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Paints and varnishes — Wettability —

Part 1:
Terminology and general principles

Peintures et vernis — Mouillabilité —

Partie 1: Terminologie et principes généraux

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Contents

Page

Foreword

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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*.

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

Paints and varnishes — Wettability —

Part 1:
Terminology and general principles

1 Scope

The ISO 19403 series specifies optical test methods

— for the measurement of the contact angle,

— for the determination of the free surface 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, and

— for the checking of the measurement arrangement with reference materials.

It can be applied for the characterization of substrates, coatings and coating materials.

The applicability can be restricted for liquids with non-Newtonian rheology[1].

This document specifies terms and definitions and defines the general principles.

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*

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:

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

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

3.1 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 areas on the surface. The significance limits can be specified by the user in accordance with standard laboratory methods.

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1)   This term is defined in DIN 1342-1.

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 areas 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

3.1.5
surface tension
σ_l
interfacial tension of a liquid surface in equilibrium with its vapour phase

Note 1 to entry: The surface tension is indicated as force per length unit (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.

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

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

Note 1 to entry: See Figure 1.

3.1.8
base line
<for flat test specimens> straight line through both *three-phase points* (3.1.7)

Note 1 to entry: See Figure 1.

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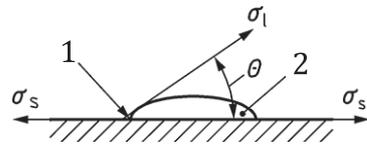angle to the *base line* (3.1.8) within the drop, formed by means of a tangent on the drop contour through one of the *three-phase points* (3.1.7)

Note 1 to entry: See Figure 1.

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

Key

1   three-phase point

2   liquid

σ_l surface tension of the liquid

σ_s surface free energy of the solid surface

σ_{sl} interfacial energy between solid surface and liquid

θ contact angle

Figure 1 — Wetting

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

3.1.11
wetting
adhesive contact between solid and liquid

3.1.12
wettability
degree of *wetting* (3.1.11)

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

## 3.2   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.

Note 2 to entry: See Figure 2.
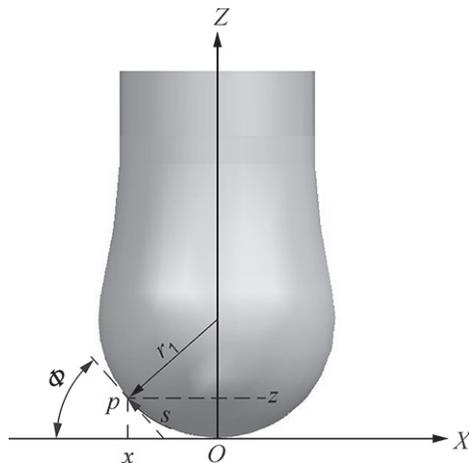
Key

r_1 main curvature radius

X, Z axes of coordinates

x, z Cartesian coordinates of a drop contour point

s arc length from the origin to the drop contour coordinate point

p drop contour coordinate point

Φ tangent angle in p to the X-axis

Figure 2 — Pendant drop

3.2.2
Young-Laplace equation
equation which describes the pressure difference, Δp, above and below a curved surface in dependence on the *surface tension* (3.1.5) or interfacial tension, 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

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

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".

Note 2 to entry: The "Bond number", B, is a non-dimensional number describing the relationship of gravitation and curvature. In physics, it is inserted above the considerations of the Navier-Stokes equations for the description of movements of fluids[5].

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[4].

4 General principles

4.1 Principles for the determination of the surface free energy

A liquid making contact with a solid surface is referred to as wetting. In consequence, the liquid 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 1). For a contact angle $\theta = 0$, 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 [7] and [8]). The forces acting on the horizontal drop at the three-phase point (see Figure 1) are described in the state of equilibrium by means of the Young equation as shown in Formula (1):

$$\sigma_s = \sigma_{sl} + \sigma_l \cdot \cos\theta \tag{1}$$

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

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

The location of the thermodynamic state of 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 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 [7] and [8], the interfacial energy, σ_{sl}, 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)[7][8] take account of these interactions as the doubled sum of the geometrical 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 (3):

$$\sigma_{sl} = \sigma_s + \sigma_l - 2\left(\sqrt{\sigma_s^d \cdot \sigma_l^d} + \sqrt{\sigma_s^p \cdot \sigma_l^p} \right) \tag{3}$$

After inserting Formula (1) and adapting to the general linear Formula (4):

$$y = m \cdot x + b \tag{4}$$

Formula (5) results:

$$\frac{(1 + \cos\theta) \cdot \sigma_l}{2\sqrt{\sigma_l^d}} = \sqrt{\sigma_s^p} \cdot \sqrt{\frac{\sigma_l^p}{\sigma_l^d}} + \sqrt{\sigma_s^d} \tag{5}$$

From the square of the gradient, m, the polar fraction of the surface free energy of the solid, σ_s^p, results. 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 3 shows an example of an interpretation in accordance with References [7] and [8].
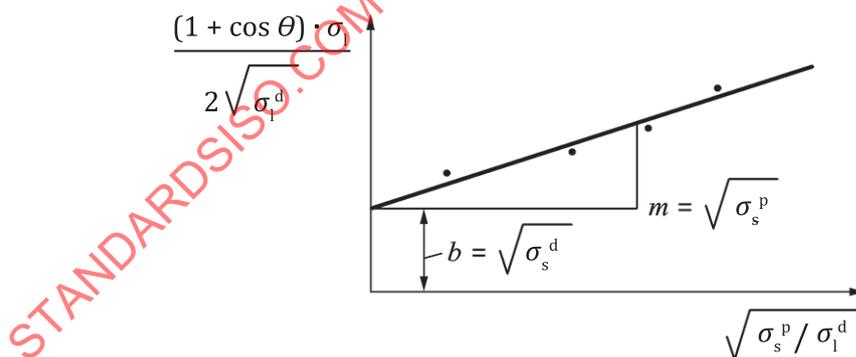

Figure 3 — Example of an interpretation in accordance with References [7] and [8]

4.2 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 respective height at the drop, compensates the Laplace pressure, which results from the curvature of the drop contour at that point. The Laplace pressure results from the main curvature radiuses, vertically standing on top of each other, as shown in Formula (6):

$$\Delta p = \sigma \cdot \left(\frac{l}{r_1} + \frac{l}{r_2} \right) \tag{6}$$

Formula (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 2). 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 (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 (7):

$$\Delta p_{apex} - \Delta p_p = z \cdot \Delta \rho \cdot g \tag{7}$$

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 (8) and (9):

$$\Delta p_{apex} = \sigma \left(k_{apex,1} + k_{apex,2} \right) \tag{8}$$

$$\Delta p_p = \sigma \left(k_{p,1} + k_{p,2} \right) \tag{9}$$

where

$k_{apex,1}$ and $k_{apex,2}$ are the main curvatures at the apex;

$k_{p,1}$ and $k_{p,2}$ are the main curvatures at point, $P(x,z)$.

The main curvatures at the apex are equal in all directions due to the axial symmetry of the drop ($\to k_{apex}$). From differential geometry, the analytic terms for the curvatures of the main normal intersections at point, $P(x,z)$:

$$k_{p,1} = \frac{d\Phi}{ds} = \left(\frac{d^2 z}{dx^2} \right) \left[1 + \left(\frac{dz}{dx} \right)^2 \right]^{-3/2} \tag{10}$$