International Standard ISO 5351/2

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Cellulose in dilute solutions — Determination of limiting viscosity number — Part 2 : Method in iron(III) sodium tartrate complex ($EWNN_{mod\ NaCl}$) solution

Cellulose en solutions diluées — Détermination de l'indice de viscosité limite — Partie 2 — Méthode utilisant une solution du complexe fer(III)-tartrate de sodium ($EWNN_{mod\ NaCl}$)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up 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.

International Standard ISO 5351/2 was developed by Technical Committee ISO/TC 6, *Paper, board and pulps*, and was circulated to the member bodies in January 1980.

It has been approved by the member bodies of the following countries :

Austria	France	Romania
Belgium	Germany, F.R.	South Africa, Rep. of
Brazil	Hungary	Spain
Chile	India	Sweden
China	Kenya	Turkey
Czechoslovakia	Korea, Rep. of	United Kingdom
Egypt. Arab Rep. of	Norway	USA
Finland	Philippines	

No member body expressed disapproval of the document.

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0 Introduction

The viscosity (or dynamic viscosity), symbol η, of a fluid is defined by the Newtonian equation

$$\tau = \eta \cdot \dot{\gamma}$$

where

τ is the shear stress;

η is the viscosity;

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

In non-Newtonian behaviour, normally the case with high-polymer solutions such as cellulose, the ratio of the shear stress to the velocity gradient varies with the shear stress.

The data required for evaluation of the limiting viscosity number of cellulose in dilute solutions (for definitions and symbols, see clause 4) are derived by means of a capillary-tube viscometer. The results of these measurements are seriously affected by the shear rate. The solution to the problem that thereby arises can be sought either by determination of the viscometric properties at so low a concentration of cellulose that the effect of shear rate is small, or by determination at a shear rate closely reproducible in different laboratories. In this document, the first condition, low concentration of cellulose, is applied.

1 Scope and field of application

This part of ISO 5351 specifies a method for the determination of the limiting viscosity number of cellulose in dilute iron(III) sodium tartrate complex ($EWNN_{mod\ NaCl}$) solution.

This method is applicable to EWNN-soluble samples of cellulose, for instance in pulps and textiles.

NOTE — The viscosity test is a means for determining the extent of cellulose degradation produced by cooking and bleaching. This degradation greatly affects the suitability of pulp for dissolving purposes and papermaking.

ISO 5351/1 specifies a method for the determination of the limiting viscosity number of cellulose in dilute cupri-ethylenediamine (CED) solution.

2 References

ISO 638, *Pulps — Determination of dry matter content.*

ISO 1833, *Textiles — Binary fibre mixtures — Quantitative chemical analysis.*

ISO 5089, *Textiles — Preparation of laboratory test samples and test specimens for chemical testing.*

ISO/TR 5090, *Textiles — Methods for the removal of non-fibrous matter prior to quantitative analysis of fibre mixtures.*

3 Principle

Measurement of the times of efflux of the diluted solvent and solution of cellulose through a capillary-tube viscometer at a specified concentation at 20 °C. Calculation by Schulz-Blaschke formula of the limiting viscosity number from these measurements, and from the known concentration of the solution.

4 Definitions

For the purposes of this International Standard, the following definitions apply.

4.1 shear rate, G : The velocity gradient of a fluid layer, parallel to the direction of flow, at the periphery of the capillary, defined by the equation

$$G = \frac{4V}{\pi r^3 t_f}$$

where

V is the volume between two arbitrary calibration marks of the viscometer, in millilitres;

r is the radius of the capillary tube, in centimetres;

t_f is the efflux time of the fluid, in seconds.

4.2 viscosity ratio : The ratio of the viscosities η and η_0 of the polymer solution of stated concentration and of the solvent respectively at the same temperature :

$$\frac{\eta}{\eta_0}$$

This ratio, as a number, is dimensionless.

4.3 viscosity relative increment : The viscosity ratio (4.2) minus one :

$$\frac{\eta}{\eta_0} - 1 = \frac{\eta - \eta_0}{\eta_0}$$

As a number, it is dimensionless.

