

Measuring and Understanding the Ageing of Kraft Insulating Paper in Power Transformers

Key Words: Degradation, paper, furfural, cresol, degree of polymerization, transformer, chemical analysis

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In time, it is hoped that a combination of techniques will result in the development of improved life prediction models.

INTRODUCTION

Power transformers are typically insulated with some 12 tonnes (12,192 kg) of paper and 40 tonnes (40,642 kg) of mineral oil, and the life of a transformer is ultimately determined by that of the solid insulation, although other factors may cause it to fail early. Transformers are currently monitored by sampling the oil at regular but infrequent intervals and analyzing for dissolved gases, such as hydrogen and hydrocarbons like methane, ethane, acetylene and carbon monoxide (often referred to as dissolved gas analysis, or DGA). Changes in the relative ratios of certain critical gases provide empirical information about the state of the transformer through the widely used Rodger's ratios [1]. Unfortunately, the major source of these gases is the hydrocarbon oil, and the results are therefore not specific to the paper condition. Insulation life expectancy has been estimated by accelerated laboratory studies of paper ageing, from the relationship of the change in the degree of polymerization (DP) of cellulose in the paper with time [2].

Current research into paper ageing, such as that being carried out at the University of Surrey, UK and a number of other centers throughout the world, is aimed at developing condition monitoring and life prediction techniques. Measurement of the concentration and distribution of degradation products, such as 2-furaldehyde (commonly referred to as furfural), in the oil provides data that can complement traditional DGA analyses, because they apply specifically to paper ageing. The long-term objective is to generate a model that can be used to assess the current condition of Kraft insulating paper in power transformers and then predict its remaining life. In order to relate the standing concentrations of such products to paper condition, it is necessary to understand the chemistry of the degradation of cellulose and to derive chemical and physical models of the breakdown process. To this end, established methods of studying polymer ageing processes are being adapted to study cellulose degradation in paper insulation.

Early studies, reported in the literature, include the work of Shroff and Stannett [2], who measured changes in the DP of paper with time, and in conjunction with Burton and others [3] empirically related the LOG(DP) to the furfural concentration in the oil. More recently, Unsworth and Mitchell [4] and Darveniza and others [5] have developed furfural analysis techniques and have investigated the use of size exclusion chromatography to assess the ageing of the paper in a transformer [6]. Unsworth and Mitchell also investigated the stability of the furan products of degradation and attempted to correlate their concentration in the oil to the tensile strength of the paper, since it is ultimately loss of tensile strength that determines the life expectancy of the insulation. The whole area of insulation ageing, monitoring, and life prediction has recently been reviewed by Emsley and Stevens [7, 8].

In this paper we discuss the application of a number of techniques that are currently being developed for use in life assessment/condition monitoring of transformer insulation, and we illustrate possible applications with some recent data. These include: high performance liquid chromatography (HPLC) of the oil to measure the product concentrations; size

exclusion chromatography (SEC) of the paper to measure changes in molecular weight distribution (related to the degree of polymerization, DP) and computer modeling of the degradation process to relate chemical degradation rates to changes in physical properties, such as tensile strength, which is of critical importance in assessing the probability of damage to the paper under fault conditions. We also revisit the use of DP measurement as a means of assessing insulation life and present results that illustrate problems that we have identified in obtaining consistent data. We describe a method, developed from the British and American standards, which enables us to obtain reproducible results with a known variance.

The aims of this paper are to present a limited review of techniques that are relatively new to the transformer monitoring field, to provide some recent results from this laboratory to demonstrate their potential application, and to show the need for a range of new tools, if we are to improve our ability to assess the condition of transformers and the remanent life of their insulation. Further results from laboratory ageing experiments and their correlation to operating transformers will be reported later.

HPLC ANALYSIS OF TRANSFORMER OIL FOR PRODUCTS OF PAPER DEGRADATION

Method

Most electrical transformers have oil sampling points, so that obtaining a few milliliters of oil is relatively easy. For analysis, 5 ml of oil is diluted with an equal volume of hexane and injected onto a silica pre-column (Waters Sep-Pak). The oil is washed off with hexane and the polar degradation products are retained. They are then eluted from the silica using an 80:20 water acetonitrile mixture and injected onto a reverse phase, C₁₈ column; the products are analyzed using a UV diode array detector.

