

Degradation of cellulosic insulation in power transformers. Part 1: Factors affecting the measurement of the average viscometric degree of polymerisation of new and aged electrical papers

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Abstract: The degree of polymerisation (DP) of electrical insulation paper is an invaluable tool for assessing its condition and is extensively used in laboratory tests to assess the life expectancy of transformer insulation. Accurate and reproducible determinations are essential if the results are to be used to calculate a meaningful life. Publication IEC 450 was prepared in 1974 as a standard for the measurement of the DP of new and aged electrical papers (the equivalent US standard is ASTM D4243). However, experience across a number of laboratories has indicated the need for further clarification in the experimental method, whichever standard is adopted. Errors arise during preparation of solutions, measurement of viscosity and calculation of DP, due to oxidative degradation of the solution, inconsistencies in the measurement temperature and the conversion of intrinsic viscosity to DP using the Mark Houwink Sakurada relationship. This paper quantifies errors associated with DP measurement which are not described in existing standards.

1 Introduction

The degree of polymerisation (DP) has traditionally been used as the primary indicator of the condition of insulation paper in electrical transformers (and cables). The paper deteriorates with age, leaving the insulation vulnerable to stresses generated by thermal, mechanical and electrical transients. Water, heat and oxygen all contribute to the degradation process, reducing the DP of the paper and with it, the mechanical strength. The paper (initial DP ~1300) is expected to last the lifetime of the transformer (25–40 years), but at a DP of 150–200 the mechanical strength of the paper can be reduced to 20% of its initial value [1]. This point is regarded as the end of life criterion for transformer insulation, because at any lower DP the paper loses all its mechanical strength, although its dielectric constant is not greatly affected. Degradation of the paper can cause the transformer to fail by several mechanisms:

- the brittle paper can break away from the transformer windings and block ducts;
- water is a product of degradation and builds up in the paper, reducing its resistivity;
- in the extreme, local carbonising of the paper increases the conductivity to cause overheating and conductor faults.

Ageing of the paper insulation determines the ultimate life of the transformer, although other factors can cause it to fail earlier.

The DP can be calculated from the viscosity of dilute polymer solutions, following early studies of solution viscometry first carried out by Staudinger [2]. The limiting viscosity number (intrinsic viscosity) of a polymer in a dilute solution is related to the volume of the hydrodynamic sphere of the molecule in solution [3], which is highly dependent on its shape and largely determined by the type of polymer. Thus, a branched polymer with the same molecular weight as a linear polymer can have a different hydrodynamic volume. Intermolecular interactions occur in more concentrated solutions, which also affect the hydrodynamic volume, and the relationship between viscosity and the molecular weight is generally only valid for solutions of 0.1% or less. Standard methods ASTM D1795-90 [4] and BSI 6306 [5] exist to measure the DP of cellulose (the main constituent of insulation paper) in cupriethylene-diamine solvent (Cuen). Other solvents have been used, for example the cadmium equivalent Cadoxen, but have not been incorporated into the standards. Methods have also been written that are specific to transformer paper, ASTM D4243-86 [6] and IEC 450 [7].

A study of the errors associated with the measurement was initiated after the National Grid Company found that a recent series of round robin tests in different laboratories, using these two very similar standards, produced up to a 40% difference in the measured DP of nominally identical samples. The ASTM D4243-86 and IEC 450 methods were used as a starting point for the investigation. The effects of air exposure of the solution, temperature of the measurement, and the parameters of the conversion function from intrinsic viscosity to DP (the Mark Houwink Sakurada relationship) were quantified and the results are reported here.

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1.1 Relating viscosity to molecular weight

The viscosity of a dilute polymer solution is related to the molecular weight, M_w , by the Mark Houwink Sakurada (MHS) equation: $[\eta] = K\overline{M}_w^\alpha$ where K and α are constants related to the solvent and polymer type, and $[\eta]$ is the intrinsic viscosity or limiting viscosity number, expressed in units of inverse concentration (dl/g). The measurement of the specific viscosity of a dilute polymer solution, its relationship to the intrinsic viscosity, and the Mark Houwink Sakurada equation can be found in any standard polymer textbook [8].

