



# Standard Test Method for Measurement of Average Viscometric Degree of Polymerization of New and Aged Electrical Papers and Boards<sup>1</sup>

This standard is issued under the fixed designation D 4243; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method describes a standard procedure for determining the average viscometric degree of polymerization (abbreviated  $\overline{DP}_v$ ) of new or aged electrical papers. The determination is made by measuring the intrinsic viscosity of a solution of the paper in an appropriate solvent.

1.2 The degree of polymerization (or the degree of condensation) of a particular cellulose molecule is the number of anhydro- $\beta$ -glucose monomers,  $C_6H_{10}O_5$ , in the cellulose molecule. Within a sample of paper, not all the cellulose molecules 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 other methods.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.* See Section 9

## 2. Referenced Documents

### 2.1 ASTM Standards:

**D 445** Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity)<sup>2</sup>

**D 1711** Terminology Relating to Electrical Insulation<sup>3</sup>

### 2.2 Other Document:

IEC Publication 450 Measurement of the Average Viscometric Degree of Polymerization of New and Aged Electrical Papers<sup>4</sup>

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology **D 1711**.

## 4. Summary of Test Method

4.1 This test method measures the specific viscosity of a solution of the paper in cupriethylene-diamine. From this measurement the intrinsic viscosity of the solution is deduced, and from this the degree of polymerization is easily calculated.

4.2 This test method follows very closely the procedures specified in **IEC Publication 450**.

## 5. Significance and Use

5.1 This test method may be applied to all papers made from unmodified cellulose, as used in transformer, cable, or capacitor manufacture. It applies to new or aged papers. For information, Appendix X2 shows an example of statistical distribution of  $\overline{DP}_v$  values for new papers intended for the insulation of transformers, together with information relative to cable and capacitor papers. Nevertheless, where evaluating the decomposition stage of aged papers, take care to use, as a reference, the  $\overline{DP}_v$  value of the new paper of the very same origin;  $\overline{DP}_v$  of new papers being a function, among other factors, of their specific gravity and of their manufacturing process.

5.2 This test method can also be used for the determination of the intrinsic viscosity of solutions of chemically modified papers, provided that these dissolve completely in the selection solvent. This test method should be used with caution when it is applied to papers with mineral fillers.

## 6. Interferences

6.1 Lignins, that are present in measurable amounts in most papers and boards, may have an effect on the test results, depending upon concentration and composition. For this reason, it is important in aging studies to use as a reference samples of the unaged paper as mentioned in **5.1**.

6.2 Under some conditions of heat and atmosphere, cross linking of cellulose molecules may occur, resulting in erratic test values. This effect has been observed for capacitor tissue in

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 10.03.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 10.01.

<sup>4</sup> Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

vacuum at temperatures as low as 110°C and for other papers aged in air at higher temperatures.

## 7. Apparatus

### 7.1 Apparatus for Solution:

7.1.1 *Round-Bottomed 50-mL Flask*, preferably with a short narrow neck, or a narrow-necked 50-mL Erlenmeyer flask.

7.1.2 *Rubber Stopper*, fitting the neck of the flask, through which passes a capillary tube fitted with a small-bore cock glass cock; or a ground stopper, fitted with a small-bore cock may be used with a ground-neck flask.

7.1.3 *Glass Balls*, 4 to 6-mm diameter, that shall not be able to enter the bore of the cock.

7.1.4 *Mechanical Stirrer*, to rotate the solution flask with a uniform circular motion with a horizontal axis between 20 and 40 r/min. The flask shall be mounted so that its axis is normal to the axis of rotation, and the radius of gyration shall not be greater than 200 mm.

### 7.2 Apparatus for Measurement of Viscosity:

7.2.1 *Apparatus for Measurement of Kinematic Viscosity*, as described in Test Method D 445. The viscometer shall have a calibration constant,  $C$ , of from 0.00010 or 0.00013 St/s ( $10 \times 10^{-9}$  to  $13 \times 10^{-9}$  m<sup>2</sup>/s<sup>2</sup>).

7.2.2 This constant shall be determined by measuring the efflux-time  $T$  (seconds) of a liquid of known dynamic viscosity (Ns/m<sup>2</sup>) and density  $\rho$  (g/cm<sup>3</sup>). It is given by the formula:

$$C = \frac{\eta}{\rho \cdot T} \quad (1)$$

7.2.3 *Constant-Temperature Water Bath*, regulated at  $20 \pm 0.1^\circ\text{C}$ .

7.2.4 *Stopwatch*, with an accuracy of 0.1 s.

7.3 *Apparatus for Measurement of Water Content of Paper Sample:*

7.3.1 *Weighing Containers*, impermeable to water vapor, with airtight lids.

