International Standard 307

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Plastics — Polyamides — Determination of viscosity number

Plastiques — Polyamides — Détermination de l'indice de viscosité

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Foreword

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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 307 was developed by Technical Committee ISO/TC 61, *Plastics*, and was circulated to the member bodies in May 1982.

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

Australia	Hungary	South Africa, Rep. of
Austria	India	Spain
Belgium	Iran	Sri Lanka
Brazil	Iraq	Sweden
Canada	Israel	Switzerland
China	Italy	Tanzania
Czechoslovakia	Japan	United Kingdom
Egypt, Arab Rep. of	Korea, Rep. of	USA
Finland	Netherlands	USSR
France	Poland	
Germany, F.R.	Romania	

No member body expressed disapproval of the document.

This second edition cancels and replaces the first edition (i.e. ISO 307-1977).

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Plastics — Polyamides — Determination of viscosity number

1 Scope and field of application

This International Standard specifies a method for the determination of the viscosity number of dilute solutions of polyamides in certain specified solvents. The method is applicable to the polyamides designated PA 6, PA 66, PA 69, PA 610, PA 612, PA 6(3)T, PA 11 and PA 12, as defined in ISO 1874/1, as well as to copolyamides and other polyamides that are soluble in one of the specified solvents under the specified conditions.

The method is not applicable to polyamides produced by anionic polymerization of lactams or produced with crosslinking agents; such polyamides are normally insoluble in the specified solvents.

The viscosity number is determined by the general procedure specified in ISO 1628/1, observing the particular conditions specified in this International Standard.

The determination of the viscosity number of a polyamide provides a measure of the relative molecular mass of the polymer.

2 References

ISO 599, *Plastics — Polyamides — Determination of matter extractable by boiling methanol.*

ISO/R 960, *Plastics — Determination of the water content in polyamides.*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks.*

ISO 1628/1, *Plastics — 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)]

ISO 1874/1, *Plastics — Polyamide homopolymers for moulding and extrusion — Part 1 : Designation.* [2)]

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

ISO 3451/4, *Plastics — Determination of ash — Part 4 : Polyamides.* [3)]

3 Definition

viscosity number (of a polymer) : The value given by the formula

$$\left(\frac{\eta}{\eta_o} - 1\right)\frac{1}{\varrho_P}$$

where

η is the viscosity of a solution of the polymer in the solvent;

η_o is the viscosity of the solvent, expressed in the same units as η;

ϱ_P is the concentration of the polymer in the solution.

The viscosity number is usually expressed in millilitres per gram.

NOTE — For further definitions relating to the viscometry of polymer solutions, see ISO 1628/1.

4 Principle

Measurement at 25 °C of the times of flow of the solvent and of a solution of the polyamide at a concentration of 0,005 g/ml, the same viscometer being used for both measurements. Calculation of the viscosity number from these measurements and from the known concentration of the solution.

1) At present at the stage of draft. (Partial revision of ISO/R 1628-1970.)

2) At present at the stage of draft. (Partial revision of ISO/R 1874-1971.)

3) At present at the stage of draft.

5 Reagents and materials

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

WARNING — Avoid contact with the skin and inhalation of any vapours of the solvents and cleaning liquids.

5.1 Solvents

5.1.1 Sulfuric acid, 96 ± 0,15 % (m/m) solution.

5.1.2 Formic acid, 90 ± 0,15 % (m/m) solution.

The solvent shall be stored in a brown glass bottle. Its concentration shall be checked at least every 2 weeks.

5.1.3 *m*-**Cresol,** meeting the following specifications :

Appearance : clear and colourless

m-cresol content : 99 % (m/m) min.

o-cresol content : 0,3 % (m/m) max.

Water content : 0,13 % (m/m) max.

m-cresol of the required purity can be obtained by distillation of chemically pure *m*-cresol, preferably in vacuo.

To avoid oxidation, nitrogen shall preferably be used for pressure compensation. Its purity may be checked by gas chromatography. The solvent shall be stored in a brown glass bottle.

5.2 Cleaning liquids

5.2.1 Chromic acid solution, prepared by mixing equal volumes of sulfuric acid (ϱ = 1,84 g/ml) and a saturated solution of potassium dichromate. If required, the chromic acid solution may be replaced by other, equally effective cleaning liquids.