Application

The results from four transformers, which were closely monitored over a period of several years, were reported previously. The results can be summarized in terms of the level of furfural in an "average" transformer, which is estimated as about 1 ppm, rising at about 0.01 ppm/year, whereas a transformer operating toward the top of its allowable temperature range had a standing furfural concentration of about 5 ppm, increasing at 0.1 ppm/year [7]. In a transformer that overheated due to failure of the coolant circuit, the product levels rose to over 10 ppm, and in a transformer that failed electrically with a discharge across the phenol formaldehyde screening between the LV and HV windings, the cresol level (a product of degradation of the resin) rose sharply prior to failure. The results indicate that the rate of increase of the product levels is as important a parameter as the standing concentration.

Subsequent analyses on a larger population of transformers, with more sensitive equipment, are reported in Fig. 1. They show that a realistic "normal" level of furfural is 100 to 1000 ppb and that other products tend to be an order of magnitude

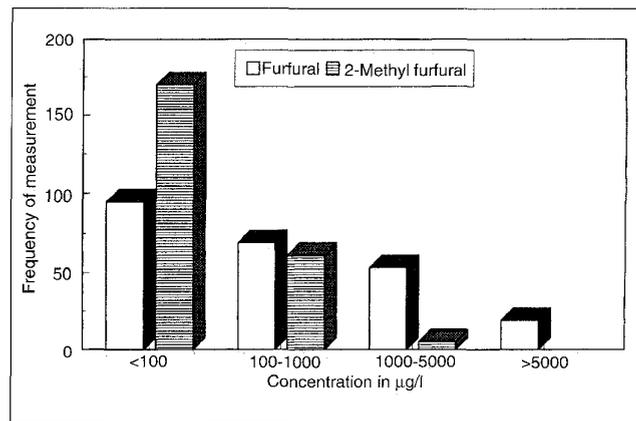


Fig. 1 Distribution of ageing products in a total of 236 analyses from a population of approximately 200 different transformers

lower in concentration. We are coming to regard figures at about the 1-2 ppm level as the upper limits of normal behavior and anything over 5 ppm as a cause for concern.

Furfural analysis (FFA) therefore provides a possible complementary technique to DGA, which is specific to the ageing of paper. Correlations with insulation condition and life are being sought through accelerated laboratory ageing experiments, the use of model compounds, such as polysaccharides and new techniques, such as size exclusion chromatography and computer modeling, all of which are discussed in more detail later.

MEASUREMENT OF THE DP OF PAPER

Modifications to the Measurement Method

The DP measurement by viscometry is notoriously variable, and not all the sources of error are adequately discussed in the standards (e.g., ASTM D 1795-90, D 4243-86, BS 6306). We have investigated the technique in some detail, using the solvent cupriethylene diamine (CUEN) in order to define the main sources of error. The five main sources are:

1. Ambient temperature during dissolution

At temperatures above about 20°C, incomplete dissolution of the sample occurs and the copper tends to fall out of solution. The problem can generally be overcome by pre-cooling the sample to 4°C.

2. Exposure to air

The solution is air (oxygen) sensitive and the DP apparently decreases at a rate of 0.5% of the initial DP per hour as soon as it is exposed to the air. Fig. 2 shows the effect of a) repeated measurements on a single sample in an Ubbelohde viscometer over a period of 5-6 hours, and b) leaving the solution exposed to the air in a beaker. The higher rate of change in the latter sample could either be due to a higher efficiency of aeration or shear degradation effects in the sample arising from repeated passage through the capillary.

