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Guidelines for the standardization of methods for the determination of viscosity number and limiting viscosity number of polymers in dilute solution -- Part 1: General conditions

Plastiques -- Principes directeurs pour la normalisation des méthodes de détermination de l'indice de viscosité et de l'indice limite de viscosité des polymères en solution diluée - - Partie 1: Conditions générales

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Guidelines for the standardization of methods for the determination of viscosity number and limiting viscosity number of polymers in dilute solution —
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Plastiques — Principes directeurs pour la normalisation des méthodes de détermination de l'indice de viscosité et de l'indice limite de viscosité des polymères en solution diluée — Partie 1: Conditions générales

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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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 1628/1 was prepared by Technical Committee ISO/TC 61, *Plastics*.

This International Standard cancels and replaces ISO Recommendation R 1628-1970, of which it constitutes a technical revision.

INTERNATIONAL STANDARD   ISO 1628/1-1984 (E)

Guidelines for the standardization of methods for the determination of viscosity number and limiting viscosity number of polymers in dilute solution — Part 1: General conditions

1 Scope and field of application

This part of ISO 1628 defines the general conditions for determining the viscosity number and limiting viscosity number of organic polymers in dilute solution.

It is intended to be used as a guide in the development of standards for measuring the viscosities of individual types of polymers.

Furthermore, this International Standard may serve as a guide in measuring and reporting the viscosities of polymers for which no separate standards exist.

Annexes A and B give details for cleaning the apparatus and on the most important sources of error.

2 References

ISO 31/3, *Quantities and units of mechanics.*

ISO 3105, *Glass capillary kinematic viscometers — Specification and operating instructions.*

ISO 3205, *Preferred test temperatures.*

3 Definitions and units

3.1 Definitions applicable to any liquid

3.1.1 viscosity; dynamic viscosity, η:

The viscosity of a fluid sheared between two parallel planes, one of which moves relative to the other in rectilinear and uniform motion in its own plane, is defined by the Newton equation:

$$\tau = \eta \cdot \dot{\gamma} \qquad \qquad \ldots \quad (1)$$

where

τ is the shear stress;

η is the viscosity;

$\dot{\gamma} = \dfrac{dv}{dz}$ is the velocity gradient or rate of shear (v is the velocity of one plane relative to the other and z the co-ordinate perpendicular to the two planes).

See ISO 31/3.

NOTE — Viscosity is usually taken to mean "Newtonian viscosity", in which case the ratio of shearing stress to the velocity gradient is constant. In non-Newtonian behaviour, which is the usual case with high polymer solutions, the ratio varies with the shear rate. Such ratios are often called "apparent viscosities" at the corresponding shear rate.

The dimensions of viscosity are:

$$ML^{-1}T^{-1}$$

and the units are:

— International System: Pa·s

— For practical use, the sub-multiple 10^{-3} Pa·s is more convenient; this sub-unit corresponds to the centipoise (cP) unit which is no longer recommended.

3.1.2 viscosity/density ratio; kinematic viscosity, ν:

This ratio is defined by the equation:

$$\nu = \frac{\eta}{\varrho} \qquad \qquad \ldots \quad (2)$$

where ϱ is the density of the fluid at the temperature at which the viscosity is measured.

Its dimensions are:

$$L^2 T^{-1}$$

and its units are:

— International System: $m^2 \cdot s^{-1}$

— For practical use, the use of the sub-multiple 10^{-6} $m^2 \cdot s^{-1}$, i.e. $mm^2 \cdot s^{-1}$, is more convenient; this sub-unit corresponds to the centistoke (cSt) unit which is no longer recommended.

3.2 Definitions applicable to polymer solutions

3.2.1 viscosity ratio (formerly called relative viscosity): The ratio of the viscosities of the polymer solution (of stated concentration) η and of the pure solvent η_0, at the same temperature:

$$\frac{\eta}{\eta_0} \qquad \qquad \ldots \quad (3)$$

Being a number, it is dimensionless.

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3.2.2 viscosity ratio increment (formerly called specific viscosity): Viscosity ratio minus one:

$$\left(\frac{\eta}{\eta_0}\right) - 1 = \frac{\eta - \eta_0}{\eta_0} \qquad \ldots (4)$$

Being a number it is dimensionless.

