IEC 60450

Edition 2.1 2007-07

INTERNATIONAL STANDARD

NORME INTERNATIONALE

Measurement of the average viscometric degree of polymerization of new and aged cellulosic electrically insulating materials

Mesure du degré de polymérisation moyen viscosimétrique des matériaux isolants cellulosiques neufs et vieillis à usage électrique

IEC 60450:2004+A1:2007

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

COMMISSION ELECTROTECHNIQUE INTERNATIONALE

ICS 17.220.99; 29.035.01

ISBN 2-8318-9234-1

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

MEASUREMENT OF THE AVERAGE VISCOMETRIC DEGREE OF POLYMERIZATION OF NEW AND AGED CELLULOSIC ELECTRICALLY INSULATING MATERIALS

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International Standard IEC 60450 has been prepared by subcommittee 15E: Methods of test, of IEC technical committee 15: Insulating materials.

This second edition cancels and replaces the first edition, published in 1974, and constitutes a technical revision. Experience has indicated the need for improved description of the experimental method. It describes a revised procedure that overcomes the limitations of the first edition.

This consolidated version of IEC 60450 consists of the second edition (2004) [documents 15E/229/FDIS and 15E/235/RVD] and its amendment 1 (2007) [documents 112/49/CDV and 112/66/RVC].

The technical content is therefore identical to the base edition and its amendment(s) and has been prepared for user convenience.

It bears the edition number 2.1.

A vertical line in the margin shows where the base publication has been modified by amendment 1.

This publication has been drafted in accordance with the ISO/IEC Directives, Part 3.

The committee has decided that the contents of the base publication and its amendments will remain unchanged until the maintenance result date indicated on the IEC web site under "http://webstore.iec.ch" in the data related to the specific publication. At this date, the publication will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

INTRODUCTION

Experience has indicated the need for an improved description of the experimental method for the reproducible determination of the average viscometric degree of polymerization of new and aged cellulosic electrically insulating material.

The major error appears to arise from oxidative degradation occurring during processing and effluxing. Other significant factors include the need to ensure that all of the material is dissolved and used, as well as the effect of the speed of effluxing.

MEASUREMENT OF THE AVERAGE VISCOMETRIC DEGREE OF POLYMERIZATION OF NEW AND AGED CELLULOSIC ELECTRICALLY INSULATING MATERIALS

1 Scope

This International standard describes a standardized method for the determination of the average viscometric degree of polymerization ($\overline{DP}_v$) of new and aged cellulosic electrically insulating materials. It may be applied to all cellulosic insulating materials such as those used in transformer, cable or capacitor manufacturing.

The methods described can also be used for the determination of the intrinsic viscosity of solutions of chemically modified kraft papers, provided that these dissolve completely in the selected solvent.

Caution should be taken if the method is applied to loaded kraft papers.

NOTE Within a sample of material, all the cellulose molecules do not have the same degree of polymerization so that the mean value measured by viscometric methods is not necessarily the same as that which may be obtained by, for instance, osmotic or ultra centrifuging methods.

2 Normative references

The following referenced documents are indispensable for the application 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.

IEC 60814, *Insulating liquids – Oil-impregnated paper and pressboard – Determination of water by automatic coulometric Karl Fischer titration*

ISO 287, *Paper and board – Determination of moisture content – Oven-drying method*

ISO 3105, *Glass capillary kinematic viscometers – Specifications and operating instructions*

3 Terms, definitions and symbols

For the purposes of this document, the following terms, definitions and symbols apply.

3.1 Terms and definitions

3.1.1
degree of polymerization of a cellulose molecule
number of anhydrous-β-glucose monomers, $C_6H_{10}O_5$, in the cellulose molecule

NOTE Figure 1 shows the chemical structure of cellulose.

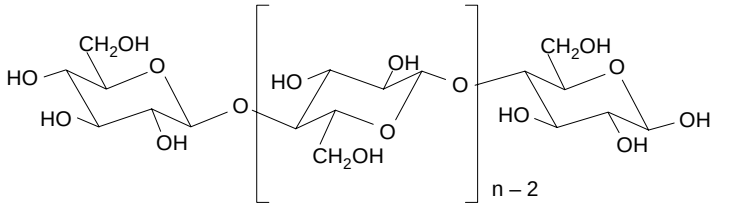

Figure 1 – Chemical structure of cellulose

3.1.2
Cuen
1 mol/l aqueous solution of bis(ethylenediamine)copper(II) hydroxide $Cu(H_2NCH_2CH_2NH_2)_2(OH)_2$. [CAS 14552-35-3][1]

NOTE In some countries the abbreviation CED is used for bis(ethylenediamine)copper(II) hydroxide.