3. Effects of shear rate

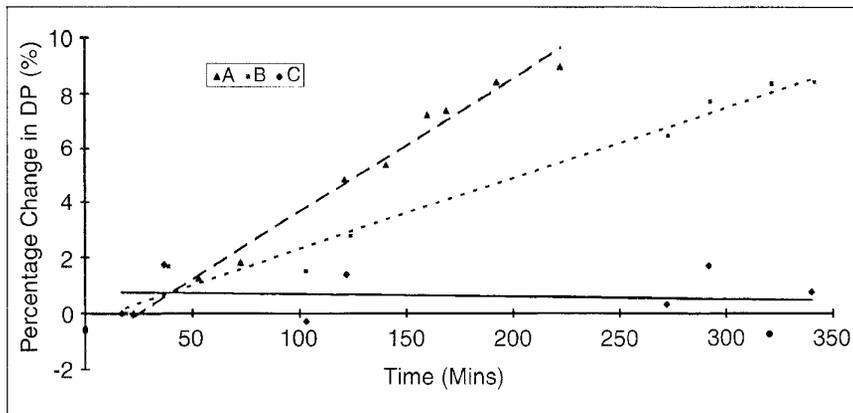


Fig. 2. Effects of air exposure during viscosity measurement on the calculated DP of a virgin transformer paper at 20°C. The first points are plotted at a time corresponding to the end of the first measurement.
 A-repeat measurements on a single sample in an Ubbelohde viscometer
 B-single measurements from a sample stored in an open beaker
 C-single measurements from a control sample stored under nitrogen

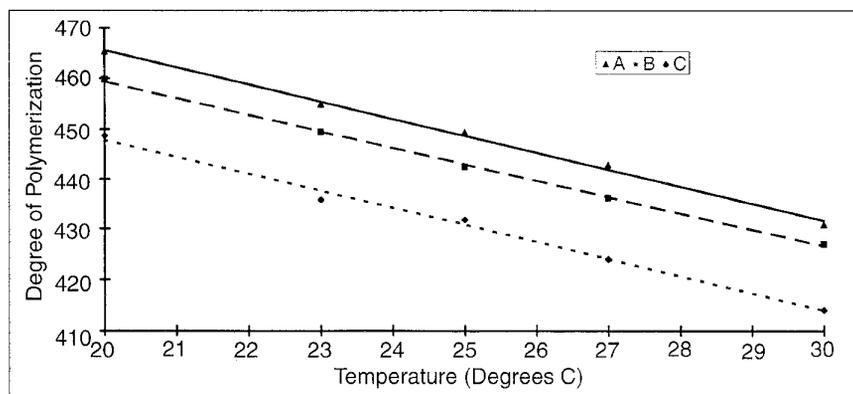


Fig. 3 Variation of calculated DP with the viscosity measurement temperature of three paper samples from a transformer

It has been reported that, at shear stresses greater than about 200 Nm², the measured viscosity is dependent on the rate of shear in the viscometer [9]. At high shear rates, the measured efflux time and hence the calculated DP are too low, but the correct choice of capillary size, as specified in the tube manufacturer's manual, and corrections as specified in the standards, which correct to infinite dilution, do result in reproducible results. However, particularly with unstable solutions, such as Kraft paper in CUEN, there is the additional problem that repeat measurements on the same sample may reduce the viscosity by degrading the salvation of the cellulose in the solution. Comparative measurements must, therefore, always be made under the same conditions.

4. Temperature of the viscosity measurement

Fig. 3 shows the effect of measurement temperature on the calculated DP of a sample, where the viscosity was measured over the temperature range 20° to 30°C. The samples were left in the viscometer tube between measurements, while the bath temperature re-equilibrated, so, allowing for air degradation

over this period, it is estimated that the calculated DP is decreased by approximately 1% per 3°C increase in the bath temperature. ASTM 4243-86 for Kraft paper specifies 20°C. Other cellulose standards, ASTM D 1795-90 and BSI 6306, recommend 25°C. Neither temperature is easy to maintain accurately, because each is so close to ambient temperature. We used a water bath, which utilizes a cooler working in conjunction with a heater.

5. The concentration times the viscosity product for the solution

The standards require specific values for ηc , where ηc = intrinsic viscosity x concentration. The ASTM standard specifies, whereas British and European standards specify between 1 and 1.5. Fig. 4 shows the importance of the choice of ηc . In the range 0.7 to 1.8, the mean value obtained was independent of ηc , but the reproducibility increased with increasing values of ηc . A variance of 1.2% was observed at 0.7 ηc , compared with 0.3% at 1.7 ηc . However, at ηc values greater than 1.0, we sometimes observed difficulties in obtaining complete dissolution, particularly of new or relatively new paper.