2 Experimental investigation of DP measurement by viscosity

The measurement of DP is affected by (i) the preparation of the solution, (ii) the measurement of viscosity, and (iii) the parameters of the Mark Houwink Sakurada equation.

- Important factors in the preparation of the sample are the removal of oil from the paper and correct measurement of the dry weight of sample, the concentration of the polymer in solution and oxidative and mechanical degradation during mixing.
- Important factors in the measurement of viscosity are shear degradation effects in the viscometer tube, degradation of the solution and/or polymer in solution by oxygen, and the temperature of analysis.
- A number of different values for the MHS equation parameters exist in the literature for calculating the DP from the viscosity measurements and it is important to ensure that the correct, or at least consistent, values are used.

Kraft paper samples in this study were taken from a scrapped transformer (identified as 3B6, 3B23 and 3B47) and from accelerated laboratory ageing experiments (about 1500 h in dry insulating oil at 160°C). In addition, as-received Kraft paper was used, supplied by Tullis Russell Papermakers.

2.1 Effects of sample preparation

2.1.1 Removal of insulation oil from the paper: Transformer insulation is impregnated with oil, and it is necessary to remove any residual oil and measure the moisture content of the paper to obtain an accurate dry weight value. Hexane is one of the de-oiling solvents suggested in ASTM D4243-86 and IEC 450, because of its ease of evaporation, but benzene or chloroform can also be used. Paper samples were washed in cold hexane and also by hot Soxhlet extraction. Table 1 shows the results of the analysis of insulation samples from the three transformer windings. The deviation about the mean value DP is quite large. Therefore, although the average DP for sample 3B47 was measured as 451.4 after hot washing and a sample from the same winding prepared using cold hexane gave a DP of 470.0, the DP of the cold-washed sample falls within the 95% confidence limits of the hot data. The temperature of washing is not therefore important when using hexane but hot washing is quicker and more convenient.

Table 1: Effects of oil extraction from paper in hot and cold hexane

Sample	DP average hot hexane	95% confidence limits of mean	95% confidence limits of data	Standard deviation	DP average cold hexane
3B6	439.2	7.22	30.64	15.63	417.0
3B23	447.9	8.38	35.57	18.14	452.3
3B47	451.4	6.99	27.99	14.28	470.0

2.1.2 Concentration of paper in solution: The Mark Houwink Sakurada relationship of the viscosity of a polymer solution to molecular weight is only valid for dilute solutions (approx. 0.1–1.0%), because the relationship of DP to intrinsic viscosity deviates from linearity outside these limits. ASTM D 1795-90 and BSI 6306 therefore state that the intrinsic viscosity (dl/g) multiplied by concentration (g/dl) should remain within limits of $1 < [\eta]c < 1.5$. However, ASTM D4243-86 specifies that the value of $[\eta]c$ should always be below 1. At this level, the concentration of paper in solution is very low and the dry mass of paper is difficult to determine accurately.

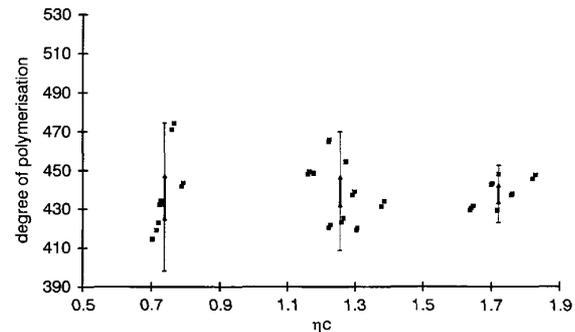


Fig. 1 Effect of paper concentration in solution on accuracy of DP measurements
 ↑ 95% confidence limits on the mean
 ↑ 95% confidence limits on the data
 ■ sample data

