INTERNATIONAL STANDARD

ISO 1409

Sixth edition
2020-08

Plastics/rubber — Polymer dispersions and rubber latices (natural and synthetic) — Determination of surface tension

Plastiques/caoutchouc — Dispersions de polymères et latex de caoutchouc (naturel et synthétique) — Détermination de la tension superficielle

Reference number
ISO 1409:2020(E)

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

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry*.

This sixth edition cancels and replaces the fifth edition (ISO 1409:2006), which has been technically revised.

The main changes compared to the previous edition are as follows:

- extension of Clause 1 and Clause 4;
- inclusion in Clause 1 that method A is the preferred method in case of dispute;
- inclusion of the tensiometer (Wilhelmy type) and glass dish or vessel in 6.2 and 6.3;
- inclusion of the procedure of the new method B in 8.2;
- expression of the test results according to the new method B in 9.2;
- inclusion of the precision data for method B in Annex A.

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.

Plastics/rubber — Polymer dispersions and rubber latices (natural and synthetic) — Determination of surface tension

1 Scope

This document specifies two methods for the determination of the surface tension of polymer dispersions and rubber latices (natural and synthetic).

- Method A is the ring method (Du Noüy ring method).
- Method B is the plate method (Wilhelmy plate method).

Method A is suitable valid for polymer dispersions and rubber latices with a viscosity less than 200 mPa·s.

Method B is not suitable for polymer dispersions and rubber latices containing cationic surfactants.

Methods A and B are also suitable for prevulcanized latices and compounded material.

In case of dispute, the preferred method is method A (the ring 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 123, *Rubber latex — Sampling*

ISO 124, *Latex, rubber — Determination of total solids content*

ISO 705, *Rubber latex — Determination of density between 5 degrees C and 40 degrees C*

ISO 1652, *Rubber latex — Determination of apparent viscosity by the Brookfield test method*

ISO 2555, *Plastics — Resins in the liquid state or as emulsions or dispersions — Determination of apparent viscosity using a single cylinder type rotational viscometer method*

ISO 3219, *Plastics — Polymers/resins in the liquid state or as emulsions or dispersions — Determination of viscosity using a rotational viscometer with defined shear rate*

3 Terms and definitions

No terms and definitions are listed in this document.

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/

4 Principle

4.1 Method A

Method A is suitable valid for polymer dispersions and rubber latices with a viscosity less than 200 mPa·s. To achieve this, the dispersion or latex is diluted with water to a mass fraction of total solids of 40 %. If necessary, the total solid content is further reduced to ensure that the viscosity is under the specified limit.

A horizontally suspended ring of thin wire is attached to a "Du Noüy type" tensiometer and immersed in the liquid under test, then slowly pulled out. Just before the ring detaches itself from the surface of the liquid, the force required reaches a maximum. This force is measured by a torsion balance, inductive pick-up or some other suitable measuring device.

4.2 Method B

When a liquid is brought into contact with the edge of the plate which is suspended from the “Wilhelmy type” tensiometer, the plate is pulled down into the liquid due to the surface tension. The instrument applies an upward vertical force to the plate so that the plate reaches the force balance. This vertical force is measured and used to calculate the surface tension of the liquid.

5 Reagents

5.1 Distilled water, carbon-dioxide-free, or water of equivalent purity (grade 3 as defined in ISO 3696).

5.2 Toluene, of recognized analytical purity.

6 Apparatus

6.1 Tensiometer (Du Noüy type), with a platinum or platinum-iridium alloy ring of either 60 mm or 40 mm nominal circumference (corresponding to 9,55 mm or 6,37 mm internal radius, respectively) and made of wire having a nominal radius of 0,185 mm.

6.2 Tensiometer (Wilhelmy type), with a flat, thin plate made of platinum or platinum-iridium alloy, and the size suitable for the tensiometer.

6.3 Glass dish or vessel, of 50 cm^3 capacity, with an internal diameter of at least 45 mm or suitable for the thermostat of the tensiometer.

6.4 Thermostatic bath, or some other means of adjusting the temperature of the test sample to 23 °C ± 1 °C (27 °C ± 1 °C for tropical countries).

NOTE The temperature coefficient of rubber latices over the temperature range 20 °C to 30 °C is –0,1 mN/m per degree Celsius.