4.4 viscosity number : The ratio of the viscosity relative increment (4.3) to the polymer concentration c in the solution :

$$\frac{\eta - \eta_0}{\eta_0 \cdot c}$$

Its unit is the millilitre per gram.

4.5 limiting viscosity number (L.V.N.), $[\eta]$: The limiting value of the viscosity number (4.4) at infinite dilution :

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_0}{\eta_0 \cdot c}$$

Its unit is the millilitre per gram.[1)]

5 Reagent

Iron(III) sodium tartrate complex solution ($EWNN_{mod\ NaCl}$).

Iron(III) sodium tartrate complex dissolved in dilute sodium hydroxide solution, for convenience referred to as iron sodium tartrate complex solution, and prepared as described in annex A.

6 Apparatus

Ordinary laboratory apparatus and

6.1 Constant-temperature bath, capable of being controlled at 20 ± 0,1 °C, accommodating the dissolving flasks (6.2) and the viscometer (6.5).

6.2 Conical flasks, with plastics stoppers, capacity 50 ml.

6.3 Balance, accurate to ± 0,1 mg.

6.4 Timing device, capable of being read to the nearest 0,1 s.

6.5 Capillary-tube viscometer, length of capillary tube at least 90 mm, for example an Ubbelohde viscometer of type 1 a.

6.6 Shaking machine, accommodating the dissolving flasks (6.2).

7 Pretreatment of test samples

7.1 Pulp samples

Take a sample corresponding to approximately 10 g of oven-dry mass. Split and tear the pulp into pieces of about 5 mm × 5 mm in size.

7.2 Textile samples

7.2.1 Generally

Prepare the sample as specified in ISO 5089.

Extract a sample of at least 3 g of air-dry mass in a Soxhlet apparatus with light petroleum for 1 h at a minimum rate of 6 cycles per hour. Allow the light petroleum to evaporate from the sample; soak the specimen in cold distilled or deionized water for 1 h, and then in a fresh portion of water at 65 ± 5 °C for a further 1 h. In both cases, use a liquor/specimen ratioof 100 : 1. Agitate the liquor from time to time. Remove the excess water from the sample by squeezing, suction or by means of a centrifuge and then allow the sample to become air-dry. For additional information, see ISO 1833 and ISO/TR 5090.

7.2.2 For bast fibres

Prepare the sample as described in annex B.

8 Procedure

8.1 Weighing of sample

8.1.1 If the approximate limiting viscosity number of the sample is known, weigh, to an accuracy of ± 0,5 mg, into the dissolving flask (6.2), an amount of the sample so chosen that the value of the viscosity ratio becomes 1,1 to 1,5 (see the note).

8.1.2 If the approximate value of the limiting viscosity number of the sample is not known, test a sample of 15 to 20 mg.

1) The SI unit of $[\eta]$ is the cubic metre per kilogram. Information from ISO/TC 61, *Plastics*, indicates plans in TC 61 to adopt this unit in practice.

8.1.3 If the viscosity ratio so obtained is not within the range specified, make the test by choice of the correct amount according to the value of the viscosity ratio so derived. At the same time, weigh out a separate sample, for determination of the dry matter in accordance with ISO 638 or ISO 1833 sub-clause 1.7.

NOTE — For routine analytical purposes, a constant amount of 15 to 20 mg of the sample may be used.

8.2 Preparation of test solution

With a pipette, add 50,0 ml of the EWNN solution (clause 5) to the sample. Close the flask, and shake it by hand for about 5 s. Transfer the flask to the shaking machine (6.6) and continue the shaking for about 16 h (see note 1). Take care to preclude raising of the temperature of the solution above 18 °C (see note 2).

NOTES

1 For the routine analysis of a large number of samples, the flasks may conveniently be put in the shaker and shaken overnight. For $[\eta]$ values below 1 000 ml/g, the shaking time is reducible to 2 h.