3.2.3 viscosity number, V.N. (formerly called reduced viscosity): The ratio of the viscosity ratio increment to the polymer concentration in the solution:

$$V.N. = \frac{\eta - \eta_0}{\eta_0 \, c} \qquad \ldots (5)$$

Its dimensions are

$M^{-1}L^3$

and its units are:

— International System: m^3/kg

— For practical use, a sub-multiple is more convenient: ml/g (1 ml/g $= 10^{-3}$ m^3/kg)

The viscosity number is usually determined at low concentration (less than 0,01 g/ml) except in the case of low molecular weight polymers for which higher concentrations may be necessary.

3.2.4 logarithmic viscosity number (formerly called inherent viscosity): The ratio of the natural logarithm of the viscosity ratio to the polymer concentration in the solution:

$$\frac{\ln\left(\dfrac{\eta}{\eta_0}\right)}{c} \qquad \ldots (6)$$

The dimensions and units are the same as those given in 3.2.3.

The logarithmic viscosity number is usually determined at low concentration (less than 0,01 g/ml), except in the case of low molar mass polymers, for which higher concentrations may be necessary.

3.2.5 limiting viscosity number (formerly intrinsic viscosity) (symbol [η]): The limiting value of the viscosity number or of the logarithmic viscosity number at infinite dilution:

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta - \eta_0}{\eta_0 \, c}\right)$$

$$[\eta] = \lim_{c \to 0} \frac{\ln\left(\dfrac{\eta}{\eta_0}\right)}{c} \qquad \ldots (7)$$

The dimensions and units are the same as those given in 3.2.3.

NOTE — The effect of the shear rate on the functions defined in clauses 3.2.1 to 3.2.5 has been neglected, since this effect is usually negligible for values of the viscosity number, logarithmic viscosity

number and limiting viscosity less than 500 ml/g. Strictly speaking, all these functions should be defined at the limiting (preferably infinitely small) value of the shear rate.

4 Measurements

The data needed for the evaluation of the functions defined in 3.2 are obtained by means of a capillary tube viscometer. The efflux times of a given volume of solvent (t_0) and of solution (t) are measured at fixed temperature and atmospheric pressure conditions in the same viscometer. The efflux time of a liquid is related to its viscosity by the Poiseuille-Hagenbach-Couette equation:

$$v = \frac{\eta}{\varrho} = kt - \left(\frac{A}{t}\right) \qquad \ldots (8)$$

where

k is a constant of the viscometer;

A is a parameter of the kinetic energy correction;

ϱ is the density of the liquid.

This equation can be reduced to

$$v = \frac{\eta}{\varrho} = kt \qquad \ldots (9)$$

if the kinetic energy correction $\dfrac{A}{t}$ can be disregarded.

In this International Standard, the term $\dfrac{A}{t}$ is considered to be negligible when it is smaller than 3 % of the viscosity of the solvent (see annex B). If this condition is accepted and if the densities of the solvent (ϱ_0) and of the solution (ϱ) differ by less than 0,5 %, the viscosity ratio $\dfrac{\eta}{\eta_0}$ will be given by the "efflux time ratio" $\dfrac{t}{t_0}$.

5 Apparatus

5.1 Capillary viscometer, suspended level, Ubbelohde the type. The use of a viscometer having the dimensions given in the figure is strongly recommended; furthermore, it is strongly recommended that the other essential viscometer dimensions are chosen from among those indicated in table 1. The choice is determined by the viscosity/density ratio of the solvent at the temperature of measurement, as indicated in table 1. The next smaller viscometer can also be used.

NOTE — Other types of viscosimeters listed in ISO 3105 may be used provided they give equivalent results to the Ubbelohde viscometers specified in clause 5.1. However, in cases of dispute, the Ubbelohde viscometers shall be used.

5.2 Viscometer holders, to hold the viscometers firmly in the thermostatic bath in the vertical position.

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Table 1 — Ubbelohde viscometers recommended for the determination of the dilute solution viscosity of polymers

Viscosity/density ratio of solvent at temperature of measurement	Diameter of capillary	Volume of reservoir C	Internal diameter of tube P	Viscometer model according to ISO 3105
mm²/s	mm (± 2 %)	ml (± 5 %)	mm (± 5 %)	
0,15 to 0,30	0,24	1,0	6,0	0
0,31 to 0,50	0,36	2,0	6,0	0C
0,51 to 0,75	0,46	3,0	6,0	0B
0,76 to 1,50	0,58	4,0	6,0	1
1,51 to 2,50	0,73	4,0	6,0	1C
2,51 to 5,00	0,88	4,0	6,0	1B
5,01 to 15,00	1,03	4,0	6,0	2

5.3 Thermostatic bath

A transparent liquid or vapour bath of sufficient depth that during the measurement, no portion of the sample will be less than 20 mm below the surface of the bath medium or less than 20 mm above the bottom of the bath.

