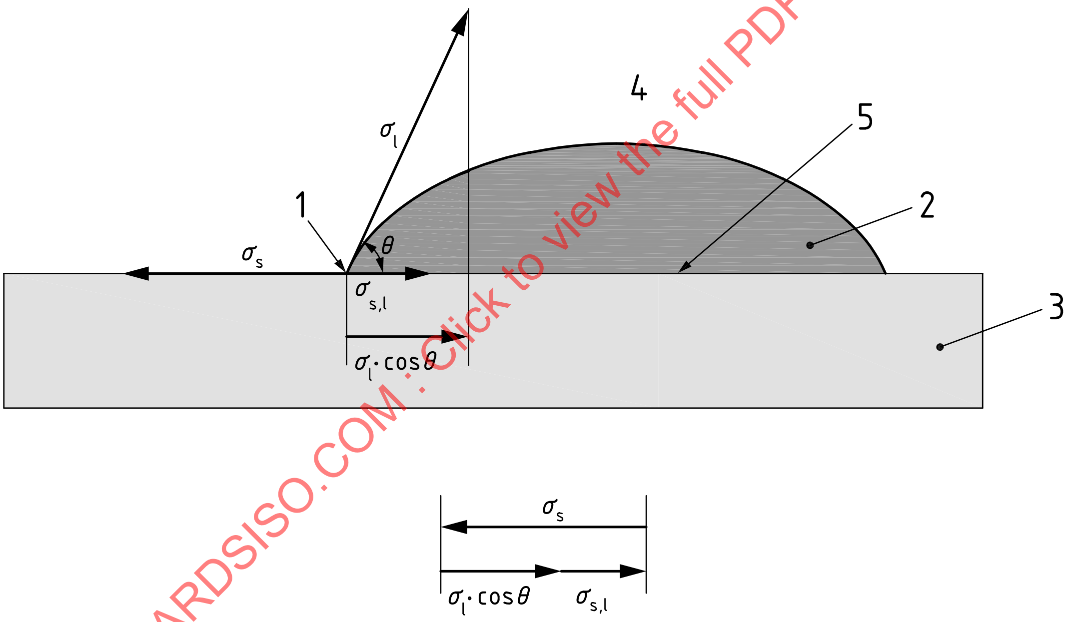
General principles

A.1 Principles for the determination of the surface free energy

A liquid lying on a solid surface forms a typical drop shape. The characteristic property of the drop is the angle, which is formed by the tangent on the contour at the three-phase point with the solid surface (see Figure A.1). For a contact angle θ = 0°, a surface is completely wetted.

The description of the wettability of a solid surface with a liquid is based on the adsorption theory (see References [9] and [10]). The forces acting on the sessile drop at the three-phase point (see Figure A.1) are described in the state of equilibrium by means of the Young equation, Formula (A.1):

$$\sigma_\mathrm{s} = \sigma_\mathrm{s,l} + \sigma_\mathrm{l} \cdot \cos\theta \qquad \text{(A.1)}$$



Key

1	three-phase point
2	liquid phase
3	solid phase
4	gas phase
5	base line
σ_l	surface tension of the liquid surface
σ_s	surface free energy of the solid surface
$\sigma_\mathrm{s,l}$	interfacial energy between solid surface and liquid surface
θ	contact angle

Figure A.1 — Wetting equilibrium

NOTE Thermodynamic equilibrium contact angle on a smooth and homogeneous surface is also called Young contact angle. The necessary condition for Young contact angle is that the surface is ideal (i.e. smooth and homogeneous).

The Dupré-Young equation defines the thermodynamic work of adhesion W_{ad} during wetting as shown in Formula (A.2):

$$W_{ad} = \sigma_l + \sigma_l \cdot \cos\theta = \sigma_l \cdot (1 + \cos\theta) \tag{A.2}$$

The thermodynamic equilibrium, which causes the formation of the static contact angle, depends on the temperature, as well as on pressure and other thermodynamic state variables. Since the interfacial free energy and surface free energy are based on different forces between atoms or molecules, it is necessary to take the polarity into account in order to assess the wettability. The model described in the following is based on the assumption that mainly polar and disperse interactions predominate.

Examples for polar interactions are as follows:

- ionic interactions;
- dipole-dipole interactions;
- hydrogen bonds;
- electron-pair acceptor and donor interactions (Lewis acid-base interactions).

The London interactions are part of the non-polar (disperse) interactions.

In accordance with References [9] and [10] the interfacial energy, $\sigma_{s,l}$, between a solid (s for “solid”) and a liquid (l for “liquid”) results from the sum of the surface tensions of both phases ($\sigma_s + \sigma_l$), reduced by the disperse and polar interactions at the phase interface.