Fig. 1 shows the results of a number of repeat measurements of DP on samples taken from laboratory aged paper, at three target $[\eta]c$ values of 0.7, 1.1 and 1.7. The horizontal spread of the data shows the difficulty of making up identical solutions, due to errors in getting the same dry weight, after removal of oil and moisture from the paper. However, the actual concentration in each solution is taken into account in calculating the DP. Thus, if all the samples had the same DP (which is far from certain) and the errors in measuring the viscosity and concentration were zero, the vertical variation would be reduced to zero. The fact that it is not zero is significant and indicates (i) the natural variation in DP, and (ii) the intrinsic errors in the measurement technique. The extent of vertical variation therefore defines the maximum errors in any single determination. It is greatest at $[\eta]c$ of 0.7 with a relative standard deviation on the DP (rsd) of 1.23%, which decreases to an rsd of 0.73% at an $[\eta]c$ of 1.1, and to 0.39% at an $[\eta]c$ of 1.7.

An $[\eta]c$ value of 1–1.5 was chosen for the remainder of the study because incomplete dissolution was sometimes observed at higher concentrations, particularly for samples with high DPs.

2.1.3 Mechanical degradation: A polymer in solution will have a tendency to undergo mechanical degradation when shaken/mixed over a long period of time, and some paper samples dissolve more slowly than others, depending on the extent of degradation and type of paper.

Measured DP values of nominally identical samples shaken (or exposed to ultrasound) for 10 or 20 hours fell within the normal scatter of results. It was impossible to identify any difference between using a mechanical shaker or an ultrasonic bath to aid dissolution, or any effect of duration of sample preparation, provided the samples were maintained under nitrogen.

2.1.4 Oxidative degradation of the solution: Paper dissolution depends on the formation of complex bonds between the polymer and the solvent. In Cuen/cellulose solutions these are prone to oxidative degradation, and studies by Henley [9] have shown that the viscosity of the solution and therefore the apparent DP decreases over time during storage. Therefore, dissolution and storage under nitrogen is essential if accurate results are to be obtained. Neither ASTM D4243-86 nor IEC 450 mention the use of nitrogen to reduce the effect of oxidative degradation. Fig. 2 shows that the DP of all three transformer samples apparently decreased with time, when the samples were left in the viscometer tube and the viscosity measured repeatedly. The rates of degradation are approximately the same at these low DP values, 2.5 DP/h, so the calculated DP decreased by about 14 during the six hour period (a change of ~3%), whereas the kinematic viscosity of the Cuen solvent (blank) did not change significantly.

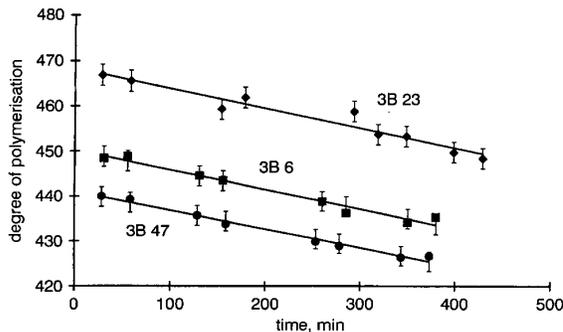


Fig. 2 Apparent decrease in DP of aged transformer paper during repeat determinations due to oxidative degradation of solution. The error bars were calculated from the standard deviations on the mean in Fig. 1 and show that the results are significant compared to the experimental errors

To quantify the effects of degradation of Kraft paper in solution, the deterioration of an as received Kraft paper solution stored under nitrogen was compared to one exposed to the atmosphere. A batch of as received paper dissolved in the standard solvent (Cuen) was divided into three separate samples and their viscosity measured at intervals over the period of a day. The first was added to a viscometer tube and its viscosity measured repeatedly, which means it was subjected to repeated shear, as well as continuous exposure to the atmosphere. A second sample was left in a beaker on the bench, exposed to the surroundings, and the viscosity of fresh aliquots measured periodically. The third sample was stored under nitrogen and again fresh aliquots were used for each measurement.