6.5 Bunsen or ethanol lamp, or some other means of heating and cleaning the ring or plate.

7 Sampling

Carry out the sampling in accordance with one of the methods specified in ISO 123.

8 Procedure

8.1 Method A

8.1.1 Preparation of apparatus

Clean the dish or vessel (6.3) carefully, since any contamination may lead to variable results. Clean the ring of the tensiometer (6.1) by washing in water (5.1) and then heating in the oxidizing section of a Bunsen or ethanol flame (6.5). Take extreme care to avoid touching or distorting the tensiometer ring when handling it. Ensure that the ring remains parallel to the surface of the liquid during the determination. Failure to observe these precautions will lead to inaccurate results.

8.1.2 Calibration

Carefully calibrate the tensiometer scale against a standard mass or a reference liquid such as distilled water (5.1) or toluene (5.2) in accordance with the manufacturer's instructions, so that the scale reads in mN/m.

Calibration is generally carried out against a standard mass. It should be noted that the calculation of the results (see Clause 9) requires different correction factors depending on the method of calibration.

8.1.3 Preparation of the test sample

8.1.3.1 If the total solids content of the test sample of latex or polymer dispersion is not known, determine it in accordance with ISO 124. If the mass fraction of total solids is greater than 40 %, dilute the test sample to a mass fraction of total solids of 40 % ± 1 % with water (5.1). If it is suspected that the viscosity of the diluted test sample is still greater than 200 mPa·s, determine it by the appropriate method given in ISO 1652, ISO 2555 or ISO 3219. If necessary, dilute the test sample further until the viscosity is less than 200 mPa·s, noting the final total solids content.

NOTE Dilution to a mass fraction of 40 % has a negligible effect on the surface tension of polymer dispersions and rubber latices. In some cases, the surface tension at a higher total solids content can be required, in which case this can be measured by the method as specified with little loss of accuracy, provided that the viscosity is less than 200 mPa·s.

If the density of the diluted test sample of latex or polymer dispersion is not known, determine it in accordance with ISO 705.

8.1.3.2 Using the thermostatic bath (6.4), adjust the temperature of the diluted test sample to 23 °C ± 1 °C (or 27 °C ± 1 °C in tropical countries).

8.1.3.3 Take approximately 25 cm^3 of the diluted test sample, using a pipette with its tip well below the surface of the liquid, and transfer it to the dish or vessel (6.3). Remove any air bubbles from the surface of the sample by wiping with a piece of hard filter paper. Measure the surface tension immediately to avoid errors due to the formation of surface skin.

8.1.4 Determination

With the tensiometer protected from air currents, place the dish or vessel containing the diluted test sample on the adjustable platform of the instrument beneath the ring of the tensiometer. Adjust the instrument, following the manufacturer's guidelines, so that the beam is in the balance position when the ring is dry and the scale reading is zero. Raise the platform until the liquid makes contact with the ring and then immerse the ring to a depth of approximately 5 mm.

Slowly lower the platform by means of the platform-adjusting screw, and simultaneously increase the torsion in the wire, proportioning these two adjustments so that the beam remains exactly in its balance position. As the film adhering to the ring approaches its breaking point, proceed very slowly with adjustments.

For determinations with an automatic tensiometer, regulate the penetration depth of the ring to approximately 5 mm below the surface of the liquid and adjust the rate of movement of the dish or vessel to 10 mm/min.

Record the maximum scale reading just prior to the point at which the ring separates from the dispersion or latex (this is of particular importance with undiluted latices or polymer dispersions of high viscosity).

Immediately raise the dish again before the film breaks, re-submerging the ring. Repeat the determination three times for a total of four determinations.

Should the film break, clean the ring as described in 8.1.1 and repeat the determination.

Discount the first reading and record the average of the next three readings, which should agree to within ±0,5 mN/m of the median value.

8.2 Method B

8.2.1 Preparation of apparatus

Clean the dish or vessel (6.3) carefully. The surface of the plate (6.2) should be roughened enough to obtain a perfect wetting and with no bright spots on the plate. Rinse the plate thoroughly by washing in water (5.1), then heating in the oxidizing section of a gas burner or Bunsen (6.5) until the plate is clean. Hang the plate on the instrument after cooling to room temperature. Make sure that the lower edge of the plate is exactly straight by checking whether the light gap between the edge of the plate and the surface of the liquid is parallel and not wedge-shaped. Ensure that the plate remains parallel to the surface of the liquid during the determination.