Valid is: $\sigma_l = \sigma_l^p + \sigma_l^d$ and $\sigma_s = \sigma_s^p + \sigma_s^d$ with the index *p* (polar fraction) and the index *d* (disperse fraction).

Owens, Wendt, Rabel and Kaelble (OWRK)[9][10] take account of these interactions as the doubled sum of the geometric mean values of the disperse $\left(\sqrt{\sigma_s^d \cdot \sigma_l^d}\right)$ and the polar tension components $\left(\sqrt{\sigma_s^p \cdot \sigma_l^p}\right)$ of the individual phases and describe Formula (A.3):

$$\sigma_{s,l} = \sigma_s + \sigma_l - 2\left(\sqrt{\sigma_s^d \cdot \sigma_l^d} + \sqrt{\sigma_s^p \cdot \sigma_l^p}\right) \tag{A.3}$$

After inserting in Formula (A.1) it is possible to rewrite the equation such that the tension components of the solid are separated from the known tension components of the liquid. Formula (A.4) results:

$$\frac{(1+\cos\theta)\cdot\sigma_l}{2\sqrt{\sigma_l^d}} = \sqrt{\sigma_s^p} \cdot \sqrt{\frac{\sigma_l^p}{\sigma_l^d}} + \sqrt{\sigma_s^d} \tag{A.4}$$

By equating coefficients with the general linear Formula (A.5)

$$Y = m \cdot X + b \tag{A.5}$$

it becomes obvious that when plotting $Y = \frac{(1+\cos\theta)\cdot\sigma_l}{2\sqrt{\sigma_l^d}}$ versus $X = \sqrt{\sigma_l^p / \sigma_l^d}$ from the square of the slope, *m*, the polar fraction of the surface free energy of the solid, σ_s^p, results and from the square of the ordinate section, *b*, the disperse fraction, σ_s^d, results. From the sum of both fractions, the total surface free energy of the solid, σ_s, results.

Figure A.2 shows an example of an interpretation in accordance with References [9] and [10].

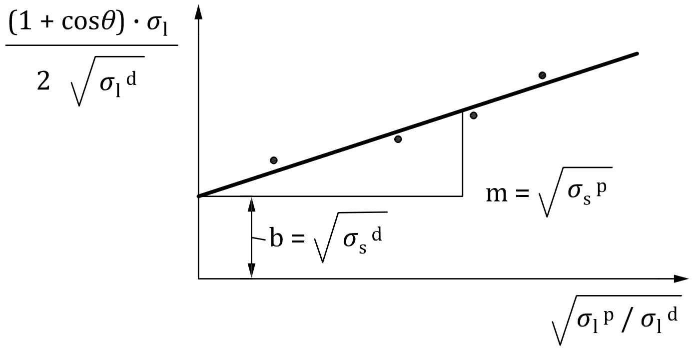


Figure A.2 — Example of an interpretation

A.2 Principles for the measurement of the surface tension at the pendant drop

In case of a drop of liquid pendant from a hollow needle, the drop forms a characteristic shape within the equilibrium of forces, from which the surface tension can be obtained.

The gravitation, depending on the height of a given point on the drop, compensates the Laplace pressure, which results from the curvature of the drop surface or interface at that point. The Laplace pressure results from the main curvature radiuses, vertically standing on top of each other, as shown in Formula (A.6):

$$\Delta p=\sigma\cdot\left(\frac{1}{r_1}+\frac{1}{r_2}\right) \qquad (A.6)$$

Formula (A.6) describes the difference between the pressure below and above a curved surface section of a drop with the main curvature radiuses, r_1 and r_2 (see Figure 1). The difference, Δp, is the pressure difference between the inside and the outside of the drop. It is caused by the surface-minimized specific energy, the surface tension.

In case of a pendant drop which is rotation-symmetrically in direction of the Z-axis, an analytic-geometrical description of the main curvature radiuses is possible, based on Formula (A.6). The tangent at the intersection of the Z-axis with the apex of the drop forms the X-axis. The drop profile is given by pairs of values (x,z) in the xz-plane.

Within the equilibrium of forces, this relationship is valid, as shown in Formula (A.7):

$$\Delta p_{\text{apex}}-\Delta p_{\text{p}}=z\cdot\Delta\rho\cdot g \qquad (A.7)$$

where

Δp_{apex} is the pressure difference at the apex;

Δp_{p} is the pressure difference at point, P (x,z);

$\Delta\rho$ is the density difference between drop liquid and ambient phase;

g is the local acceleration of gravity.

With the main curvatures, k, (reciprocal values of the main curvature radiuses, r) and the Young-Laplace formula, this results in Formulae (A.8) and (A.9):

$$\Delta p_{\text{apex}}=\sigma\left(k_{\text{apex},1}+k_{\text{apex},2}\right) \qquad (A.8)$$