Fig. 3 shows the effects of shear and oxidative degradation. It clearly shows the need to store the solution under nitrogen to avoid oxidative degradation, and the enhancement to degradation due to shear effects when the solution is passed through the viscometer tube repeatedly. The DP of the sample left *in situ* decreased at a rate of approximately 38 DP per hour, compared to 21 DP/h for the sample exposed to air in a beaker. There is no measurable deterioration in the DP of the sample sealed under nitrogen.

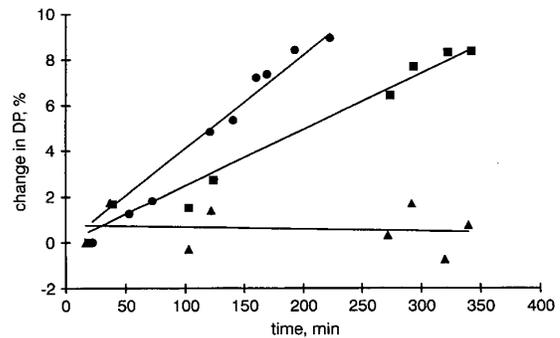


Fig. 3 Combined effect of shear and oxidative degradation on DP determination of Cuen solutions of paper aged in laboratory
 ● air exposed in situ
 ■ air exposed in beaker
 ▲ stored under nitrogen

2.2 Viscosity determination

2.2.1 Temperature of analysis and efflux time:

The viscosity and the MHS constants of a solution are dependent on temperature. ASTM D1795-90 and BSI 6306 specify $25 \pm 0.1^\circ\text{C}$ for cellulose and ASTM D4243-86 and IEC 450 specify $20 \pm 0.1^\circ\text{C}$. The DPs of the three transformer paper samples were measured at 20 and 25°C . The values at 20°C were, on average, ~1.8% higher than those at 25°C , indicating a small effect of measurement temperature.

A second possible error related to the measurement of viscosity is the efflux time through the viscometer (the time taken for the sample solution to pass through the 'timing marks'), which is determined by the viscosity of the solution and the choice of viscometer tubes. The higher the concentration the longer, and therefore more accurate, the efflux times. For instance, an error of 10 seconds at an efflux time of 30 minutes will give an error of about 0.45% in a DP of 400, compared to 1.6% at an efflux time of 15 minutes. ASTM 4243-86 recommends an efflux time of 100 seconds for the blank solution (50:50 Cuen/water) and viscometer tube constants of approximately 0.1 – 0.13 cSt/s. However, the calibration certificates for the Ubbelohde tubes from the manufacturers (Schott Geräte) stipulate that the efflux time must be greater than 300 seconds to ensure accurate and reproducible measurements. The efflux time for the blank solution was approximately 460 seconds in the tubes used for measurements reported here (approximately 0.003 cSt/s) and solution efflux times ranged from 15 to 30 minutes.

2.2.2 Source of Kraft paper: The reproducibility of the calculated DP of transformer insulation was compared to that of paper samples aged under laboratory ageing conditions, because the type of paper and the degree of ageing found on a particular winding can vary. For example two thicknesses of Kraft paper were found on the transformer windings 3B6, 23 and 47, (0.124 mm and 0.051 mm), and the DPs were, in all cases, lower for the thinner paper. The results are shown in Table 2.

2.2.3 Mark Houwink Sakurada constants: The DP calculated from a solution viscosity measurement can differ significantly depending on the Mark Houwink Sakurada constants used in the data analysis. ASTM D4243-86 quotes values of $\alpha = 1$ and $k = 0.0075$; ASTM D1795-90 quotes an approximate conversion to the DP of cellulose, which involves multiplying the intrinsic viscosity by 190; BSI 6306 does not quote any conversion values.