NOTE Any contamination can lead to variable results and failure to observe these precautions leads to inaccurate results.

8.2.2 Calibration

8.2.2.1 Calibrate the tensiometer (6.2) scale against standard mass or distilled water (5.1) in accordance with the manufacturer's instructions, so that the scale will read in mN/m.

8.2.2.2 If the calibration is carried out against distilled water, determine the surface tension of distilled water, the result should be 72,28 mN/m ± 0,30 mN/m at 23 °C or 71,66 mN/m ± 0,30 mN/m at 27 °C.

8.2.3 Preparation of the test sample

8.2.3.1 Using the thermostatic bath (6.4), adjust the temperature of the test sample to 23 °C ± 1 °C (or 27 °C ± 1 °C in tropical countries).

8.2.3.2 Rinse the dish or vessel (6.3) with a small amount of the test sample, and then transfer approximately 30 cm^3 of the test sample to the dish or vessel by a pipette with its tip well below the surface of the liquid. Make sure the depth of the test sample is at least 10 mm. Remove any air bubbles from the surface of the sample by wiping with a piece of hard filter paper. Measure the surface tension immediately to avoid errors due to the formation of surface skin.

NOTE For the polymer dispersions or rubber latices with high viscosity, the equilibration time of the surface tension can be longer, and it can be shortened by diluting the test sample to a mass fraction of total solids of 40 % ± 1 % with water.

8.2.4 Determination

8.2.4.1 General

Two alternative plate methods are specified, which can be chosen according to the instruments:

- method B1: carry out the measurement when the pre-wetted plate is suddenly caught by the liquid;
- method B2: immerse the plate in the liquid to a certain depth, and then carry out the measurement when the plate is pulled back into contact with the surface of the liquid.

8.2.4.2 Method B1

Adjust the instrument following the manufacturer's instructions.

Place the dish or vessel containing the test sample on the adjustable platform of the instrument beneath the plate of the tensiometer and tare the reading to zero.

After pre-wetting the plate in the liquid to a depth of 2 mm to 5 mm according to the manufacturer's instructions, pull the plate out of the liquid.

Raise the platform slowly until the plate is suddenly caught by the liquid. Record the stable reading from the tensiometer. Lower the platform until the plate separates from the liquid. Repeat the determination of contact separation another two times without taring the reading to zero and cleaning the plate.

Discount the first reading and record the average of the next two readings, which difference should be within ±0,5 mN/m.

8.2.4.3 Method B2

Adjust the instrument following the manufacturer's instructions.

Place the dish or vessel containing the test sample on the adjustable platform of the instrument beneath the plate of the tensiometer and tare the reading to zero.

Raise the platform until the lower edge of the plate is just submerged and mark the position of the platform according to the manufacturer's instructions.

Raise the platform another 2 mm to 5 mm to ensure the wetting of the plate.

Lower the platform until it is located exactly to the marked position again, that is the lower edge of the plate comes into contact with the surface of the liquid again. Record the stable reading from the tensiometer.

After lowering the platform until the plate separates from the liquid, tare the reading to zero and repeat the determination without cleaning the plate.

Make at least three measurements until the difference between two successive readings is not greater than ±0,5 mN/m. Discount the first reading and record the average of the last two readings.

For method B1 or method B2, if an automatic tensiometer that can display the change of surface tension in real time is used for measurement, adjust the instrument and set the parameters following the manufacturer's instructions. Some recommended values are given in Table 1 and the typical surface tension curve is given in Figure 1. For Table 1, the test result is the mean value of the last five readings when the maximum measuring time is reached.