6. The (Mark Houwink) constants used to convert viscosity to DP

Here there are over half a dozen values quoted in the literature, which can result in differences of $\pm 40\%$ in the estimated DP. The DPs calculated for a single

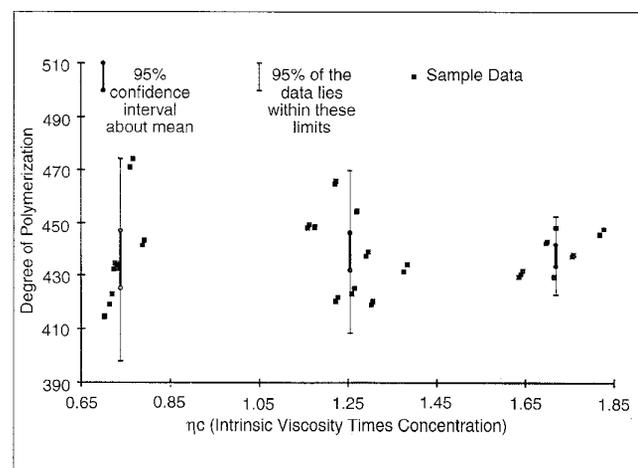


Fig. 4 Reproducibility of calculated DP of paper at different values of ηc (viscosity x concentration)

Table I Variation of the DP, depending on the Mark Houwink constants used. Transformer sample with average intrinsic viscosity of 3.320 dl/g			
Mark Houwink Constants		DP	Reference
a	k		
1	0.0059	562.71	S. Newman, L. Loeb, C.M. Conrad, (1953) J. Polym. Sci, Vol. 10, pg 463
0.9	0.0098	647.16	M. Marx, (1955) Makromol. Chem., Vol. 16, pg 157
0.9	0.0082	788.91	M. Marx, (1956) Papier, Vol. 10, pg 135
1	0.0058	572.41	S. Claesson, W. Bergmann, G. Jayme, (1959) Svensk, Papperstidn., Vol. 62, pg 141
1	0.00248	1338.71	G. Meyerhoft, (1961) Fortsch. Hochpolymer Forsch, Vol. 3, pg 59
0.76	0.0244	642.04	M. Marx-Figini, (1962) Papier, Vol. 16, pg 551
1	0.00448	741.07	M. Marx-Figini, (1962) Papier, Vol. 16, pg 551
1	0.0075	442.67	ASTM 4243-86/IEC 450
N/A	N/A	630.80	ASTM 1795-90 Approximate DP can be calculated from intrinsic viscosity * 190

The DP is calculated from the Mark Houwink equation as follows:

$$[\eta] = k \overline{DP}^a$$

where $[\eta]$ = intrinsic viscosity

sample using a range of constants listed in the Polymer Handbook [10] are given in Table I.

In addition to the techniques and constraints specified in the standards, we find that, to obtain consistent results, with 95% confidence limits better than $\pm 2\%$, it is essential to:

- pre-cool the solvent to 4°C
- dissolve the paper in the solvent under nitrogen at an ambient temperature not greater than 20°C and maintain the nitrogen blanket throughout the mixing
- measure the viscosity immediately on exposure to air
- maintain the temperature constant to $\pm 0.2^\circ\text{C}$ during the measurement. ASTM 4243-86 for Kraft paper specifies 20°C
- use a consistent value of the ηc product, not more than 1; otherwise, virgin paper may not dissolve quantitatively
- use a consistent set of Mark Houwink constants, e.g., for Kraft paper, ASTM 4243-86: $a = 1$, $k = 0.0075$

Ageing Kinetics from DP Measurements

DP has been used in numerous studies of the degradation of cellulose under a variety of conditions, and simple, mathematical models have been developed to describe the kinetics of the reaction. The simplest of these was derived by Ekamstam [11] from early statistical studies of Kuhn and co-workers [12, 13]. According to his analysis, the reciprocal DP should be directly proportional to the degradation time. Emsley and Stevens have