3.1.3
paper
cellulosic electrically insulating material, such as paper, presspaper, pressboard and components made thereof

NOTE In the present document such paper is termed “paper”.

3.2 Symbols

Symbols used in this standard are shown in Table 1.

Table 1 – Symbols

Symbol	Definition
α	Mark Houwink constant of the cellulose monomer
c_{Cu}	Molarity of copper in Cuen solution
c_{En}	Molarity of ethylenediamine in Cuen solution
C_0, C_1 and C_2	Constants for viscometer tubes 0, 1 and 2 respectively
c	Concentration of solution
$\overline{DP_v}$	Average viscometric degree of polymerization
ν	Kinematic viscosity of solution
ν_0	Kinematic viscosity of solvent
K	Mark Houwink characteristic constant of the polymer/solvent system
k	Constant in Martin's formula
m_D	Mass of dry paper
m_T	Mass of swollen paper in tared vessel
m_{H_2O}	Mass of added water
ρ_{H_2O}	Density of water
v_{H_2O}	Volume of added water
v_{Cu}	Volume of added Cuen
$[\nu]$	Intrinsic viscosity
ν_s	Specific viscosity
t_{1A}, t_{1B}	Efflux time for tests A and B on dissolved specimen 1
t_{2A}, t_{2B}	Efflux time for tests A and B on dissolved specimen 2
t_{0A}, t_{0B}	Efflux time for tests A and B on pure solvent
t_0	Efflux time for diluted Cuen solvent (50 % Cuen and 50 % water)
t_S	Efflux time for Cuen dissolved specimen

[1] Chemical Abstracts Service (CAS) Registry numbers®

4 Principle

The specific viscosity ν_s of a solution of the paper in Cuen is determined. From this result the intrinsic viscosity $[\nu]$ of the solution is deduced, and from this the degree of polymerization is calculated.

NOTE Solutions of cellulose are non-Newtonian fluids. Their viscosity decreases as the flow velocity increases (sometimes known as "structural viscosity"). Although the viscosity of dilute solutions varies only slightly with the gradient of the velocity modulus, the use of conditions outside those specified in this standard may result in unacceptable errors.

Specific viscosity ν_s is defined by

$$\nu_s = \frac{\text{viscosity of paper solution} - \text{viscosity of solvent}}{\text{viscosity of solvent}} \quad (1)$$

Intrinsic viscosity $[\nu]$ is defined by

$$\nu = \lim_{c \to 0} \left[\frac{\nu_s}{c} \right] \quad (2)$$

where c is the concentration of the solution.

The average viscometric degree of polymerization $\overline{DP_\nu}$ (the ratio of the mean molecular mass indicated viscometrically to the molecular mass of the monomeric unit) is related to the intrinsic viscosity $[\nu]$ by the equation:

$$[\nu] = K \overline{DP_\nu}^{\alpha} \quad (3)$$

K and α being characteristic Mark Houwink coefficients of the polymer-solvent system (paper/Cuen) and of the monomer respectively.

The intrinsic viscosity $[\nu]$ is calculated from the specific viscosity ν_s and the concentration c by Martin's empirical formula:

$$\nu_s = [\nu] \cdot c \cdot 10^{k[\nu] \cdot c} \quad (4)$$

where k is Martin's constant. For kraft papers k = 0,14.

5 Apparatus and reagents

NOTE 1 Apparatus and reagents for the preparation of Cuen are given separately in Annexes A and B.

During the analysis, unless otherwise specified, use only reagents of recognized analytical grade and only distilled /de-ionized water or equivalent quality.

A glass fronted, thermostatically controlled bath, suitable for the immersion of the viscometer tubes, capable of maintaining a temperature of 20 °C to within ±0,1 K and fitted with appropriate means for illuminating the tubes. It shall be fitted with a means of displaying the temperature to within an accuracy of ±0,05 K.

NOTE 2 To obtain the required degree of temperature stability, it may be necessary to use a refrigeration unit in addition to the bath heater.

Calibrated capillary type viscometer tubes according to ISO 3105 with a capillary constant of 0,005 or 0,01. Non calibrated tubes can be used as long as the viscosities of the Cuen solvent and solution of paper in Cuen are measured in the same tube.

A timer/stopwatch capable of measuring to within an accuracy of ±0,1 s.

Suitable blender or grinder to “activate” the paper sample to allow dissolution.

Suitable vials (typically 25 ml to 50 ml) with lids (not paper) that make an effective seal for the preparation of paper/Cuen solution. Alternative glass containers can be used. However, these shall be sealed during dissolution to minimize oxidative degradation of the Cuen.

Cuen (see Annex A).

Distilled or de-ionized water.

Low oxygen content nitrogen supply (minimum 99,9 % nitrogen).