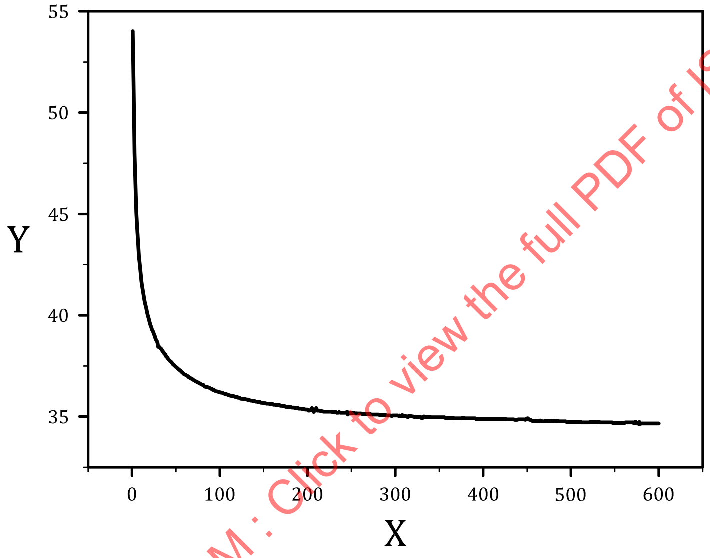
NOTE Table 1 shows only the recommended maximum measuring time. Before the formation of the surface skin, the maximum measuring time for different test sample can be determined according to the surface tension curve.

Table 1 — Parameters of automatic tensiometer

Parameters		Set value
Maximum measuring time, s	XSBRL[a]	600
	NRL, CRL and NBRL[b]	300
Value interval, s		1
Immersion depth, mm		2
Surface detection speed, mm/min		10
Values for mean		5
Standard deviation		Not set

[a] XSBRL is carboxylated styrene-butadiene rubber latices.

[b] NRL is natural rubber latices. CRL is chloroprene rubber latices. NBRL is nitrile latices.



Key

X time, s

Y surface tension, mN/m

Figure 1 — Typical surface tension curve

9 Expression of results

9.1 Method A

9.1.1 Calibration against standard mass

If (as is usual) the tensiometer has been calibrated against a standard mass, the reading, σ, shall be corrected by a factor depending on the dimensions of the ring and the density of the liquid according to Formula (1):

$$\sigma = M \times F \quad (1)$$

where

M is the scale reading, in mN/m;

F is the factor calculated from Formula (2).

$$F = 0{,}725 + \sqrt{\frac{0{,}036\,78M}{R^2\rho} + P} \quad (2)$$

where

R is the mean radius, in mm;

ρ is the density of the liquid, in Mg/m^3;

P is a constant calculated from Formula (3).

$$P = 0{,}045\,34 - \frac{1{,}679r}{R} \quad (3)$$

where r is the radius of the wire, in mm.

NOTE 1 Some formulae for calculating F include the gravitational constant G. This has been incorporated directly into the constant 0,036 78 to avoid possible confusion over units.

NOTE 2 For standard rings of 60 mm or 40 mm nominal circumference (R = 9,55 mm or 6,37 mm, respectively) and wire of nominal radius 0,185 mm, P will be given by:

P_{60} = +0,012 82 or

P_{40} = −0,003 43

NOTE 3 “Surface tension” and “surface free energy” are synonymous and have equal numerical values when expressed in mN/m and mJ/m^2, respectively.

NOTE 4 Since it might not be practical to calculate the factor F separately for each sample tested, it is convenient to create tables for a correction index $\Delta\sigma$ depending on the wire dimensions (see Annex B).

9.1.2 Calibration against a standard liquid

If the calibration has been carried out using a reference liquid, then the surface tension, σ′, expressed in mN/m, is given by Formula (4):

$$\sigma' = M' \times F' \quad (4)$$

where

M' is the reading for the diluted test sample, in mN/m, on the scale calibrated with the reference liquid;

F' is a factor calculated from Formula (5).

$$F' = F \times \sigma'' / M'' \quad (5)$$

where

F is calculated according to Formula (2);

σ'' is the known surface tension of the reference liquid, in mN/m ;

M'' is the actual scale reading recorded for the reference liquid, in mN/m.

It is particularly important to read the equipment manufacturer's instructions carefully if using this procedure, as some corrections may have been built into the equipment. For this reason, calculated corrections are not given in Annex B.

9.2 Method B

The surface tension, σ, expressed in mN/m, is calculated using Formula (6):

$$\sigma = \frac{F_0}{2(l+t)\cos\theta} \tag{6}$$

where

F_0 is the measured force, in mN;

l is the length of plate, in m;

t is the thickness of plate, in m;

θ is the contact angle between the plate and the liquid, in °.