re-analyzed a wide range of results reported in the literature and have shown that cellulose degradation fits this model, at least for the majority of the reaction, until the DP approaches a limiting value of about 200 [14]. 200 is widely found to be a limiting value for the DP of semi-crystalline cellulose under a variety of ageing conditions and is thought to correspond to breakdown to the basic crystallite size (see [12] for further discussion). The logarithm of the slope of the graph can be directly related to reciprocal absolute temperature via the Arrhenius relationship. A series of parallel lines are generated, with intercepts that increase as the environment becomes increasingly more aggressive. Extrapolation of these lines to, for instance, transformer temperatures, allows the lifetime of the paper to be predicted under specific reaction conditions [7, 14]. Clearly, in reality, the extrapolation is not this simple, because the conditions are neither constant nor well defined, and we cannot be sure that reaction mechanisms at operating temperatures are the same as at the elevated temperatures of laboratory experiments. Furthermore, Hill et al. [6] have recently shown that, if the number average molecular weight, calculated from size exclusion chromatography (see next section), is used instead of the DP calculated from solution viscosity, a different activation energy is obtained and therefore a different extrapolation to working temperatures. A new model is needed that takes into account both the complexity of paper structure, possible changes in ageing mechanisms, and the varying operating conditions of a real transformer.

SIZE EXCLUSION CHROMATOGRAPHY OF PAPER

The DP gives us no more than an approximate estimate of the average chain length of the cellulose, and its variation during ageing is a very coarse measure of the changes occurring. Size exclusion chromatography has the potential to provide a full picture of the changes occurring at the macromolecular level. It has been used previously for the study of cellulose ageing [15, 16], and a technique using dimethyl acetamide and lithium chloride (DMAc/LiCl) as a solvent originally developed by Ekmanis [17] has recently been improved for extracting cellulose from plants by Timpa [18]. Darveniza et al. [5, 6] have demonstrated that the cellulose and hemicellulose fractions of Kraft paper can be separated and that they degrade differently. They have also demonstrated the importance of considering the whole molecular weight distribution and not just the viscosity average molecular weight, measured by more traditional methods [6].

Size exclusion chromatography separates the polymer molecules into decreasing order of size (strictly speaking, hydrodynamic volume) during their passage through the column and detects cellulose in the eluent by measuring, for instance, the refractive index change. The system is calibrated against known standards with a narrow molecular weight distribution. If a refractive index alone is used for detection, the results are relative to the standard material (usually polystyrene or polysaccharide). Absolute molecular weights can be obtained by the use of a dual detector system, such as the Waters 150 CV, used in our laboratory, which incorporates a viscometer in series with the refractometer. A universal calibration can then be applied for any particular solvent system [18, 19], although care must be taken in applying universal calibration to a degrading system, because the hydrodynamic volume of cellulose in the solvent may well change with age.

Because refractive index is used for detection, the standard CUEN solution, which is dark blue, is not suitable for size exclusion chromatography. Alternative, colorless solvents are dimethyl acetamide/lithium chloride and the cadmium version of CUEN (CADOXEN, cadmium tris(ethylene diamine) hydroxide). However, we have so far failed to obtain a quantitative solution of Kraft paper in DMAc/LiCl, because, we think, the presence of lignin and CADOXEN destroys our columns in two to three weeks. Darveniza et al. [5, 6] have overcome the problems by derivatizing the paper with phenyl isocyanate to render the cellulose soluble in tetrahydrofuran (THF), but there is a slight danger with this approach of degrading the sample during derivatization.

An alternative approach to direct measurements on Kraft paper is to use polysaccharides, which are soluble in water, as models for the degradation process. Fig. 5 shows a typical SEC picture of the degradation of a high molecular weight polysaccharide. It can be seen that the main peak decreases in height and its position shifts to a slightly lower molecular weight. A new, low molecular weight peak appears and gradually shifts to lower values. DP measurements would show a significant shift to lower DP, due to the influence of the low molecular weight component. Further work is required to obtain similar