5.2.2 Acetone, freshly distilled.

6 Apparatus

6.1 Vacuum drying cabinet, pressure less than 100 kPa.

6.2 Balance, accurate to 0,1 mg.

6.3 Volumetric flask, capacity 50 ml, complying with the requirements of ISO 1042, fitted with a ground glass stopper.

6.4 Shaking apparatus or **magnetic stirrer.**

6.5 Sintered glass filter with a pore size index between 40 and 100 µm (grade P 100), or **stainless steel sieve** with apertures of about 0,075 mm².

6.6 Viscometers, of the suspended-level Ubbelohde type, complying with the requirements of ISO 3105. The essential dimensions of the viscometers are shown in figure 1. For use with the formic acid solution (5.1.2) the inside diameter of the capillary shall be 0,58 mm ± 2 % (complying with the requirements of type 1 of ISO 3105). For use with the sulfuric acid solution (5.1.1) or *m*-cresol (5.1.3) the inside diameter of the capillary shall be 1,03 mm ± 2 % (complying with the requirements of type 2 of ISO 3105).

Other types of viscometers listed in ISO 3105 may be used, provided that the results are equivalent to those of the Ubbelohde viscometers specified above. However, in case of dispute, the Ubbelohde viscometers shall be used.

6.7 Thermostatic bath, capable of being maintained at 25 ± 0,05 °C.

6.8 Stop-watch, accurate to 0,1 s.

7 Preparation of test sample

7.1 Determination of extractable matter content

The content of extractable matter must be known. In principle, ISO 599, comprising extraction with boiling methanol, shall be used for this purpose. For polymers which themselves are soluble in boiling methanol, the same procedure shall be followed, using a different solvent. The latter shall be capable of dissolving the corresponding monomers and oligomers and of swelling, though not dissolving, the polymer.

7.2 Polyamides with extractable matter content not greater than 2,00 % (m/m)

No pretreatment is needed to remove the extractable matter from the sample.

7.3 Polyamides with extractable matter content greater than 2,00 % (m/m)

The ground polymer remaining after the extraction shall be dried by heating for 3 h at 80 to 100 °C under vacuum and used as the test sample.

8 Calculation of mass of test portion

8.1 Polyamides with extractable matter content not greater than 2,00 % (m/m)

Calculate the mass, m_c, in milligrams, of the test portion as follows :

$$m_c = \frac{250}{1 - \frac{w(\%)_1 + w(\%)_2 + w(\%)_3}{100}}$$

where

$w(\%)_1$ is the water content of the sample, expressed as a percentage by mass, determined according to ISO/R 960;

$w(\%)_2$ is the content of inorganic materials (for example fillers or glass fibres) of the sample, expressed as a percentage by mass, determined according to ISO 3451/4;

$w(\%)_3$ is the content of other materials (for example other polymers such as polyolefins or additives, such as flame-retardants) expressed as a percentage by mass, determined by appropriate methods.

The corrections for $w(\%)_1$, $w(\%)_2$ and $w(\%)_3$ need only be applied if they exceed 0,5 % (m/m) each.

8.2 Polyamides with extractable matter content greater than 2,00 % (m/m)

Use the material extracted and dried according to 7.3 as the test sample. Calculate the mass, m_c, in milligrams, of the test portion as follows :

$$m_c = \frac{250}{1 - \frac{w(\%)_2 + w(\%)_3}{100 - w(\%)_4}}$$

where

m_c, $w(\%)_2$ and $w(\%)_3$ have the same meanings as in 8.1;

$w(\%)_4$ is the content of extractable matter of the sample, expressed as a percentage by mass.

It has been assumed in this calculation that $w(\%)_2$ and $w(\%)_3$ have been determined in the unextracted sample and that the extracted and dried material will be kept dry, so that no correction for moisture in the test sample is required.

NOTE — When dissolved in 50 ml of solvent, a test portion weighing exactly m_c mg will give a solution containing (almost) exactly 5 mg of polymer per millilitre. For practical reasons masses of the test portion of $(m_c \pm 5)$ mg are allowed. The resulting actual polymer concentration is taken into account in the calculation of the viscosity number.

