UDC 678.675

Ref. No.: ISO/R 600 - 1967 (E)

ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION
R 600

PLASTICS

DETERMINATION OF THE VISCOSITY RATIO OF POLYAMIDES IN CONCENTRATED SOLUTION

1st EDITION
August 1967

For each individual country the only valid standard is the national standard of that country.

Printed in Switzerland

Also issued in French and Russian. Copies to be obtained through the national standards organizations.

BRIEF HISTORY

The ISO Recommendation R 600, *Plastics – Determination of the viscosity ratio of polyamides in concentrated solution,* was drawn up by Technical Committee ISO/TC 61, *Plastics,* the Secretariat of which is held by the United States of America Standards Institute (USASI).

Work on this question by the Technical Committee began in 1960 and led, in 1961, to the adoption of a Draft ISO Recommendation.

This first Draft ISO Recommendation (N° 513) was circulated in June 1962 to all the ISO Member Bodies for enquiry. As the results of this consultation were not considered satisfactory, the Technical Committee presented a second Draft ISO Recommendation which was circulated to all the Member Bodies in July 1964 and which was approved, subject to a few modifications of an editorial nature by the following Member Bodies:

Austria
Belgium
Canada
Chile
Czechoslovakia
Denmark
Finland
Germany
India
Italy
Japan
Korea, Rep. of
Netherlands
New Zealand
Poland
Romania
South Africa
  Rep. of
Sweden
U.A.R.
United Kingdom
U.S.A.
U.S.S.R.

One Member Body opposed the approval of the Draft:

France

The second Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in August 1967, to accept it as an ISO RECOMMENDATION.

ISO Recommendation R 600 August 1967

PLASTICS

DETERMINATION OF THE VISCOSITY RATIO OF POLYAMIDES IN CONCENTRATED SOLUTION

1. SCOPE

1.1 This ISO Recommendation describes a test method for determining the viscosity ratio of a solution of polyamides in formic acid. The method is applicable to those polyamides only that are soluble and do not degrade in formic acid in the specified conditions and which give reproducible results under the conditions of test described below. The times of flow of the solvent and of a solution containing 8.4% by mass (11 g/100 ml) of polyamide in the solvent are measured at 25 °C by conventional methods and the viscosity ratio is calculated from these measurements. Mathematical corrections for kinetic energy are small in this method and are not applied.

1.2 If a substantial amount of monomer* is known to be present in the sample, the amount should be determined in accordance with ISO Recommendation R 599* and indicated in the test report. The presence of monomer affects considerably the determination of viscosity ratio of certain types of polyamides. If the sample contains an additive or filler which would affect the viscosity measurement, it should be removed by a procedure agreed between the contracting parties.

1.3 This method is intended for use in specifications for polyamides for the purpose of comparing different types or for control purpose during manufacture. To get an insight into the molecular structure of polyamides, viscosity is normally determined in dilute solution in accordance with ISO Recommendation R 307, *Determination of the viscosity number of polyamides in dilute solution.*

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* In this text, monomer is understood as "monomer and low molecular mass polymer" in accordance with ISO Recommendation R 599, *Plastics — Determination of the percentage of extractable materials in polyamides.*