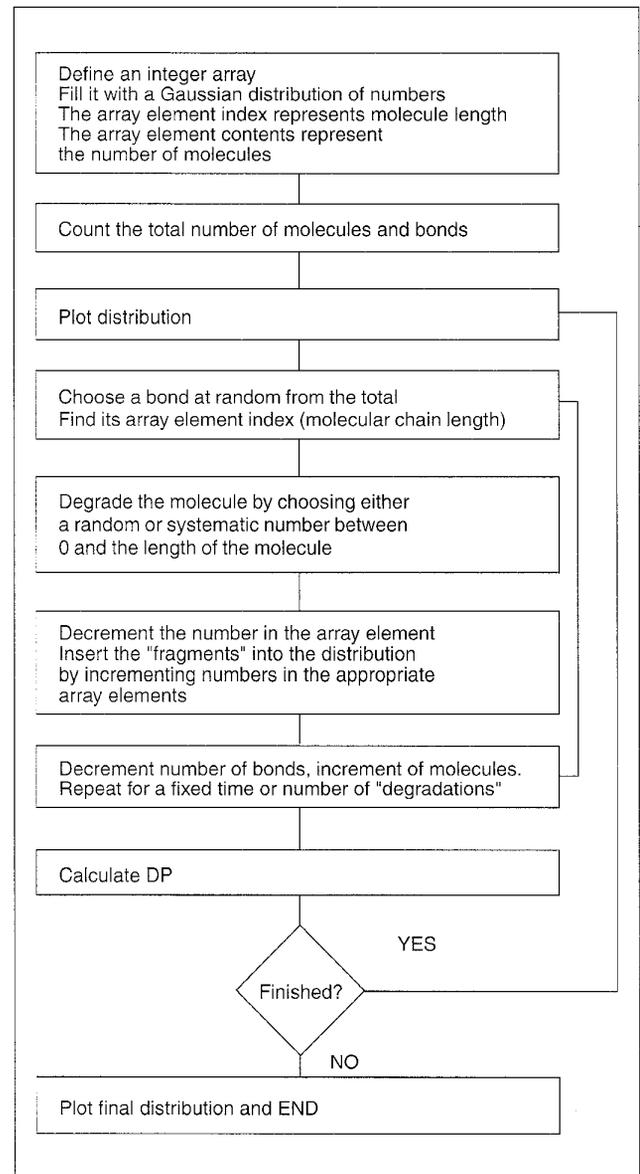


Fig. 5 Flow diagram for the computer modeling of cellulose degradation

data for insulating paper and to understand the significance of MWD in terms of, for instance, changes of mechanical strength and the formation of ageing products such as 2-furaldehyde.

COMPUTER MODELING OF DEGRADATION

The mathematical models of degradation referenced above, due to Kuhn and Ekamstam, implicitly assume that degradation occurs randomly in the cellulose—a randomly chosen chain, breaking at a random position along its length. All the chain linkages are assumed to be the same, with an equal chance of breaking. No account is taken of complicating factors such as fibril formation, chain entanglements, etc., for the simple reason that to do so would make the mathematics too complex to handle. Computers, however, can simulate the degradation

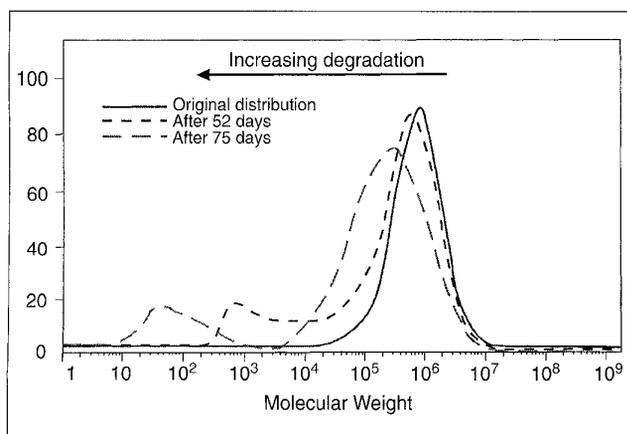


Fig. 6 Degradation of a polysaccharide narrow MW standard in water at ambient temperature

process, using standard random number generators and can handle far more complex situations.