Acetone minimum 99,0 % pure.

Pentane or hexane minimum 99,0 % .

20 % aqueous nitric acid.

Vented drying oven thermostatically controlled to 105 °C ± 2 K.

Analytical balance capable of weighing 20 g to within ±0,1 mg.

Soxhlet extractor.

Pipette to deliver ±0,1 ml.

Mechanical shaker capable of holding the glass vials used to prepare the paper/Cuen solutions or a magnetic stirrer can be used to dissolve the paper/Cuen solution.

6 Specimens

6.1 Preparation of specimens

The paper under evaluation shall only be handled with gloves or forceps. It shall not be touched by hand.

Pressboard with a thickness greater than 1 mm, shall be split into layers of less than 1 mm.

The samples shall be cut into pieces sufficiently small to facilitate the subsequent processes. For very thin paper, the material may be cut into small pieces using scissors.

6.1.1 Impregnated papers

Impregnated papers shall be degreased before weighing and absorbing solution.

Wash a sufficient amount of the paper under evaluation so as to give a degreased mass of approximately 3 g in a Soxhlet using pentane or hexane for a minimum of five washings, or by rinsing in five portions of fresh pentane or hexane in an appropriate glass vessel. Allow the degreased material to dry and leave it exposed to the atmosphere until equilibrium with the atmospheric humidity is reached. Two portions of the paper are separated, one for use in the $\overline{DP}_v$ determination and one for use in the moisture determination.

6.1.2 Non-impregnated papers

Take a sample having an approximate mass of 3 g and continue with the test procedures. Two portions of the paper are separated, one for use in the $\overline{DP}_v$ determination and one for use in the moisture determination.

7 Experimental procedure

7.1 Measurement of water content of paper

Measure the water content according to ISO 287 or IEC 60814.

The water content shall be measured at the same time as the Cuen/paper solution is prepared.

7.2 Determination of viscosity

7.2.1 Number of test specimens

One specimen shall be used in a preliminary experiment to obtain data on which to base a valid test.

One specimen shall be used for each valid test, unless otherwise specified. If $[\nu] \cdot c$ of the preliminary experiment is outside of the range 0,5 to 1,5, two test specimens shall be used.

7.2.2 Concentration of the solution

The concentration of the solution to be used is dependent upon the expected $\overline{DP}_v$ value as given in the following table.

Table 2 – $\overline{DP}_v$ values of specimen

Specimen condition	Expected $\overline{DP}_v$	Approximate resulting concentration g/dl or %
New	1 000 to 2 000	0,05 to 0,15
Good	650 to 1 000	0,08 to 0,25
Average	350 to 650	0,15 to 0,45
Aged	< 350	0,25 to 0,80

NOTE The purpose of this operation is to achieve a fixed value of the product's intrinsic viscosity and concentration which is in the range $0,5 \leq [\nu] \cdot c \leq 1,5$. The higher the product of $[\nu] \cdot c$ the more accurate its precision.

7.2.3 Fibre separation

The cellulose fibres need to be separated in order to facilitate dissolution in Cuen. Two techniques are described as follows.

7.2.3.1 Dry fluffing

Fluff the material in a suitable blender or grinder. Ensure enough sample remains after fluffing as some sample may be lost during the process. The temperature rise during fluffing must not cause any detrimental effect to the specimen.

The fluffed sample is left to acclimatize with the atmospheric humidity before determining the water content.

Weigh the necessary amount of sample to the nearest 0,1 mg according to Table 2 and place it in a suitable vessel for dissolution. Calculate the mass of dry paper as m_D.

Add water and allow the fibres to disperse.

7.2.3.2 Wet mulching

Weigh the necessary amount of sample to the nearest 0,1 mg and place in the blender cup with sufficient distilled/de-ionized water to cover it. Mulch the paper by operating the blender at approximately 18 000 r/min for about 30 s or until the fibres are well separated. After mulching, remove the excess water by either centrifuging or using a Grade 3 sintered glass filter.

Place the swollen paper in a tared vial and weigh it to within ±0,1 mg (m_T). Calculate the total mass of water (i.e. original mass of water plus the mass of water remaining after mulching) by subtracting the dry paper mass (m_D) and the tare mass from m_T.

Calculate the quantity of water required to make the total water content up to 10,000 g. Selecting this amount to within ±0,5 mg, use a sufficient amount of this water to rinse any residual paper out of the centrifuge/filter into the vial and then place the remainder of the water into the vial. Alternatively, make up to 10,000 g, then weigh to within ±0,5 mg and calculate the concentration.