Dimensions in millimetres

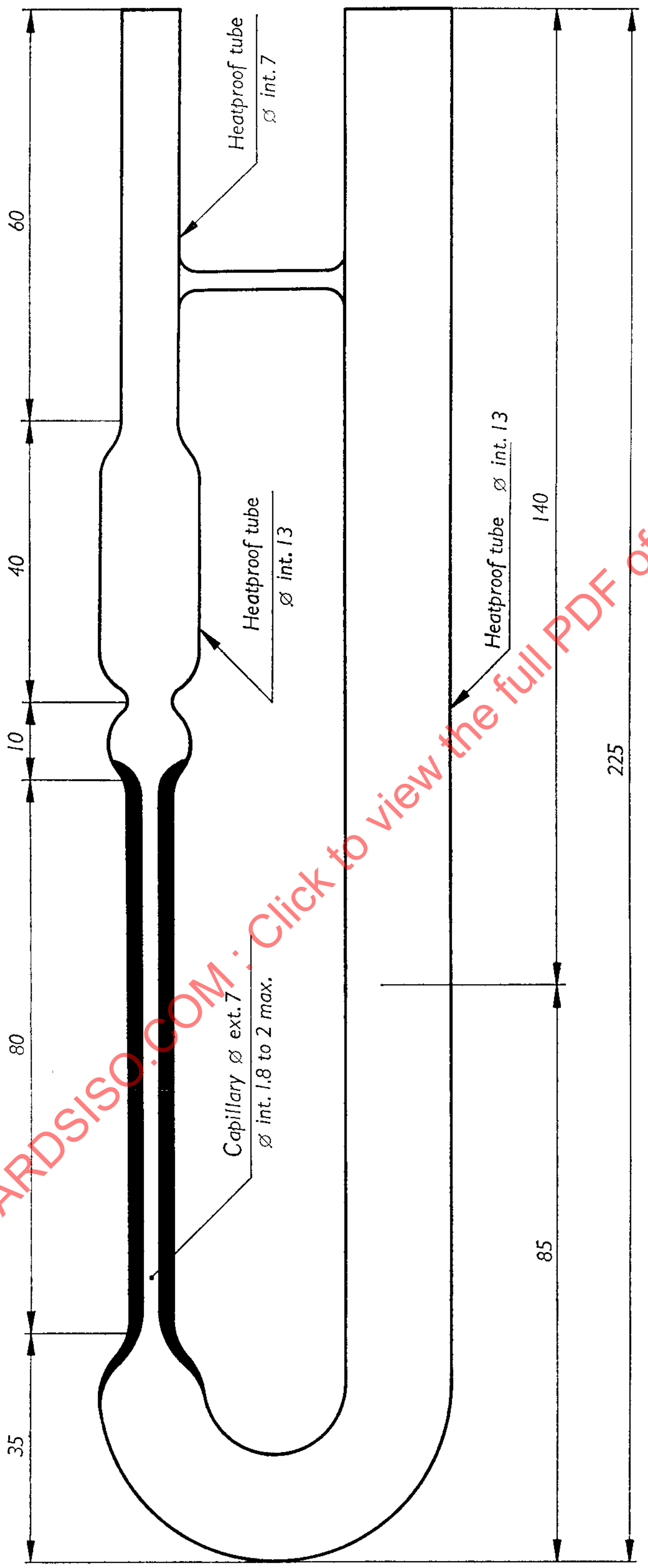

FIGURE — **Viscometer for viscosity ratio**

2. REAGENTS

2.1 The solvent and chemicals should consist of the following.

2.1.1 *Formic acid solvent,* containing 90 ± 0.2% by mass of chemically pure formic acid, the remainder being water (see Annex A, page 9).

2.1.2 *Glycerol,* analytical grade.

2.1.3 *Cleaning liquids,* (distilled water, concentrated sulphuric acid, saturated aqueous solution of potassium dichromate, chemically pure hydrochloric acid, ethanol and acetone).

2.2 Safety measures

When cleaning viscometers which have previously been used for viscosity determinations, care should be taken to ensure that the viscometers are first washed out with the solvent and with water before attempting to clean them with concentrated sulphuric acid and potassium dichromate mixture.

3. APPARATUS

The apparatus should consist of the following:

(*a*) *Pycnometer.*

(*b*) *Water-bath,* maintained at 25 ± 0.1 °C.

(*c*) *Viscometer,* type Ostwald, with a flow time for water of 10 to 15 seconds (for measuring the viscosity of the polyamide solution) (see Figure, page 4).

(*d*) *Viscometer,* type Ostwald, with a flow time for water of 100 to 200 seconds (for measuring the viscosity of formic acid).

(For these two viscometers any other type that can be shown to give the same results may be used with appropriate modification of procedure).

(*e*) *Stop-watch,* reading to 0.1 second.

(*f*) *Pipette,* 7 ml type Ostwald.

(*g*) *Burette.*

(*h*) *Flask,* 150 ml, fitted with ground-glass stopper.

(*i*) *Brown glass bottle,* connected to an automatic burette and fitted with a calcium chloride tube on the air inlet.

(*j*) *Balance,* to weigh to 0.0001 g.

(*k*) *Suitable means* for reducing coarse materials to a finer state of division.

(*l*) *Mechanical stirrer.*

(*m*) *Oven,* maintained at 125 °C or vacuum oven (2 mm mercury) at 100 °C.

(*n*) *Sieve,* stainless steel, mesh openings 3.15 mm.

4. PREPARATION OF SAMPLE

The sample should be in the form of small pieces or powder that pass through the sieve with mesh openings 3.15 mm. The water content, determined in accordance with ISO Recommendation R . . . * should be lower than 1.0% and, if necessary, the sample should be dried by a suitable method. For instance, if the polymer does not contain sublimable monomer, it may be dried in a vacuum oven at a temperature not higher than 80 °C for about 24 hours.

5. PROCEDURE

5.1 Calculate the constants of the viscometers with the aid of mixtures of glycerol and water of known viscosity (see Annex B, page 10).