2 Dependent upon the room temperature, this may be done by refrigeration of the sample to 0 to 4 °C and isolation of the dissolving flasks with suitable covers, or more safely by direct cooling with water during the shaking.

8.3 Determination of efflux times

Keep the dissolving flask containing the solution in the constant-temperature bath (6.1), until a temperature of 20 ± 0,1 °C is reached. Immerse the viscometer (6.5) in the constant-temperature bath, fix it in a vertical position, and allow it to stand until equilibrium temperature is reached. Rinse the viscometer twice with the test solution prior to each determination. For temperature adjustment, apply suction to draw the solution once or twice to the maximum liquid level of the viscometer.

Draw a portion of the test solution into the viscometer by suction. Allow the fluid to drain. When the meniscus is at the upper mark on the upper bulb, start the timing device (6.4), and measure the efflux time (t) for the fluid to drain to the lower mark on the bulb. Measure the efflux time several times to an accuracy of ± 0,1 s. Measure, as described above, the efflux time (t_0) of the solvent.

Make at least two determinations the results of which shall agree within ± 2,5 %. If the deviation exceeds this, the test shall be repeated.

9 Calculation

The limiting viscosity number is given, in millilitres per gram, by the Schulz-Blaschke formula :

$$(\text{L.V.N.}) = [\eta] = \frac{\left(\frac{\eta - \eta_0}{\eta_0 \cdot c}\right)}{1 + k_\eta \cdot \left(\frac{\eta - \eta_0}{\eta_0}\right)}$$

where

$\frac{\eta - \eta_0}{\eta_0 \cdot c} = \frac{t - t_0}{t_0 \cdot c}$ is the viscosity number, in millilitres per gram;

$\frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0}$ is the viscosity relative increment (dimensionless);

k is an empirical constant (for the cellulose-EWNN system, $k = 0{,}3$);

c is the concentration (oven-dry basis), in grams per millilitre, of the cellulose in the solvent.

Example of calculation

For a spruce sulphite pulp, the following data were obtained :

$t = 74{,}2$ s

$t_0 = 56{,}2$ s

Accordingly, the viscosity ratio, $\frac{\eta}{\eta_0} = 1{,}320$, and the viscosity relative increment

$$\frac{\eta - \eta_0}{\eta_0} = \frac{\eta}{\eta_0} - 1 = 0{,}320$$

For a cellulose concentration of $c = 0{,}304 \times 10^{-3}$ g/ml, the Schulz-Blaschke formula yields a limiting viscosity number L.N.V. = $[\eta]$ = 950 ml/g.

10 Test report

The test report shall include the following particulars :

a) reference to this International Standard;

b) all the information necessary for complete identification of the sample;

c) preliminary treatment, such as purification;

d) type and constants of the viscometer;

e) the result, expressed in millilitres per gram;

f) any unusual features observed in the course of the test;

g) any operations not specified in this International Standard, or in the International Standards to which reference is made, or regarded as optional, which might have affected the results.

Annex A

Preparation of the iron(III) sodium tartrate complex solution

(Forms part of the standard.)

A.1 Reagents

During the preparation, use only reagents of recognized analytical grade and only distilled or deionized water.

A.1.1 Ferric chloride hexahydrate ($FeCl_3.6H_2O$).

A.1.2 Sodium tartrate dihydrate [$Na_2(C_4H_4O_6).2H_2O$].

A.1.3 Sodium hydroxide solution, containing 96,0 g of sodium hydroxide (NaOH) per 180 mi of water.

A.2 Apparatus

It is necessary to exclude daylight during preparation of the solvent, to prevent photo-chemical reactions. The apparatus illustrated in the figure has been found suitable.

The apparatus comprises a 10 litre vessel made of stainless steel, covered with a black poly(methyl methacrylate) fitting lid. Holes are provided in the lid to accommodate a thermometer, stirrer, dropping funnel and powder funnel. For temperature adjustment, the vessel is placed in a cooling bath of ice and water.