7.2.4 Dissolution of specimen

Before use, the Cuen solution sample shall be inspected, refurbished and verified as follows:

- ensure that the solution contains no precipitate by filtering or decanting;
- using the method described in Annex C, verify that the ratio $\frac{c_{En}}{c_{Cu}} = 2{,}0 \pm 0{,}1$
- in the event of non-conformance, reject the solution and prepare a new sample.

Transfer into the same vial the same volume (±0,1 ml, using a pipette) of Cuen as the quantity of water already added to the cellulose fibres.

If there is some contact between the solution and the atmospheric air in the vial, flush the vial with nitrogen and shake by hand to ensure good mixing of the components. Flush the vial again with nitrogen and seal it to ensure a low oxygen environment. Preferably the vial should be flushed with nitrogen throughout the whole time of dissolution.

NOTE 1 The solution is placed in a nitrogen environment and sealed in the vial because the alkaline solvent is susceptible to oxidative degradation.

Mechanically shake or stir the specimen until dissolution is complete.

NOTE 2 The time taken is dependent upon the type of paper and the extent of degradation.

a) For heavily aged papers ($\overline{DP}_v < 350$) a shaking time of 1h to 2 h is usually adequate.

b) For most papers ($\overline{DP}_v > 350$) shaking for a period of 16 h (overnight) usually ensures complete dissolution.

c) Some types of new or nearly new papers do not dissolve easily at room temperature. The dissolution rate may be increased by using a magnetic stirrer to stir the specimen at 4 °C, in a refrigerator overnight. The use of a few glass balls can also aid the dispersion of the cellulose fibres.

When testing heavily degraded papers ($\overline{DP}_v < 150$) they should be tested immediately after dissolution.

7.2.5 Determination of the viscosity

7.2.5.1 Selection and filling of the viscometer tube

Select a viscometer tube and support it in a constant temperature bath at 20 °C ± 0,1 K.

Ensure that the viscometer tube is dry, dust free and flushed thoroughly with nitrogen.

Fill the viscometer according to the manufacturer’s instructions. Figure 2 gives an example of a viscometer.

During the filling and the following measurement procedure, visually observe the solution to determine the presence of any undissolved matter. In the event of finding undissolved matter, reject the solution and repeat the experiment.

Wait for 5 min to 10 min before the first measurement of the viscosity, until the solution has reached its temperature equilibrium.

7.2.5.2 Measurement procedure

An Ubbelohde viscometer is used as an example (see Figure 2). For other viscometers, see ISO 3105 as well as the manufacturer’s instructions.

Seal the ventilation tube (1) with a finger, a stopper or with plastic film and apply a vacuum to the capillary tube (2) until the lower reservoir (10), the working capillary (6), the timing bulb (5), and the upper reservoir (4) are filled.

Remove the vacuum and seal.

Ensure that the liquid separates at the lower end of the capillary.

Measure and record the time interval (t_{1A}, efflux time) with an accuracy of ±0,5 s for the upper meniscus to travel between the two timing marks M_1 and M_2 on the timing bulb (5).

Repeat the measurement on the same specimen and record as t_{1B}. Record the percentage difference between the two results.

Inspect the results to assess whether the efflux time is within the allowable range and whether the two results lie within 1 % of each other.

Record the details of the tube constant that was used and the efflux times (C_1, t_{1A} and t_{1B}).

Clean the viscometer tube in accordance with 7.2.5.3.

By taking note of the results of the first experiment, repeat the procedure using a second specimen selected to give:

- optimum paper mass based on an accurate knowledge of the original water content,
- optimum viscometer tube to give efflux times in the allowable range.

In the event that the two results obtained from the second experiment do not lie within 1 % of each other, clean the viscometer tube and repeat with a new specimen of the same solution.

In the event that no two results lie within 2 % of each other, the two results that lie closest together shall be accepted and recorded along with details of the tube constant used as C_2, t_{2A} and t_{2B}. The test report shall indicate the poor agreement between results.

7.2.5.3 Viscometer tube cleaning

Viscometer tubes shall be cleaned in the following manner:

a) dispose of the Cuen/paper sample, as appropriate;

b) rinse the viscometer tube thoroughly with distilled water;

c) if possible, soak in 20 % (aqueous) nitric acid for a minimum of 30 min, between two test, or alternatively between two tests wash the viscometer first with water and then with acetone and at the end of the working day soak it in 20 % (aqueous) nitric acid and leave it overnight;

d) rinse with distilled water;

e) rinse with acetone to help dry the tube;

f) finally either blow dry with clean compressed air or dry in a suitable oven.

7.2.5.4 Solvent measurements

In the same manner measure the efflux time for the diluted solvent alone, 50 % Cuen and 50 % of distilled/de-ionized water. Record the details of the tube constant used and the times as (C_0, t_{0A} and t_{0B}).