7.3.2 *Ventilated Drying Oven*, thermostatically controlled at  $105 \pm 2^\circ\text{C}$ .

7.3.3 *Desiccator*.

## 8. Reagents

### 8.1 Cupriethylene-Diamine Solution:

8.1.1 The formula ascribed to cupriethylene-diamine (CED) is:



This implies a molar ratio of 2 between the concentration of ethylene-diamine and the concentration of copper:

$$(C_{\text{ED}}/C_{\text{Cu}}) = 2 \quad (3)$$

8.1.2 Cupriethylene-diamine solution may be purchased commercially at several different concentrations. At a concentration greater than 1 M it may be kept for one year in the dark. It is diluted to 1 M when required for use. Alternatively the CED solution can be made in the laboratory at its working strength of 1 M by the methods described in Annex A1.

8.1.3 The 1 M solution will keep only for a limited time. As often as necessary the solution should be checked by:

8.1.3.1 Using the method described in Annex A2 to verify that the ratio

$$C_{\text{ED}}/C_{\text{Cu}} = 2.0 \pm 0.1. \quad (4)$$

8.1.3.2 Verify that there is no precipitate in the solution. Any precipitate should be removed by filtering or by decanting.

## 9. Preparation of Specimens

### 9.1 Impregnated Papers:

9.1.1 Using a Soxhlet extractor, degrease the paper with hexane or, if necessary, with chloroform.

9.1.1.1 *Caution*—Chloroform is toxic, and hexane is flammable. Adequate precautions must be taken to avoid exposure to vapors and to prevent fire.

9.1.2 Allow the solvent to evaporate in air at room temperature.

9.1.3 Cut the sample into small pieces (1 or 2 mm<sup>2</sup>) with scissors, using gloves to avoid touching the paper.

9.1.4 Keep the sample in a controlled-humidity atmosphere until it reaches equilibrium water content before removing the material required for test purposes.

### 9.2 Nonimpregnated Papers:

9.2.1 Cut the sample into small pieces (1 or 2 mm<sup>2</sup>) with scissors, using gloves to avoid touching the paper.

9.2.2 Keep the sample in a controlled-humidity atmosphere until it reaches equilibrium water content before removing the material required for test purposes.

## 10. Procedure

### 10.1 Determination of Viscosity:

10.1.1 *Test Specimen*—Weigh to the nearest 0.1 mg an amount ( $m$ ) of paper, in equilibrium with the controlled atmosphere, of about:

10.1.1.1 125 mg when  $\overline{DP}_v$  lies between 100 and 300,

10.1.1.2 50 mg when  $\overline{DP}_v$  lies between 300 and 700, and

10.1.1.3 25 mg when  $\overline{DP}_v$  lies between 700 and 1500.

### 10.1.2 Solution:

10.1.2.1 Put a few glass balls in the flask.

10.1.2.2 Add the weighed test specimen.

10.1.2.3 Carefully shake or stir by hand to ensure the small pieces of paper are separated and evenly distributed.

10.1.2.4 Add 22.5 mL of distilled water.

10.1.2.5 Again shake or stir by hand to disintegrate and wet all the paper completely.

10.1.2.6 Leave for ½ h to allow thorough impregnation with water.

10.1.2.7 Add 22.5 mL of 1 M solution of cupriethylene-diamine.

10.1.2.8 Add a number of glass balls so that, when the stopper with capillary tube, and so forth, is fitted, the liquid will entirely fill the flask and reach the bore of the cock. Do not allow any pieces of paper to enter the capillary, for such paper will not be dissolved.

10.1.2.9 Close the cock.

10.1.2.10 Allow the specimen to dissolve with mechanical stirring as described in 7.1.4. The preferred solution time is 2 h; however, when the specimen is not satisfactorily dissolved, the solution time may be increased to a maximum of 18 h. For a specimen of an aged paper, there is little risk of further measurable degradation due to this increase of solution time.

### 10.1.3 Measurement of Viscosity:

10.1.3.1 After the period of stirring and before filling the viscometer, allow the solution to stand for 1 h at the temperature of measurement,  $20 \pm 0.1^\circ\text{C}$ .

10.1.3.2 Take the required volume of solution and transfer it to the viscometer reservoir. Assemble the viscometer and place the assembly in the thermostatic bath.

10.1.3.3 Wait 15 min before beginning the measurements. Then raise the liquid level above the upper mark of the viscometer either by means of air pressure or slight vacuum. Measure the efflux time between the upper and lower marks. Make three successive measurements. The difference between the maximum and minimum time of flow shall be less than 0.5 s. If this repeatability is not achieved, clean the viscometer as described in 10.1.4. Take a second specimen of the solution that has been kept at the measurement temperature and make a further series of three measurements. If again the difference is not less than 0.5 s, take a new specimen of paper and prepare a fresh solution.