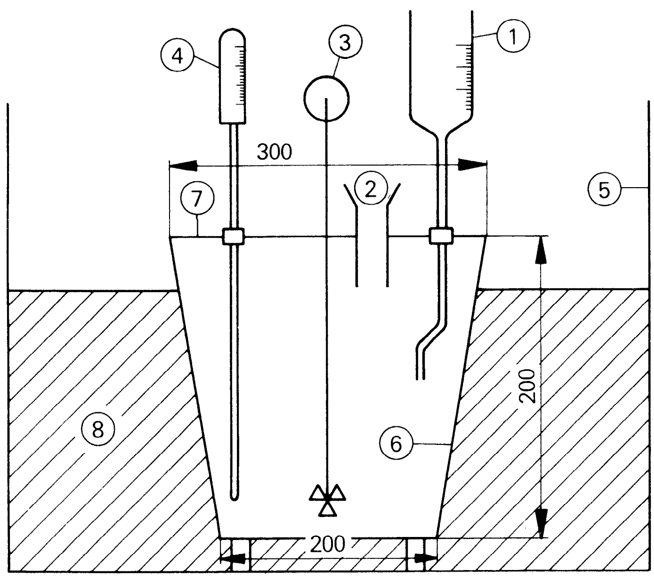
A.3 Preparation of the EWNN solution (see the note)

Pour 217,09 g of the sodium tartrate (A.1.2) and 550 ml of distilled water into the stainless steel container. Place the black lid upon the vessel. Dissolve the sodium tartrate with vigorous stirring. Add 81,09 g of the iron(III) chloride (A.1.1) through the powder funnel, rinse the funnel with a small amount of water, and then replace by a rubber stopper. Continue the mixing at room temperature until completely dissolved. Continue stirring and add ice-water and ice to the cooling bath, and cool the solution to 15 to 20 °C. As soon as this temperature range has been reached, continue stirring and add 96 g of sodium hydroxide, dissolved in 180 ml of distilled water (A.1.3), drop by drop through the dropping funnel. The temperature shall not rise above 20 °C during the addition of the sodium hydroxide solution (A.1.3). Rinse the dropping funnel with distilled water.

Pour the solution into a 1 litre one-mark volumetric flask, rinse the preparation vessel with distilled water, pour the rinsing water into the volumetric flask, and dilute to the mark. Shake the flask immediately to prevent any hydrolysis at the solution/water interface. The EWNN solution is light green, and fully transparent. It is immediately ready for viscometry.

NOTE — The amounts of chemicals given are for the preparation of 1 litre of EWNN solution.

Dimensions in millimetres



1. Dropping funnel for the addition of sodium hydroxide
2. Powder funnel for the introduction of iron(III) chloride (to be closed with a rubber stopcock after addition of the reagent
3. Stirrer
4. Thermometer
5. Cooling bath vessel
6. Jacket made from stainless steel
7. Cover made from black opaque poly(methyl methacrylate)
8. Ice and water

Figure — Apparatus for preparation of iron(III) sodium tartrate complex solution

Annex B

Pretreatment of bast fibres

(Forms part of the standard.)

Any fragments of straw, anasa and boll which the samples may contain shall be removed manually before the determination.

Moreover, in as much as bast fibres contain, depending on their degree of retting and the treatments they have undergone, from 10 % to 40 % (*m*/*m*) non-cellulosic substances, it is necessary to remove these substances by treatment of the sample in a boiling sodium hydroxide solution, followed by neutralization according to the following procedure :

Boil for 15 min, in a flask equipped with a reflux coolant, a quantity of 1,5 mol/l sodium hydroxide solution corresponding to a bath ratio of 100 : 1. The air having thus been removed from the solution, introduce the sample, keep it constantly immersed, using any appropriate device, and continue the boiling for 1 h.

Rinse the sample, constantly kept immersed, by continuous siphoning for 5 min with distilled or deionized water.

Immerse the sample in a solution of 0,1 mol/l acetic acid for 10 min and then rinse with distilled or deionized water until neutralization.

Wring the sample and then dry it without exceeding a temperature of 60 °C.