Table 2: Difference in average DP of thick and thin papers from the same transformer

Sample	DP average thick	95% confidence limits	Standard deviation	DP average thin
3B6	439.2	7.224	15.637	395.8
3B23	447.9	8.384	18.148	318.7
3B47	451.4	6.997	14.281	382.1

Table 3: Mark Houwink Sagurada constants for cellulose/Cuen from the literature

MHS constants		DP	Ref.
α	k		
1	0.0059	562.71	[11]
0.9	0.0098	647.16	[12]
0.9	0.0082	788.91	[13]
1	0.0058	572.41	[14]
1	0.00248	1338.71	[15]
0.76	0.0244	642.04	[16]
1	0.00448	741.07	[16]
1	0.0075	442.67	[6, 7]
n/a	n/a	630.80	[4]*

DP calculated as intrinsic viscosity $\times 190$

In order to compare the effects of conversion parameters in the MHS equation, the different constants quoted in the Polymer Handbook [10] were used to analyse the same data. Table 3 shows the variation in calculated DP (note that most of the constants are related to 100% cellulose and are not specific to insulation paper). The same intrinsic viscosity of 3.320 dl/g was used throughout, but the DP varies between 440 and 1340, which is the largest variation of any of the parameters investigated. The Mark Houwink Sakurada constants quoted for transformer insulation paper in ASTM D4243-86 and IEC 450 actually give the lowest value in Table 3.

3 Discussion

The apparent decrease in the DP of paper solutions in air indicates that the interaction between the copper complex and Kraft paper is oxygen sensitive. The effect of air exposure over a day on Cuen/water solvent itself was not significant, although it is reported to be susceptible to oxidative attack [9]. It is the complexation of the copper with the paper in solution that is susceptible and the copper falls out of solution after prolonged periods of exposure. The rate of oxidative degradation is highest at low DP values because of the presence of carbon char, which reduces the copper (2^+) ions to copper.

The DP of paper from transformer windings is more variable than that of laboratory aged paper. The relative standard deviation of the transformer samples 3B6, 3B23 and 3B47 were 3.56%, 4.05% and 3.16%, compared to 0.73% for the laboratory-aged samples. The extra scatter in the DP of the transformer samples is due to non-uniform ageing rates in the transformer and, although the thinner papers appear to have degraded quicker, the differences could be related to the position of the paper rather than thickness. The position of the papers on the winding was not known, but the thinner paper could, for instance, be the inner layer on the winding, i.e. in contact with the hot copper.

The most significant variation in DP arises from the choice of MHS constant. Clearly, trends in DP change will be observed irrespective of which particular constants are used. However, comparisons between different data sets will only be possible if consistent MHS constants are used throughout. It is interesting to note that there is even a 50% difference between ASTM D4243 and ASTM D1795.

A revised method to determine the degree of polymerisation of electrical insulation paper has been submitted to a CIGRE work group for approval, before submission to the European and British standards organisation committees. The following modifications to the existing methods are recommended:

- solutions should be mixed under nitrogen and stored under nitrogen until measured.
- $[\eta]c$ values of between 1 and 1.5 should be used to make up solutions for viscosity measurement.
- viscometer tubes should be chosen to give an efflux time for the solvent of at least 300 seconds.
- Mark Houwink Sakurada constants of $\alpha = 1$ and $k = 0.0075$ should be used to convert the intrinsic viscosity to DP.

4 Conclusions

The measurement of the degree of polymerisation of insulation paper is not well defined in the existing standard methods. Both the sample preparation and the viscosity determination must be carried out within more rigorous guidelines to minimise errors.

The most significant source of variability of result is the choice of Mark Houwink Sakurada constants to convert the intrinsic viscosity to the DP. The remaining experimental variables can, however, still cause further errors. Oxidative degradation of the solution is the next most important factor, but can be avoided if the solution is maintained under nitrogen throughout the mixing process and exposure to air is minimised during measurement of viscosity. Shear effects in the viscometer tube can also be minimised by following the manufacturer's recommendations and using slow efflux rates, which also increases the accuracy of measurement of efflux time. The concentration of the paper in solution affects the scatter in the measurement, but not the mean value of a number of repeat determinations. The temperature of the viscosity analysis does not significantly affect the DP measurement, but the viscometer tubes should be chosen to give an efflux time for the solvent of at least 300 seconds.

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