10.1.3.4 Under the same conditions, measure the flow time of the solvent. This shall be between 90 and 110 s for the viscometer constant  $C$  stated in 6.2 ( $0.00010 \leq C \leq 0.00013$ ).

10.1.4 *Cleaning the Viscometer:*

10.1.4.1 By aspiration, fill the tube with chromic-acid mixture and immediately empty it again.

10.1.4.2 Rinse thoroughly with distilled water.

10.1.4.3 Rinse twice with acetone or alcohol.

10.1.4.4 Dry by means of compressed gas from a cylinder or dust-and-oil-free compressed air.

10.1.5 Make all tests in duplicate, making up two separate solutions from separately weighed specimens.

10.2 *Determination of Water Content of Paper:*

10.2.1 *Test Specimen:*

10.2.1.1 Weigh to the nearest milligram approximately 2 g of paper in equilibrium with the controlled-humidity atmosphere, and in a closed weighing container that has been dried and tared.

10.2.1.2 If the paper sample is too small for 2 g to be reserved for determining its water content, use a smaller specimen. However, if the amount of paper is only sufficient for the viscometric measurements, its water content may be deduced from the moisture equilibrium curves and the relative humidity of the conditioning atmosphere with which the paper was in equilibrium. If equilibrium curves are not available for the particular paper tested, the following average values may be used as a first approximation for temperatures between 20 and  $27^\circ\text{C}$ .

Relative Humidity of Air, %	Water Content of Air, %
50	6
65	8

10.2.2 *Measurement of Water Content:*

10.2.2.1 After weighing, open the container and place it, with the weighed test specimen and its cap, in the oven and heat at  $105 \pm 2^\circ\text{C}$  until it reaches constant mass. This will normally require from 4 to 18 h.

10.2.2.2 After drying, replace the cap on the container and allow it to cool in a desiccator for about 45 min. After cooling, equalize the air pressures inside and outside the container by raising and lowering the cap quickly. Weigh the container with the specimen.

10.2.3 Alternative procedures may be used to determine the water content of the paper sample provided that it can be verified that the procedure used will give results that differ from the results used in 10.2.2 by no more than 0.5 %.

**11. Calculation**

11.1 *Concentration,  $c$ , of Dry Paper in the Solution:*

11.1.1 The water content  $H$  of the paper, as a proportion of the dry weight, is as follows:

$$H = (M - M_0/M_0) \tag{5}$$

where:

$M$  = mass of the test sample used for determining the water content before drying, g and

$M_0$  = mass of this sample after drying, g.

11.1.2 Knowing the mass,  $m$ , in grams of the test specimen and its water content,  $H$ , the concentration  $c$  (g/100 mL), of dry paper in the solution is given by:

$$c = (m \cdot 100/45) \cdot (1/1 + H) \tag{6}$$

11.2 *Specific Viscosity,  $\eta_s$* —The densities of the solvent and of the solution are practically identical. Thus, the specific viscosity  $\eta_s$  as defined in 4.2 is given by:

$$\eta_s = \frac{T_s - T_0}{T_0} \tag{7}$$

where:

$T_0$  = mean efflux time of the solvent, and

$T_s$  = mean efflux time of the solution.

11.3 *Intrinsic Viscosity  $[\eta]$ :*

11.3.1 The intrinsic viscosity is calculated using Martin's formula from the specific viscosity  $\eta_s$  and the concentration  $c$  (g/100 mL), of dry paper.

11.3.2 As Martin's formula does not readily lend itself to calculation of  $\eta$ , use Table 1, which contains values of the product  $[\eta] \cdot c$  as a function of  $[\eta_s]$ .

11.3.3 In Table 1,  $k = 0.14$ , which value has been found experimentally for the operating conditions described.

11.4 *Degree of Polymerization  $\overline{DP}_v$* —The average viscometric degree of polymerization  $\overline{DP}_v$  is given by the equation:

$$\overline{DP}_v^\alpha = [\eta]/K \tag{8}$$

where:

$\alpha = 1$ , and

$K = 7.5 \times 10^{-3}$ .

**12. Validity of Results**

12.1 Two conditions should be met if the results are to be considered significant:

12.1.1 Both values  $\overline{DP}_v$  should agree within 2.5 % of their mean value.

12.1.2 After measuring the viscosity, filter the solution through a fine-sintered glass filter; wash the filter and any deposit with hydrochloric acid (diluted with one part water to three parts acid), then with distilled water; dry in an oven of about  $110^\circ\text{C}$ , allow to cool in a desiccator, and weigh. The mass of any insoluble residue shall be less than 5 % of the initial weight of the specimen.

12.2 If one or both of these conditions are not met, a further series of tests shall be made. If, again, one or both requirements