9 Selection of solvent

9.1 The value of the viscosity number of a polyamide depends on the solvent used.

Three different solvents are described in this International Standard : sulfuric acid solution (5.1.1), formic acid solution (5.1.2) and *m*-cresol (5.1.3). The flow times of the solvents shall be determined at least once each day that they are used (see 10.3). If the flow time of a solvent differs by more than 1 % from the initial value at the time of preparation, the solvent shall be discarded and fresh solvent prepared.

The solvent or solvents to be used for a particular polyamide are specified below.

9.2 For PA 6, 66, 69, 610 and corresponding copolyamides, the sulfuric acid or formic acid solution shall be used as solvent, unless these polyamides contain additives that liberate gases in acidic solvents, in which case *m*-cresol shall be used as the solvent.

NOTE — Graphs for interconversion of the viscosity numbers determined in these two solvents are presented in figure 2. The reliability of the conversion is discussed in 13.1.

9.3 For PA 612, 6(3)T and corresponding copolyamides, the sulfuric acid solution or *m*-cresol shall be used as solvent.

NOTE — Graphs for interconversion of the viscosity numbers determined in these two solvents are presented in figure 3. The reliability of the conversion is discussed in 13.2.

9.4 For PA 11, PA 12 and PA 11/12 copolymers, *m*-cresol shall be used as solvent.

9.5 For other polyamides, any of the three solvents may be used.

10 Procedure

10.1 Cleaning of viscometer

Clean the viscometer (6.6) prior to the first use, again after discordant readings (for example when two successive determinations of the efflux time of the solvent differ more than 0,4 s) and, further, at intervals during regular use. For this purpose allow it to stand for at least 12 h filled with a cleaning agent (5.2), for example the chromic acid solution (5.2.1). Remove the cleaning agent, rinse the viscometer with water, then with the acetone (5.2.2) and dry, for example by a slow stream of filtered air or in the vacuum drying cabinet (6.1).

After each determination, drain the viscometer, rinse with the solvent, then with water, followed by the acetone (5.2.2) and dry as described above.

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

10.2 Preparation of test solution

Weigh, to the nearest 0,2 mg, a test portion of $(m_c \pm 5)$ mg, where m_c is the mass calculated according to clause 8, working rapidly to minimize moisture pick-up by the polymer. If the weighing takes more than 2 min, reject the material and begin another weighing.

Transfer the test portion to the 50 ml volumetric flask (6.3) and add about 40 ml of the solvent selected according to clause 9. Close the flask and shake, or stir with the magnetic stirrer (6.4) the contents until the polymer has dissolved. This may take from approximately 0,5 h to several hours, depending on the type of polyamide and the particle size of the test portion. When the sulfuric acid or formic acid solution is used as the solvent, the temperature shall not exceed 30 °C. When the *m*-cresol is used as the solvent, the temperature may be raised to 95 to 100 °C. If, in the latter case, dissolution takes more than 2 h, this shall be reported.

When dissolution is complete, cool the solution to approximately 25 °C, dilute to the mark with the solvent and mix well.

The temperature of the solution during dilution shall lie between 23 and 27 °C. If the magnetic stirrer (6.4) is used, remove it from the solution before dilution and rinse it with the solvent, adding the rinsings to the flask before further dilution.

NOTE — In the case of polyamides with extremely high relative molecular masses, solutions free from the so-called streaking phenomenon cannot always be obtained, in spite of prolonged periods of shaking or stirring. Such test solutions may only be used for mutual comparison with similar products.

10.3 Measurement of flow times

Filter the solution through the sintered glass filter (6.5) or the metal sieve into tube L of the viscometer (see figure 1). Alternatively, centrifuge the solution at a rotational frequency of approximately 50 s^{-1} and pour the clear supernatant liquid into the viscometer (6.6). The volume of liquid shall be such that, after draining, the level lies between the filling marks. Preferably, the filling should be done with the viscometer out of the thermostatic bath (6.7) to avoid contamination of the bath in case of accidental spills.

Mount the viscometer in the thermostatic bath maintained at 25 ± 0,05 °C, ensuring that tube N is vertical and that the upper graduation mark, E, is at least 30 mm below the surface of the liquid in the bath. Allow at least 15 min for the charged viscometer to attain the temperature of the bath.