A FORTRAN model has been developed [20], which allows any bond in the system to be chosen for scission. The molecular chain in which it resides is identified and the scission point in the chain is chosen systematically or at random. The structure of the program is shown in Fig. 6. Model results have been compared against our own laboratory measurement and the literature of the change of molecular weight distribution (MWD) during the ageing of polymers. One of the main conclusions to come out of our initial studies is that, although random scission statistically favors the breaking of the largest molecules, the low molecular weight peaks we observe during the degradation of polysaccharides arise as a result of systematic scission processes and not purely random ones as assumed in the mathematical models. Fig. 7(a) shows that purely random scission yields products of all possible lengths and hence, no more than an increase in the low molecular weight base line. However, systematic scission of x or $x\%$ of units from the chains yields the observed low molecular weight peak, with little change in the main peak (Fig. 7(b)). In the example, $x = 150$ units. Such a model could also explain the low molecular weight peak observed by Darveniza et al. [5, 6], since even the virgin paper is already degraded as a result of the manufacturing process.

Some early work of Mark et al. [21] reported changes in the MWD of an almost homogeneous solution of cellulose acetate, with an initial DP of 350. The initially narrow distribution first spread toward a lower molecular weight and flattened, then became progressively narrower as it moved to lower molecular weights. We can only reproduce this behavior if we bias the degradation toward the center of the molecule. Similar simulation results have recently been reported by Nguyen [22].

Mathematical theories have limited application, because real systems require far more complex models of degradation. Such models will only arise from a more detailed understanding of the chemical and physical processes occurring during degradation. It is difficult for mathematical models to allow for possibilities such as weak links in the chain, stable "domain" sizes

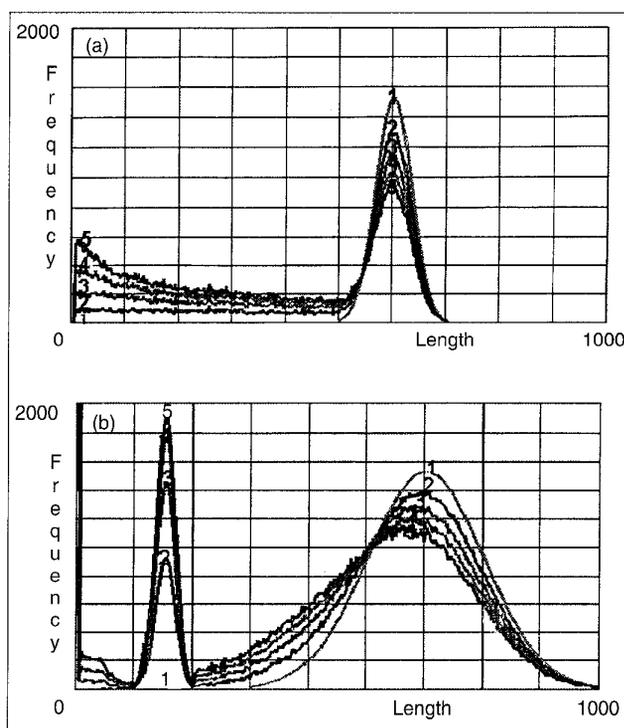


Fig. 7 Computer modeling of paper ageing a) Purely random scission b) Systematic scission, chopping 150 units per molecule

that break preferentially from the chain, and other non-random options. Techniques such as size exclusion chromatography linked to computer models of the mechanisms and the kinetics of degradation might provide the key to progress in this very difficult area.

CONCLUSIONS AND FUTURE STUDIES

- Furan-based aldehydes are typical degradation products of cellulose and can potentially be used to monitor the degradation of paper by analysis of the oil by HPLC. Normal levels of 2-furaldehyde are in the range 100 to 1000 ppb, but levels of about 1 ppm have been measured in a "normal" transformer, rising to 5 ppm in a transformer running hot and to over 10 ppm in a transformer that overheated after a cooler failure. The rate of change of concentration is as important as the absolute value.
- The DP of paper is difficult to measure reproducibly. We have developed a systematic approach, which gives results to a known accuracy, but even then the DP only gives a crude average of the molecular chain size and is a very coarse measure of degradation.
- Size exclusion chromatography (SEC) has the potential to give a far more detailed analysis of molecular weight distribution changes during cellulose ageing. Coupled with computer modeling, SEC could provide the basis of more sophisticated degradation models than are currently available from the statistical analysis of chain scission, because more complex situations can be accommodated.

- In future studies, we hope to develop correlations of tensile strength to molecular weight distribution changes and the concentrations of key degradation products in the transformer oil, with the long-term objective of generating a more comprehensive model of insulation degradation.

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