The plate is made of roughened platinum or platinum-iridium alloys and is optimally wetted so that the contact angle θ can be assumed to be zero for common liquids on clean glass or plate. That means the term cos θ has a value of 1, so that only the measured force and the wetted length of the plate need to be taken into consideration. No other correction factors are necessary for this method and the density of the liquid does not need to be known.

NOTE 1 One can be aware of the error caused by a non-zero contact angle.

NOTE 2 For most tensiometers, the size of the plate has been set in the software of the instrument and it can display the surface tension directly.

10 Precision

See Annex A.

11 Test report

The test report shall include the following information:

a) a reference to this document, i.e. ISO 1409:2020;

b) all details necessary for the identification of the sample tested;

c) the method used: method A or method B;

d) the temperature at which the test was carried out;

e) the total solids content of the test sample originally and as tested after dilution;

f) the results and the units in which they have been expressed;

g) any unusual features noted during the determination;

h) the date and place where the determination was carried out;

i) the maximum measuring time when using an automatic tensiometer;

j) any operation not included in this document or in the international standards to which reference is made, as well as any operation regarded as optional.

Annex A
(informative)

Precision

A.1 Precision of method A

With accurate operation and control, i.e. correctly following the details of the procedure, it is possible to obtain the following:

- repeatability limit: 1,0 mN/m;
- reproducibility limit: 2,0 mN/m.

The work to generate the precision data was initiated before the publication of ISO/TR 9272 in 2005. Consequently, the results are not expressed in the recommended format.

A.2 Precision of method B

A.2.1 General

An interlaboratory test programme (ITP) to determine the precision of method B was conducted using Wilhelmy type tensiometer in June and July 2018 in China, Germany and United States. The precision evaluated was a type 1 precision in accordance with method A of ISO 19983:2017, 6.7.1.

Eight laboratories participated in the ITP and one of these used two different types of analyser. For this laboratory, the data from the separate analysers were included in the ITP as data from individual laboratories. This gave a database of up to nine laboratories or pseudo-laboratories.

Three different materials (XSBRL, NBRL and NRL) were used in the ITP. A test result was taken to be the average value of three measurements. Test results from each laboratory were obtained on two different days at intervals of one week. Three measurements were repeated for each day.

A.2.2 Precision results

The precision results are given in Table A.1. These results were obtained using outlier deletion procedures as described in ISO 19983.

a) **Repeatability**: the difference between two test (value) averages, found on nominally identical material samples under normal and correct operation of the test method, exceed the tabulated repeatability on average not more than once in 20 cases.

b) **Day-to-day repeatability**: the difference between two-day test (value) averages, found on nominally identical material samples under normal and correct operation of the test method, exceed the tabulated day-to-day repeatability on average not more than once in 20 cases.

c) **Reproducibility**: the difference between two independently measured test (value) averages, found in two laboratories using normal and correct operation of the test method on nominally identical material samples, exceed the tabulated reproducibility not more than once in 20 cases.

Table A.1 — Precision data for method B

Material	Mean mN/m	Within laboratory within-day			Within laboratory day-to-day			Between laboratories			Number of laboratories[a]
		s_r	r	(r)	s_{rD}	r_D	(r_D)	s_R	R	(R)	
XSBRL	42,2	0,14	0,40	0,95	0,16	0,45	1,07	0,35	0,99	2,35	9
NBRL	31,4	0,20	0,57	1,82	0,22	0,62	1,97	0,30	0,85	2,71	9
NRL	35,3	0,17	0,48	1,36	0,25	0,71	2,01	0,35	0,99	2,80	9

[a] The final number of laboratories in the ITP after deletion of outliers.

s_r	is the repeatability standard deviation;
r	is the repeatability, in measurement units;
(r)	is the relative repeatability, in percent;
s_{rD}	is the day-to-day repeatability standard deviation;
r_D	is the day-to-day repeatability, in measurement units;
(r_D)	is the relative day-to-day repeatability, in percent;
s_R	is the reproducibility standard deviation;
R	is the reproducibility, in measurement units;
(R)	is the relative reproducibility, in percent.