The temperature control shall be such that within the range of 25 °C to 100 °C, the temperature of the bath during the period of measurement does not vary from the desired temperature by more than 0,05 °C over the length of the viscometer, or between viscometers.

At temperatures higher than 100 °C, the tolerance shall be ± 0,2 °C maximum.

5.4 Temperature measuring device

Liquid-in-glass, "total immersion" thermometers reading to 0,05 °C in the range to be used and in a known state of calibration. Other thermometric devices of at least equal precision may be used.

5.5 Timing device

Any timing device may be used provided that its readings discriminate to at least 0,2 s and that its rate is constant to ± 0,1 % over 15 min.

6 Solutions

6.1 Preparation of solutions

The dissolution of the polymer sample in the solvent shall give a "true" solution, essentially free of microgels and of associated macromolecules. Also, polymer degradation shall be minimized. For these reasons, it is necessary that the dissolution procedure be exactly defined and it is recommended that the following factors be mentioned:

a) the solvent and its pretreatment, if any;

b) the apparatus and the method of agitation used;

c) the temperature range within which the system is maintained during preparation of the solution;

d) the time interval necessary for completely dissolving the polymer without degradation, or at constant degradation;

e) the stabilizer and/or the protecting atmosphere used;

f) the conditions of filtration of the solution, if applied.

6.2 Concentration

Where no standard exists, in addition to the above factors, careful consideration shall be given to the choice of solvent and the solution concentration. The solution concentration shall be chosen so that the ratio of the efflux time of the solution (t) to the efflux time of the solvent (t_0) is at least 1,2 and less than 2,0 (see the note).

More than one concentration can therefore be used for a given polymer-solvent system, depending on the molar mass of the polymer sample under test.

The concentration is expressed preferably in grams of polymer per millilitre of solution (g/ml).

NOTE — A lower limit of 1,2 is necessary in order to have sufficient precision on the measured difference of efflux times. The upper limit of 2,0 is recommended because at high molar mass there can be, at the usual concentrations, shear effects and nonlinearity of the viscosity number in relation to concentration.

7 Temperature of measurement

The temperature shall be chosen with respect to sufficient solubility and other technical requirements but kept uniform for one particular polymer/solvent system and the temperature tolerance shall be specified. A temperature of 25 ± 0,05 °C should be chosen whenever possible. If another temperature is used, it should be chosen from the values recommended in ISO 3205 and stated in the test report.

8 Procedure

Measure successively the flow times of the solution and the solvent in the same viscometer, using the following procedure:

8.1 Setting up the apparatus

Maintain the bath at the specified test temperature.

Charge the dry, clean viscometer (see annex A) by tilting it about 30 ° from the vertical and pouring sufficient sample through tube L so that when the viscometer is returned to the vertical, the meniscus is between the filling marks. Avoid trapping air bubbles in the viscometer. The initial filling may be carried out away from the bath.

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Mount the viscometer in a holder in the bath, ensuring that tube N is vertical. Allow time for the charged viscometer to reach the same temperature as the bath. Usually 15 minutes will suffice if the measurement is made at 25 °C. At higher temperatures longer times may be necessary. Unnecessary delay should be avoided as it is found that the most consistent results are obtained shortly after temperature equilibrium is attained with a freshly charged viscometer.

8.2 Flow time measurement

When temperature equilibrium has been attained, close tube M and apply suction to tube N or pressure to tube L until the liquid reaches a level about 5 mm above mark E. Hold the liquid at this level by closing tube N.

Open tube M so that the liquid drops away from the lower end of the capillary tube R.

When the liquid is clear of the capillary end and the lower end of tube M, open tube N. Measure the flow time to the nearest 0,2 s as the time taken for the bottom of the meniscus to pass from the top edge of mark E, to the top edge of mark F. For polymer solutions containing small amounts of finely divided pigments, eg, carbon black, it may be necessary to view the top of the meniscus.

The opening and closing of the tubes may conveniently be carried out by means of taps or clips on clean flexible tubing attached to the end of the tubes, making sure no fluff or other contaminant enters the tube.

The first flow shall not be taken into account for measuring the flow time. Repeat the measurement of flow time immediately, without emptying or recharging until two successive flow times agree within 0,25 %. Take the mean of these two values as the flow time.