Close tube M and blow or draw the liquid into the upper bulb of tube N using a rubber bulb or similar equipment. Close tube N. Open tube M so that the liquid drops away from the lower end of the capillary tube. Open tube N and measure the flow time, to the nearest 0,2 s, as the time taken for the bottom of the meniscus to pass from mark E to mark F. With cloudy solutions, view the top of the meniscus. Repeat the measurement of the flow time until two successive values agree within 0,25 %. Take the mean of these two values as the flow time of the solution.

Determine the mean flow time of the solvent in the same viscometer and in the same manner as that of the solution. Measure the mean flow time only once for each series of determinations; however, measure the time at least once each day the solvent is used. If two successive determinations of the mean flow time differ more than 0,4 s, clean the viscometer (see 10.1).

With each polyamide sample, carry out at least two determinations of the viscosity number, each time using a fresh solution, until two successive values meet the repeatability requirement corresponding to the solvent used (see clause 12). Report the mean of these two values, rounded off to the nearest unit, as the viscosity number of the sample.

11 Expression of results

Calculate the viscosity number J, in millilitres per gram, from the equation :

$$J = \left(\frac{t}{t_0} - 1\right)\frac{1}{\varrho_P}$$

where

t is the flow time of the solution;

t_0 is the flow time of the solvent;

ϱ_P is the concentration of the polymer in grams per millilitre of solution.

NOTE — Density difference and kinetic energy corrections can be neglected in this method; therefore, in calculating the viscosity number of the polymer, the ratio of the viscosities of the solution and the solvent (see clause 3) can be replaced by the ratio of the corresponding times of flow. Furthermore, the concentration of the polymer may be expressed as grams per millilitre of solvent instead of grams per millilitre of solution, without introducing appreciable error.

12 Repeatability and reproducibility

The repeatability and reproducibility of the determination of the viscosity number depend on the solvent used. The values are given in the following table :

Table

Solvent	Repeatability %	Reproducibility %
Sulfuric acid solution (5.1.1)	2	5
Formic acid solution (5.1.2)	2	10
m-Cresol (5.1.3)	3	10

NOTE — The repeatabilities and reproducibilities were determined in an interlaboratory investigation carried out in 1982. Seven laboratories participated in this investigation. The programme included 11 samples of PA 6, 9 of PA 66, 3 of PA 69, 4 of PA 610, 5 of PA 612 and 2 of PA 6(3)T. The viscosity numbers of the samples were determined in duplicate in both solvents according to this International Standard.

13 Interconversion of the viscosity numbers determined in different solvents

The relation between the viscosity numbers determined in different solvents was determined in the interlaboratory investigation referred to in the note to clause 12.

13.1 Viscosity numbers in 96 % (*m*/*m*) sulfuric acid and 90 % (*m*/*m*) formic acid, respectively

Graphs of the relation between the viscosity numbers of PA 6, 66, 69 and 610 determined in the sulfuric acid solution (5.1.1) and in the formic acid solution (5.1.2) are presented in figure 2.

The value measured by one laboratory in one of the solvents will, in general, differ from the value obtained by conversion from a measurement by another laboratory in the other solvent. The 95 % confidence intervals for this difference, as percentages of the converted values, are

for PA 6 ± 9 %

for PA 66 ± 9 %

for PA 69 ± 10 %

for PA 610 ± 14 %

13.2 Viscosity numbers in 96 % (m/m) sulfuric acid and *m*-cresol, respectively

Graphs of the relation between the viscosity numbers of PA 612 and PA 6(3)T in the sulfuric acid solution (5.1.1) and in *m*-cresol (5.1.3) are presented in figure 3.

For PA 612, the 95 % confidence interval for the difference between an actually measured value and a converted value depends on the direction of the conversion. The intervals, as percentages of the converted values, are

value in *m*-cresol converted to value in 96 % (m/m) sulfuric acid : ± 17 %

value in 96 % (m/m) sulfuric acid converted to value in *m*-cresol : ± 9 %

NOTE — The interlaboratory investigation did not allow for the determination of the confidence interval(s) for the conversion of the viscosity numbers of PA 6(3)T.