5.2 Dilute the formic acid with distilled water to a concentration of 90 ± 0.2% formic acid (see Annex A, page 9).

5.3 Before it is first used and after discordant readings if any, the viscometer should be cleaned at first with the solvent and then successively with water and with a mixture of equal volumes of concentrated sulphuric acid and a saturated solution of potassium dichromate in water. After rinsing with distilled water it should be washed with 95 to 96% ethanol, followed by acetone and dried by drawing through it a stream of air free from dust. Between successive determinations, the viscometer should be washed several times with pure hydrochloric acid, followed by water and acetone and dried as described.

5.4 Immerse the viscometer for measuring the viscosity of formic acid in the water-bath maintained at 25 ± 0.1 °C and measure a suitable quantity (about 7 ml for usual viscometers) of the formic acid solvent 90% into the viscometer using an Ostwald pipette. After 15 minutes immersion, the time of flow of the formic acid should be determined four times, discarding the first measurement, by bringing the liquid above the upper mark by blowing dry air through a rubber tube and measuring the time for the surface of the liquid to sink from the upper to the lower mark. The efflux times should agree to within 0.5%, if not the test should be repeated. The time of flow is the average of three determinations. After the viscometer has been emptied, it should be cleaned, rinsed and dried as described above.

5.5 The relative density of the formic acid solvent should be determined at 25 ± 0.1 °C after 30 minutes in the water-bath using the pycnometer with 0.1% accuracy.

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* *Determination of the water content in polyamides*, at present Draft ISO Recommendation No. 1004.

5.6 Weigh about 5.5 g of dry polyamide to the nearest 0.001 g in the 150 ml flask fitted with a ground-glass stopper. By means of a burette, add formic acid solvent 90% in a suitable quantity to make up a solution containing 5.5 ± 0.001 g of the dry polyamide per 50 ml of the formic acid solvent; put the flask in the mechanical stirrer until complete dissolution is reached (45 minutes are generally sufficient). In the case of polyamides 610 it is sufficient to heat at 50 °C until it is dissolved. Immerse the viscometer for measuring the polyamide solution in the water-bath and measure a suitable quantity (about 7 ml for usual viscometers) of the polyamide solution into the viscometer using an Ostwald pipette; when certain types of viscometers are used, a preliminary filtration of the solution through coarse filter paper may be required. After 15 minutes immersion, the time of flow of the polyamide solution should be determined four times as described for the determination of the viscosity of the formic acid, discarding the first measurement. The efflux times should agree to within 0.5%; if not the test should be repeated. The time of flow is the average of three determinations. The remainder of the solution is used for determining the relative density of the solution at 25 ± 0.1 °C after 30 minutes in the water-bath. The relative density should be determined using the pycnometer with 0.1% accuracy.

6. CALCULATION AND EXPRESSION OF RESULTS

Calculate the viscosity ratio by substituting flow times, viscometer constants and relative densities in the following equations:

$$\eta_r = \frac{\eta_s}{\eta_a} = \frac{K_s}{K_a} \times \frac{T_s}{T_a} \times \frac{d_s}{d_a}$$

where

η_r = viscosity ratio,

η_s = viscosity of the solution, expressed in centipoises,

η_a = viscosity of the formic acid, expressed in centipoises,

K_s = constant of the viscometer used for measuring the viscosity of the solution,

K_a = constant of the viscometer used for measuring the viscosity of the formic acid,

d_s = relative density of the solution,

d_a = relative density of the formic acid,

T_s = time of flow of the solution, expressed in seconds,

T_a = time of flow of the formic acid, expressed in seconds.

Two independent determinations of η_s should be carried out; the results should agree within 0.30 centipoise.

7. TEST REPORT

The test report should include the following:

(*a*) Complete identification of the material tested, including type, source, manufacturer's code numbers and trade name;

(*b*) Monomer content;

(*c*) Details of treatment of the sample before the test;

(*d*) Conditions of drying;

(*e*) Type of viscometer used;

(*f*) Viscosity ratio;

(*g*) Test conditions, if any, deviating from those of the present ISO Recommendation;

(*h*) Date of tests.

ANNEX A

PREPARATION OF FORMIC ACID SOLVENT

The formic acid solution to be used should contain 90 ± 0.2% by mass of chemically pure formic acid. To prepare this solution, commercially concentrated formic acid analytical grade is diluted with distilled water to a formic acid concentration of 90% or more. The exact acid content of this solution is determined by titration with sodium hydroxide and phenolphthalein. The amount of distilled water to be added, if the solution does not already contain between 89.8 and 90.2% formic acid, should be calculated from the results of the titration. After adding this water, the acid content should be determined again by titration as indicated above. The formic acid solution should be stored in a brown bottle closed with a ground-glass stopper. In use the stopper can be connected to an automatic burette that is provided with a calcium chloride tube on the air inlet. The titre of the formic acid should be checked every two weeks.