If two successive determinations of the mean flow time of the solvent differ by more than 0,4 s, clean the viscosimeter.

WARNING NOTE — Great care must be exercised when working with hazardous liquids such as sulphuric acid.

9 Expression of results

The results are preferably expressed as a viscosity number. The viscosity number (V.N.), in millilitres per gram, is calculated from the equation

$$\text{V.N.} = \frac{t - t_0}{t_0 \, c} \qquad \ldots \text{(10)}$$

where

t is the flow time of the solution, in seconds;

t_0 is the flow time of the solvent, in seconds, in the same viscometer;

c is the concentration, in grams per millilitre.

The results can also be expressed as a limiting viscosity number $[\eta]$, for example in order to compare polymers of different average molar masses for which it has been necessary to use different concentrations (see 6.2).

The limiting viscosity number shall be calculated from the values of viscosity number obtained for concentrations c_1, c_2, c_3..., in the approximate ratio 1:2:3..., by a graphical method consisting of plotting the viscosity number values (on the ordinate axis) against the concentrations (on the abscissa) and extrapolating the curve to zero concentration. The limiting viscosity number is read off the ordinate axis.

NOTE — It is recommended that the least squares method be used for analysing the experimental values.

The limiting viscosity number $[\eta]$ can also be calculated from one value of the viscosity number for instance by the following equation:

$$[\eta] = \frac{\text{V.N.}}{1 + k' \cdot c \cdot \text{V.N.}} \qquad \ldots \text{(11)}$$

where k' is an experimental constant, usually between 0,2 and 0,3, which must be previously determined by measuring the viscosity number at two different concentrations and applying the equation

$$k' = \frac{\text{V.N.}_2 - \text{V.N.}_1}{\text{V.N.}_1 \cdot \text{V.N.}_2 \cdot (c_2 - c_1)} \qquad \ldots \text{(12)}$$

In the calculation of k' it may be preferable to use several concentrations and plot VN against c, drawing a straight line through the points and selecting two positions on this line to give values for substitution in the equation for k'.

10 Test report

The test report shall contain the following particulars:

a) a reference to this International Standard and the particular standard for the polymer tested, if one exists;

b) a complete identification of the material tested, including type, source, and manufacturer's code number;

c) concentration of material in the solution used, description of the solvent and details of making the solution;

d) details of the viscometer used;

e) temperature of test;

f) test results.

Annex A

Cleaning of apparatus

(This annex forms part of the Standard.)

It is essential for the full success of the method that all apparatus coming into contact with the liquid under test shall be scrupulously clean. Any impurities such as dust, traces of liquid or filaments in the viscometer will cause false results to be obtained.

Before test, the viscometer and all the apparatus used (glass vessels, pipettes, sintered glass filters, rubber tubing, etc) shall be cleaned. A suitable detergent may be adequate. Aqua regia may be required to remove inorganic residues from the glassware and a suitable solvent may be required to remove oil and grease. Following this, the glass apparatus shall be dried and then cleaned with freshly prepared chromic acid solution. This solution shall remain in contact with the glassware overnight at a minimum temperature of 20 °C. For more active cleaning, the chromic acid should be warmed gently on a water bath where this is possible.

Remove the chromic acid and rinse at least five times with distilled or deionized water. Dry in an electric oven at a temperature no more than 100 °C or rinse at least five times with acetone that has been distilled, dried and filtered and dry the apparatus with a slow stream of filtered dry air or, preferably, with a vacuum line.

Between successive determinations of the flow times of samples of a similar nature, the viscometer may be cleaned as follows:

Drain, thoroughly rinse with a suitable volatile solvent that has been distilled and filtered and dry with a slow stream of filtered dry air, with a vacuum line, or in an electric oven at a temperature no more than 100 °C. The effectiveness of cleaning can be checked by establishing that flow times with a given solvent and viscometer remain constant.

If the next solution to be measured is of a polymer of the same type and of a similar viscosity, it is permissible to drain the viscometer, wash it with the solution to be measured, then fill it with this solution.

It is recommended that viscometers used for silicone fluids and fluorocarbons be reserved for the exclusive use of these fluids, and that these viscometers be subjected to calibration checks at frequent intervals. Take great care that silicone fluids and fluorocarbons do not contaminate other apparatus either directly or indirectly (e.g. through the use of contaminated solvent).

WARNING NOTE — Great care must be taken when using aqua regia and chromic acid (preferably goggles and rubber gloves should be worn); wash off any splashes on the skin immediately with plenty of cold water and avoid inhaling any vapour.