14 Test report

The test report shall include the following information :

a) reference to this International Standard;

b) complete identification of the material tested;

c) if the sample contains more than 0,5 % (m/m) of other materials according to 8.1, description of the method used for their determination;

d) the solvent used;

e) if longer than 2 h, the time required to dissolve a sample in *m*-cresol at 95 to 100 °C;

f) the viscosity number (individual values and arithmetic mean of the two determinations).

Dimensions in millimetres

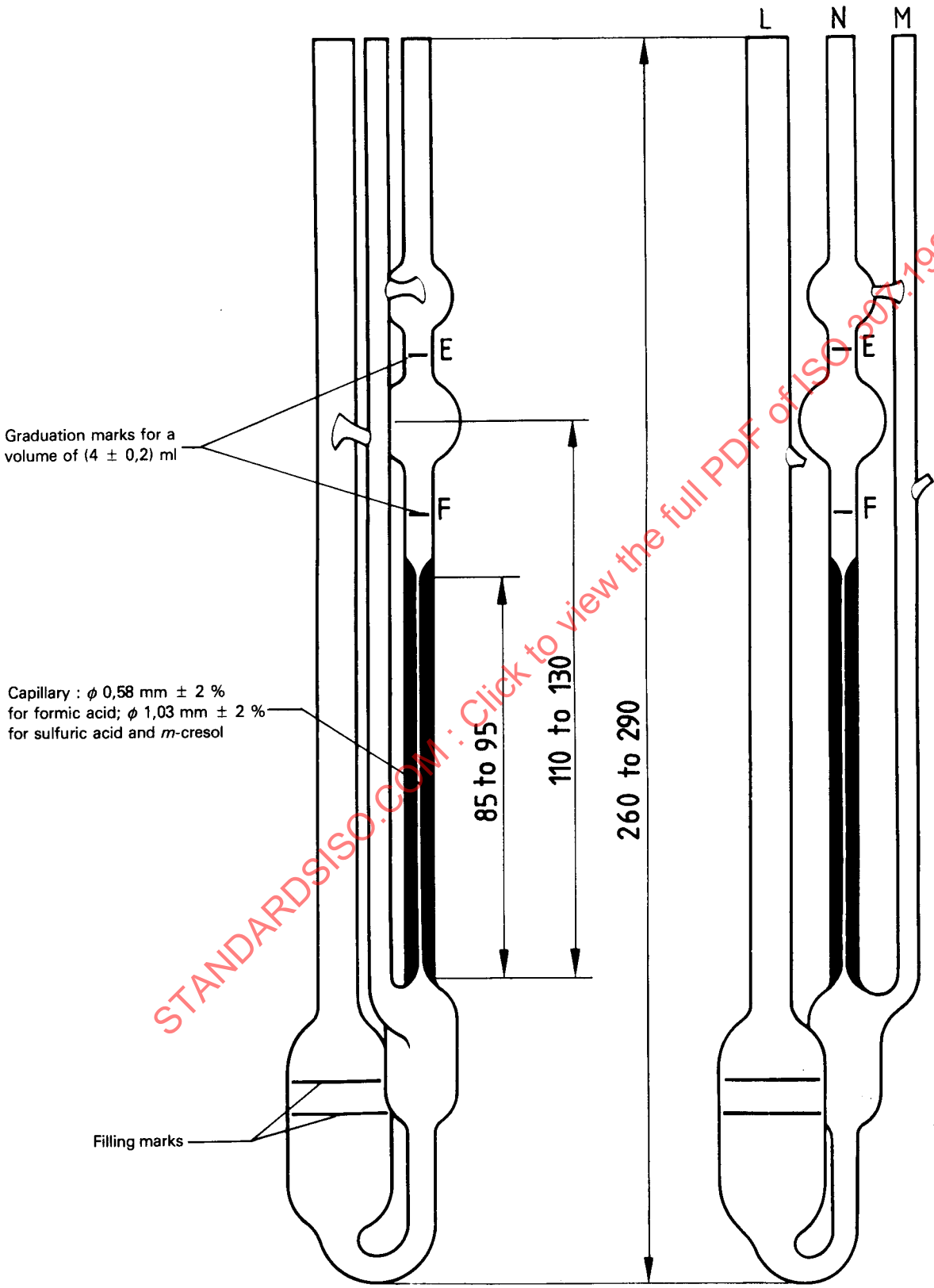

Figure 1 — Ubbelohde viscometer